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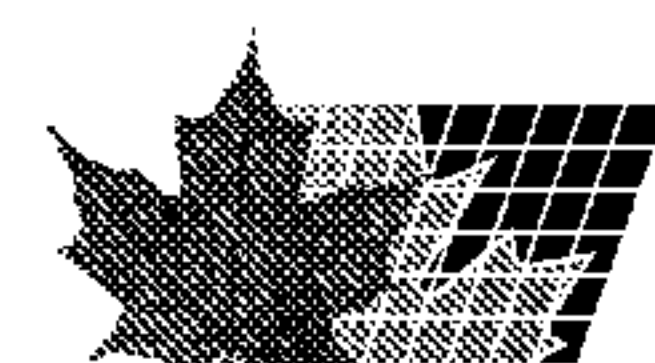
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(54) Title: MAR-RESISTANT OLIGOMERIC-BASED COATINGS FOR GLASS-PLASTIC GLAZING PRODUCTS

(57) **Abrégé/Abstract:**

This invention is glass laminate article comprising a mar-resistant clearcoat. A laminate of the present invention resists scratches, and is easily repairable and even self-healable at temperatures above about 40°C.



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(54) Title: MAR-RESISTANT OLIGOMERIC-BASED COATINGS FOR GLASS-PLASTIC GLAZING PRODUCTS

(57) Abstract: This invention is glass laminate article comprising a mar-resistant clearcoat. A laminate of the present invention resists scratches, and is easily repairable and even self-healable at temperatures above about 40°C.



**WO 2005/035241 A3**

## **TITLE**

### **MAR-RESISTANT OLIGOMERIC-BASED COATINGS FOR GLASS-PLASTIC GLAZING PRODUCTS**

5           This application claims the benefit of U.S. Provisional Application  
No. 60/499,949, filed September 2, 2003.

## **BACKGROUND OF THE INVENTION**

### **Field of the Invention**

10           This invention relates to laminated glass articles having scratch- and mar-  
resistant oligomeric coatings, and to a process for preparing such articles.

### **Description of the prior art**

          Base coat/clear coat systems are used conventionally in, for example,  
automobiles as finishes. Such systems are designed to protect the paint and finish  
15   of an automobile. Repairable mar-resistant coatings for automobile finishes are  
known and described in U.S. Pat. No. 5,827,910 and U.S. Pat. No. 6,376,596 B1,  
for example.

          Coatings for transparent glass laminates are known. For example,  
polysiloxanes can be useful as a hard coating on polyethylene terephthalate (PET)  
20   films of windshield laminates. However, polysiloxane coatings can become  
permanently scratched by sharp objects. Over time the optical qualities of a  
transparent laminate can be greatly diminished due to an accumulation of  
scratches. In addition, polysiloxane coatings cannot be applied to laminates at a  
thickness greater than 2.8 microns, otherwise cracking may develop from routine  
25   handling of the coated film.

          Repairable coatings for transparent laminates are known. For example,  
pre-formed scratch-resistant, self-repairable polyurethane sheets that can be  
adhesively applied to windshields as a two-layer coat are described in U.S. Pat.  
No. 4,784,916, U.S. Pat. No. 4,671,838, and U.S. Pat. No. 4,652,494.

30

## **SUMMARY OF THE INVENTION**

          In one aspect the present invention is a glass laminate article comprising: a  
clearcoat/polymer film bilayer wherein the clearcoat is a scratch-resistant coating



composition obtained from the combination of components (1) and (2), wherein component (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.

In another aspect, the present invention is a process for making a glass laminate article comprising the steps: combining two components, (1) and (2), to obtain a clearcoat composition; (b) coating a polymer film by applying the clearcoat composition onto the polymer film; (c) curing the clearcoat composition on the polymer film to obtain a cured coated film; and (d) laminating the cured coated film onto a stack comprising at least one layer of glass to obtain a glass laminate; wherein the clearcoat composition is a scratch-resistant coating composition and wherein component (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.

In still another embodiment, the present invention is a process for making a glass laminate article comprising the steps: combining two components, (1) and (2), to obtain a clearcoat composition; (b) coating a polymer film by applying the clearcoat composition onto the polymer film; (c) curing the clearcoat composition on the polymer film to obtain a cured coated film; and (d) applying a coat of an adhesive composition to a second side of the cured coated film, and (e) applying the cured film to a substrate by contacting the adhesive-coated surface of the cured film to a surface of the substrate comprising at least one layer of glass to obtain a glass laminate; wherein the clearcoat composition is a scratch-resistant coating composition and wherein component (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.

### **DETAILED DESCRIPTION OF THE INVENTION**

In one embodiment, the present invention is a glass laminate comprising a mar-resistant clearcoat. A glass laminate of the present invention comprises at least one layer of glass that is laminated to at least one layer of a thermoplastic polymer interlayer. The thermoplastic polymer interlayer can be any polymeric material that is known and used conventionally in the manufacture of glass laminates. For example, the thermoplastic polymer can be selected from (i) polyurethane (PU), (ii) polycarbonate (PC), (iii) polyvinylbutyral (PVB), (iv) polyesters such as polyethylene terephthalate (PET) or (v) an ethylene acid copolymer obtained from the copolymerization of ethylene with an  $\alpha,\beta$ -unsaturated carboxylic acid, or a derivative thereof. A combination of various conventional interlayer materials can be used in the practice of the present invention. Preferably, the interlayer material is selected from PVB and an ethylene acid copolymer or a derivative thereof. Suitable acid derivatives useful in the practice of the present invention are known to those skilled in the art, and include esters, salts, anhydrides, amides, and the like. Acid copolymers can be fully or partially neutralized to the salt (or partial salt). Fully or partially neutralized acid copolymers are known conventionally as ionomers. Suitable copolymers can include an optional third monomeric constituent which can be an ester of an ethylenically unsaturated carboxylic acid. Suitable acid copolymers useful in the practice of the present invention can be purchased commercially from, for example, E.I. DuPont de Nemours & Company under the tradenames of Surlyn® and Nucrel®, for example.

The laminate further comprises a second polymeric layer that is laminated to the interlayer on a second surface that is not laminated to the glass. The second polymeric layer can be any that is clear or transparent and can adhesively bond to both the interlayer and the clearcoat composition, such as polyurethane, PET, and ethylene/acid copolymers, for example. Preferred in the practice of the present invention as the second polymeric layer is PET.

The clearcoat is coated onto the second polymeric layer. The clearcoat can be formed from either (A) the combination of at least one hydroxyl-containing oligomer with at least one isocyanate oligomer, or (B) the combination of at least



one anhydride-containing oligomer with at least one epoxide-containing compound. Suitable oligomers for use in the practice of the present invention are particularly described and can be obtained as described in WO 9744402 and in U.S. Pat. No. 5,827,910.

5           Suitable hydroxy-containing oligomers can be obtained by reacting multifunctional alcohols such as pentaerythritol, hexanediol, trimethylol propane, similar compounds, or mixtures thereof, with cyclic monomeric anhydrides such as hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, and the like, and further reacting the acid oligomers thus obtained with monofunctional  
10   epoxy compounds such as butylene oxide, propylene oxide, similar compounds, or mixtures thereof. Hydroxyl-containing oligomers suitable for use in the practice of the present invention can have a molecular weight in the range of from about 300 to about 3,000. Preferably, the molecular weight of a hydroxyl-containing oligomer is in the range of from about 400 to about 2,500. More  
15   preferably, the molecular weight is in a range of from about 450 to about 2,000, and most preferably in the range of from about 500 to about 1,500.

          Suitable isocyanate oligomers are, for example: the isocyanurate trimer of hexamethylene diisocyanate; DESMODUR® 3300 available from Bayer; Tolonate® HDT available from Rhodia; and the isocyanurate trimer of isophorone  
20   diamine, and the like.

          Suitable anhydride oligomers are linear anhydrides having a structure defined by the general formula:  $R-CO-O-CO-(R'-CO-O-CO)_n-R$ , wherein R is a monosubstituted hydrocarbon group having from 2 to 50 carbon atoms, R' is a di-substituted hydrocarbon group having from 2 to 50 carbon atoms, the hydrocarbon  
25   R and R' groups containing or not containing an ether linkage, urethane linkage, or ester linkage, and n is an integer from 1 to 500. Also suitable are anhydrides having a molecular weight of less than about 2000 comprising (1) a central moiety, and (2) greater than one non-cyclic anhydride moieties bonded to each central moiety. Anhydrides suitable for use as an anhydride (b) type anhydride  
30   can be obtained by reacting multifunctional alcohols such as pentaerythritol, hexanediol, trimethylol propane, and the like, with cyclic monomeric anhydrides



such as hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, and the like, and further reacting the acid oligomers thus obtained with ketene.

Suitable epoxy oligomers are, for example, the diglycidyl ester of cyclohexane dicarboxylic acid such as Araldite® CY – 184 from Ciba Geigy, and  
5 cycloaliphatic epoxies such as ERL®– 4221, available from Union Carbide, and the like. In another embodiment, the present invention is a process for making a laminate comprising the step of preparing a clearcoat composition. A clearcoat of the present invention can be obtained by combining at least one oligomeric component (1) compound with at least one oligomeric component (2) compound.  
10 It is preferable that if component (1) is a hydroxyl-containing oligomer, that component (2) be an isocyanate-containing oligomer, and that if component (1) is an anhydride containing oligomer, that component (2) is an epoxide-containing oligomer. For example, at least one suitable hydroxyl-containing oligomer can be combined with at least one suitable isocyanate oligomer. The isocyanate and  
15 hydroxyl oligomers can be combined in a stoichiometric ratio that will result in all of the hydroxyl functionality present being reacted with the isocyanate functionality, that is, with a slight stoichiometric excess of isocyanate being present after all of the hydroxyl functionality has been reacted. Preferably, however, a stoichiometric excess of hydroxyl component is added such that some  
20 residual hydroxyl functionality remains after all of the isocyanate functionality is reacted. A molar equivalent, as used herein, is the number of moles of a reactant, such as component (1) required to completely react with one mole of the other reactant, for example component (2). The equivalent ratio is a ratio that can be easily determined by one of ordinary skill in the art by dividing the number of  
25 moles of a reactant actually present by the number of moles required for a complete reaction. The equivalent ratio of hydroxyl oligomer to isocyanate oligomer (HY:ISO) is greater than 0.60. Preferably the ratio is in the range of from about 0.70 to about 1.50, more preferably in the range of from about 0.80 to about 1.40; and most preferably in the range of from about 0.90 to about 1.35. In  
30 a particularly preferred embodiment, the equivalent ratio of the hydroxyl oligomer to the isocyanate oligomer is in the range of from about 1.10 to about 1.35 with the tetrahydroxyl oligomer. It has been found, surprisingly, that higher HY:ISO



ratios result in faster healing of scratches and nicks, and at lower temperature. An anhydride oligomer is preferably combined with an epoxide-containing oligomer in a stoichiometric ratio such that an excess of epoxy remains after all of the anhydride is reacted. Preferably, the equivalent ratio of epoxy oligomer to anhydride is at least 0.70, and preferably from about 0.70 to about 1.40. More preferably the equivalent ratio of epoxide to anhydride is from about 0.90 to about 1.30, and most preferably from about 1.00 to about 1.25.

It is preferable that the clearcoat components (1) and (2) be combined just prior to being applied to the polymer film. Preferably components (1) and (2) are combined less than about 60 minutes prior to the application to the polymer film. After application of the clearcoat to the polymer film, the coating can be allowed to sit for a period, typically less than 30 minutes, at room temperature prior to being placed in a heated environment to cure the clearcoat. The coatings can be cured at a temperature of at least about 100°C, preferably above 120°C, and most preferably above about 125°C but below about 150°C.

Cured coated polymer films obtained as described herein are optically clear films having low haziness and good see-through clarity.

A laminate comprising the cured clearcoat can be obtained by laminating the coated polymer film to a suitable material as described herein. The lamination process used herein can be any that is known or conventional in the art. However, the preferred lamination process may depend on the specific details of the lamination, including the structure of the laminate and/or the materials used to build the laminate. For example, a laminate assembly can be constructed using suitable materials and placing them in the order desired in the assembly. Preferably in the practice of the present invention a glass coverplate is used to cover and protect the exposed surface of the clearcoat film. In some cases it can be desirable to place the assembly in bag, which is in turn placed into a vacuum chamber, remove as much air as possible from the bag and chamber, and then seal the bag while still under vacuum. A laminate assembly whether vacuum-bagged or not, can then be heated in an oven set at 90-150°C for at least about 20 minutes. The oven can be an autoclave, wherein the assembly can be subjected to temperatures above about 125°C and pressures above about 12 atmospheres. The



exact time can depend on the conditions employed, but the temperature and pressure are maintained at the desirable levels for at least about 9 minutes before cooling and depressurizing the autoclave.

In a preferred embodiment, a laminate of the present invention can be  
5 obtained by coating the un-coated surface of the polymer film -- that is the surface intended to be laminated to the glass surface -- with an adhesive composition, followed by contacting the adhesive-coated surface of the polymer film with a glass surface. The adhesive can be a moisture activated adhesive. In such case, either or both the glass surface and/or the adhesive coated surface of the polymer  
10 film can be wet prior to contacting the two surfaces. In some cases it can be preferred that the glass surface is wet prior to bringing the glass into contact with the adhesive coated surface of the polymer film. In other cases it can be preferred to wet the adhesive-coated surface of the film. In still other cases it can be preferred to wet both surfaces prior to bringing them into contact with each other.  
15 For example, an aqueous mixture of Elvanol® polyvinyl alcohol, available from E. I. DuPont de Nemours and Company, can be suitable for use herein as a water activated adhesive.

Other adhesives can be used wherein water activation is not required. For example, in U.S. Pat. Pub. No. US2002/0061395 A1 is described an adhesive that  
20 is suitable for use herein. In a preferred embodiment, an adhesive that does not include water, and/or does not require activation by water, can be desirable in order to avoid problems that can result from water that is absorbed or trapped by the laminate.

In any case, suitable adhesives for the purposes of the present invention  
25 are known. For example suitable adhesives are described in U.S. Pat. No. 4, 973,511. Suitable adhesives are transparent adhesives that can include: polyester adhesives described in DuPont Technical Bulletin No. 17 entitled "Polyester Adhesives", specifically adhesives No. 46960, 46971, and 46690 therein; polyamide adhesives such as, for example "Versalon" 1140 (General Mills);  
30 and/or vinyl resin-based adhesives that are conventionally used in the construction of laminate safety glass.

In still another embodiment, the present invention is a laminate comprising a polymer film coated with a mar-resistant coating of the present invention, wherein the polymer film is adhesively bonded directly to glass, without an intervening layer of thermoplastic interlayer between the glass and the coated polymer film. For example, it can be desirable in some applications to exclude PVB from the laminate structure, and adhesively bond a coated PET film to glass.

A laminate of the present invention has excellent durability, impact resistance, toughness, and resistance by the interlayer to cuts, scratches, nicks, and the like. A laminate of the present invention that is scratched can be easily repaired by applying heat to the clearcoat layer of the laminate. A scratch produced on a coated laminate of the present invention can be removed (healed) by heating the scratched laminate to a temperature of at least about 30° for at least about 15 minutes. Preferably, the laminate surface is heated to a temperature of at least about 35°C for at least about 30 minutes, and more preferably 40°C for at least about 30 minutes. Even more preferably, a scratched laminate is heated to a temperature of at least about 60°C for at least about 45 minutes. Most preferably, a scratched laminate can be healed by heating the laminate surface to a temperature of at least about 70°C for at least about 60 minutes.

A laminate of the present invention can be useful in an automobile as windshields and/or sidelites and/or moonroofs. A laminate of the present invention can also be particularly useful in architectural applications, in buildings for example. A laminate of the present invention can be easily cleaned and is resistant to spalling, and penetration by projectiles.



## **EXAMPLES**

The Examples are for illustrative purposes only, and are not intended to limit the scope of the invention.

### **Example 1**

5           A coating formulation (A) was prepared by combining 71.1 wt% of Part 1 with 28.9 wt% of Part 2. Part 1 consists of: 56.87 wt% tetrahydroxyl oligomer (obtained as described in Procedure 1 of U.S. Pat. No. 6,376,596); 0.68 wt% of 10% BYK 301 in propylene glycol monomethyl ether acetate, available from Byk Chemie; 2.8 wt% of a mixture of 1% dibutyl tin dilaurate in methyl ethyl ketone;  
10           and 10.75 wt% butyl acetate. Part 2 is Tolonate® HDT LV, which is an isocyanurate trimer of hexamethylene diisocyanate available from Rhodia. Weight percentages are based on the total weight from the combination of Part 1 and Part 2.

### **Example 2**

          A coating formulation (B) was prepared by combining 72.04 wt% of Part 1 with 27.96 wt% of Part 2. Part 1 consists of: 28.73 wt% tetrahydroxyl oligomer (obtained as described in Procedure 1 of U.S. Pat. No. 6,376,596B1); 29.09 wt% of dihydroxyl oligomer (obtained as described in Procedure 2 of U.S. Pat. No.  
20           6,376,596B1); 0.68 wt% of 10% BYK 301 in propylene glycol monomethyl ether acetate, available from Byk Chemie; 2.77 wt% of a mixture of 1% dibutyl tin dilaurate in methyl ethyl ketone; and 10.77 wt% butyl acetate. Part 2 is Tolonate® HDT LV, which is an isocyanurate trimer of hexamethylene diisocyanate available from Rhodia. Weight percentages are based on the total  
25           weight from the combination of Part 1 and Part 2. Part 1 and Part 2 are mixed just prior to application to substrate surface.

### **Example 3**

          A coating formulation (D) was prepared by combining 65.79 wt% of Part  
30           1 with 34.21 wt% of Part 2. Part 1 consists of: 26.17 wt% anhydride resin with pendant groups (as described in Example 1A of U.S. Pat. No. 5,827,910); 24.53 wt% of linear anhydride (as described in Example 1B of U.S. Pat. No. 5,827,910);

1.23 wt% of 10% BYK 301 in propylene glycol monomethyl ether acetate, available from Byk Chemie; 1.23 wt% of a mixture of 25% tetrabutyl phosphonium chloride in propylene glycol monomethyl ether acetate; 1.45 wt% of a mixture of 25% Nix A-99 (a tertiary amine available from Union Carbide) in methyl ethyl ketone; and 7.86 wt% butyl acetate. Part 2 is diglycidyl ester of 1,2-cyclohexane dicarboxylic acid available from Ciba-Geigy as Araldite®CY-184. Weight percentages are based on the total weight from the combination of Part 1 and Part 2. Part 1 and Part 2 are mixed just prior to application to substrate surface.

10

#### **Examples 4-8**

The coating compositions A, B, and D of Examples 1-3 were each coated onto 4 mil polyethylene terephthalate films which surfaces had been previously flame treated to improve adhesion. The coated film samples were kept at room temperature for 5-10 minutes after coating, and then baked for 30 minutes at 140 °C to cure the coatings. The coating thicknesses were varied as described in Table 1. Scratch behavior, abrasion resistance, coating adhesion, and the effects of immersion in boiling water on coating adhesion and haze were tested according to the methods described below. The results of the tests are described in Tables 1 – 4 below.

20

#### **Examples 9-14**

The coating compositions A and B of Examples 1-2 were each coated – using a #30 wire wound rod fitted on a RESOURCE I lab coater device -- onto 4 mil polyethylene terephthalate films which had been previously had the surfaces flame treated to improve adhesion. The coated film samples were kept at room temperature for 10 minutes after coating, and then baked for 30 minutes at either 100°C, 120°C, or 140 °C in a hot air oven to cure the coatings. The coating thicknesses were 28 – 36 microns for the “A” composition and 32 – 37 microns for the “B” composition.

30



**Example 15 – General lamination procedure**

A glass laminate assembly is constructed as follows:  
glass/PVB/PET/clearcoat/coverplate. The coverplate can be any rigid material,  
but is generally float glass. While any surface pattern on the coverplate can be  
5 used, for optical applications a smooth surface is desirable. The multilayer  
construction can be laminated according to conventional techniques. The  
assemblies described herein are vacuum bagged according to the following  
procedure. A laminate construction is placed in a plastic bag, which is then  
placed into a vacuum chamber, which is evacuated to remove air, and thermally  
10 sealed while still under vacuum. The vacuum-bagged construction is placed in an  
autoclave and subjected to a pressure of about 17 atmospheres, and a temperature  
of about 125°C to about 150°C for 30 minutes. The chamber is depressurized and  
cooled. The laminate is removed from the bag and the coverplate is removed.

**Examples 16-21**

The cured coated films of Examples 9-14 were laminated to glass in an  
autoclave using the lamination procedure of Example 15, at an autoclave  
temperature of 140°C. Glass coverplates were used, the coverplates were washed  
with water containing 350 parts per million (ppm)  $\text{MgSO}_4$  before use to prevent  
20 sticking between the coverplate and the clearcoat. The laminates obtained were  
optically flat and smooth, and the coverplates easily removed.

**Scratch Behavior**

Scratch behavior for each sample tested was determined using a Taber  
25 Shear/Scratch Tester, Model 502, fitted with a diamond stylus lapped to a 90°  
included angle with a 0.003-inch radius tip. The stylus was positioned on the arm  
of the tester at an angle of 90° to the surface of the coated film being tested. The  
coated film sample was positioned horizontally on the disc of the tester with the  
coated side facing upward to receive the stylus. A given weight was applied to  
30 the arm by sliding the weight to a marked position along the arm. The arm with  
stylus was lowered into contact with the coated film and the disc with attached  
coated film was rotated at a speed of 0.5 inches/second. The stylus path was then

inspected for any scratch, and any visible scratch measured for width. This process was repeated using different weights on the stylus arm. After the degree of visibility and actual scratch width are recorded, the sample was heated in an oven held at 70°C for 30 minutes to determine the affect on scratch visibility and width. The results for Examples 4-8 are shown in Table 1.

TABLE 1

Example	Thickness (microns)	State <sup>1</sup>	Scratch Width <sup>a</sup> (mm)	Scratch Width <sup>b</sup> (mm)	Scratch Width <sup>c</sup> (mm)	Scratch Width <sup>d</sup> (mm)	Scratch Width <sup>e</sup> (mm)
4	30 to 40	AS	NV <sup>2</sup>	0.033	0.050	0.058	0.098
4		AH	NV	NV	0.048	0.054	0.093
5	10 to 15	AS	0.035	0.047	0.058	0.068	0.099
5		AH	NV	NV	0.043	0.054	0.071
6	30 to 40	AS	0.029	0.046	0.058	0.067	0.104
6		AH	NV	NV	NV	NV	NV
7	20	AS	NV	0.040	0.051	0.065	0.096
7		AH	NV	NV	NV	0.053	0.077
8	30 to 40	AS	NV	0.031	0.049	0.063	0.124
8		AH	NV	NV	NV	NV	NV

<sup>1</sup>AS = As Scratched; AH = After Heating at 70°C for 30 minutes.

<sup>2</sup>NV = scratch not visible

<sup>a</sup>Stylus weight 20 grams.

<sup>b</sup>Stylus weight 30 grams.

<sup>c</sup>Stylus weight 40 grams.

<sup>d</sup>Stylus weight 50 grams.

<sup>e</sup>Stylus weight 100 grams.

### Abrasion Resistance

Abrasion resistance was evaluated using the Taber Abrasion test as defined in ANSI Z-26.1, Test Number 34. In this test the sample surface is abraded by a CS-10F abrader wheel under 500 grams weight for 100 revolutions. The increase in haze of the clear sample in the abraded lane is measured and expressed as the Taber Haze in percent. The clear-coated samples were abraded on the coated sides, and measured for Taber Haze, then heated and held in an oven held at 70°C for 30 minutes. The Taber Haze was determined again after removal from the oven to determine whether heating diminished the abrasion scarring. The results are reported in Table 2.



TABLE 2

Example	Coating Thickness (microns)	Taber Haze <sup>a</sup> (%)	
		initial	after heating
4	30-40	25.8	13.6
5	10-15	38.2	24.6
6	30-40	36.2	20.8
7	20	24.2	13.1
8	30-40	23.1	11.7

<sup>a</sup>100 revolutions/500 grams

## 5 Optical Properties

To determine the optical properties of the films, film samples were immersed in boiling water for two hours and 6 hours and the Gardner Haze value determined according to the procedures of ASTM D 1003 – 61 (Reapproved 1977). The films had good see-through clarity and low haziness. The results are reported in Table 3.

TABLE 3

Example	Gardner Haze (%)		
	initial	2 hrs	6 hrs
4	1.1	3.8	12.5
6	0.6	5.5	4.0
8	1.0	8.1	12.4

## Coating Adhesion

Coating adhesion was determined according to ASTM D3359 – 87 Tape Test using PERMACEL™ tape having a peel strength against a stainless steel of 40 ounces per inch. The adhesion was measured before and after immersion in boiling water for 2 hours and for 6 hours. The results of the adhesion test are given in Table 4.

TABLE 4

Example	Coating Adhesion (% Coating Retained)		
	Initial	2 hrs	6 hrs
4	100	100	100
6	100	100	100
8	100	100	100

**Examples 22-27**

Coating formulations were prepared by combining Part 1 with Part 2 in various ratios, such that the equivalent ratio of hydroxyl to isocyanate was varied as indicated in Table 5. Part 1 consists of: 56.87 wt% tetrahydroxyl oligomer; 0.68 wt% of 10% BYK 301 in propylene glycol monomethyl ether acetate, available from Byk Chemie; 2.8 wt% of a mixture of 1% dibutyl tin dilaurate in methyl ethyl ketone; and 10.75 wt% butyl acetate. Part 2 is Tolonate® HDT LV, which is an isocyanurate trimer of hexamethylene diisocyanate available from Rhodia. Weight percentages are based on the total weight from the combination of Part 1 and Part 2.

TABLE 5

Example	Part 1	Part 2	Equivalent Ratio
22	12.30	5.00	0.95
23	14.15	5.00	1.09
24	16.00	5.00	1.24
25	12.90	5.00	0.95
26	14.85	5.00	1.09
27	16.80	5.00	1.24

**Examples 28-33**

PET clearcoated films were obtained by coating the above coating compositions at a thickness 7 mil onto PET film. Laminates were made according to the procedure of Example 15 and were evaluated for optical properties and performance after autoclaving. The laminates did not change color, remained clear and free of haze, conformed perfectly to the coverplate to yield an optically flat surface, and release readily from the coverplate with no tendency to stick. The results are tabulated in Table 6.



TABLE 6

Example	Transparency (%)	Haze (%)	Clarity (%)	20° Gloss	YID Color
C1 <sup>1</sup>	92.8	0.09	100	101.3	0.30
C2 <sup>2</sup>	89.8	0.61	99.7	153.7	1.60
28 <sup>a</sup>	91.9	1.08	99.7	99.3	1.47
29 <sup>b</sup>	91.6	0.73	99.6	104.3	1.45
30 <sup>c</sup>	91.9	0.57	99.8	103.6	1.52
31 <sup>d</sup>	91.9	0.79	99.6	103.1	1.46
32 <sup>e</sup>	91.7	0.59	99.7	105.8	1.56
33 <sup>f</sup>	91.9	1.29	99.7	103.0	1.41

<sup>1</sup>90 mil glass, not an example of the present invention<sup>2</sup>7 mil PET film, not an example of the present invention5 <sup>a</sup>Laminate obtained from film of Example 22.<sup>b</sup>Laminate obtained from film of Example 23.<sup>c</sup>Laminate obtained from film of Example 24.<sup>d</sup>Laminate obtained from film of Example 25.<sup>e</sup>Laminate obtained from film of Example 26.10 <sup>f</sup>Laminate obtained from film of Example 27.

TABLE 7

Example	Stylus Load (grams)	Scratch Visibility After heating for 1 hour at:				
		25°C	40°C	50°C	60°C	70°C
C1	50	V <sup>1</sup>	V	V	V	V
C1	100	V	V	V	V	V
C2	50	V	V	V	V	V
C2	100	V	V	V	V	V
28	50	V	V	V	V	NV
28	100	V	V	V	V	NV
29	50	V	V	V	V	NV
29	100	V	V	V	V	NV
30	50	V	V	V	NV	NV
30	100	V	V	V	V	NV
31	50	V	NV	NV	NV	NV
31	100	V	NV	NV	NV	NV
32	50	V	NV	NV	NV	NV
32	100	V	NV	NV	NV	NV
33	50	NV	NV	NV	NV	NV
33	100	V	V <sup>4</sup>	BV <sup>3,4</sup>	BV <sup>4</sup>	BV <sup>4</sup>

<sup>1</sup>V = Visible to the unaided eye.<sup>2</sup>NV = Not visible to the unaided eye.15 <sup>3</sup>BV = Barely visible to the unaided eye.<sup>4</sup>The stylus penetrated through to the PET film surface.

**Examples 34-35**

Two laminates were prepared as described in Example 15, using the coating composition described below in Table 8a. The laminates were then subjected to the XENOTEST® 1200 CPS tested conducted using ASTM G26-90 METHOD A. The samples were exposed to 1,515 MJ/m<sup>2</sup> UV radiation (300-400 nm) for a total time of 5,260 hours. The exposed laminates were measured for Gardner Haze (ASTM 1003-61), 20° gloss, and coating adhesion by the ASTM tape adhesion test (ASTM 3359-97). Results are shown in Table 8b. The samples were also visually inspected for yellowness and see-through clarity.

TABLE 8a

Coating Composition	Ex 34	Ex 35
Part 1 (Hydroxyl Oligomer)	30.0 g	30.0 g
Part 2 (isocyanate)	11.64 g	9.90 g
Equivalent Ratio Part 1/Part 2	0.95	1.12

The samples did not show any visual color change and clarity was considered good. Some hazing occurred due to the XENOTEST® water spray cycles.

TABLE 8b

Example	Haze (%)	20° Gloss		Tape Adhesion		
		control	exposed	Cross hatch	unscribed	x-scribed
34	1.6	108	96.3	30	100	100
35	2.2	124	124	100	100	100

**Example 36**

A clear 7 mil flame treated PET film was coated on one side with a water solution of an ELVANOL® PVA formulation to serve as a water-activated adhesive, and was coated on the other side with the oligomeric clearcoat described in Examples 34 (B1) to serve as a scratch resistant healable coating. The film was bonded to glass by wetting the glass and/or the film on the adhesive coated side followed by pressing the wetted film to the glass using a rubber roller or “squeegee” to remove all excess water. The glass and film bonded structure was then allowed to dry at room temperature until the adhesive was dry, that is until the moisture diffused through the PET film and the adhesive layer was “set” and the film was firmly adhered to the glass.



**Example 37**

A 7 mil clear CRONAR® PET film, flame treated on both sides, was coated on one side with a 15% water solution containing ELVANOL® type 51-05 powder using a #28 wire-wound coating rod. The coating was allowed to dry at room temperature before coating the opposite side with the clearcoat formulation described in Examples 34 (B1). The formulation was applied coated using a # 28 wire-wound coating rod. The coating was allowed to flash off solvent at room temperature and then allowed to sit at room temperature for 24 hours before the application of the clearcoated PET film to the glass (see "Glass Application Procedure", Example 39 below).

**Example 38**

A 7 mil clear CRONAR® PET film, flame treated on both sides, was coated on one side with a 15% water solution containing ELVANOL® type 51-05 powder using a #28 wire-wound coating rod. The coating was allowed to dry at room temperature before coating the opposite side with the clearcoat formulation described in Examples 35 (B2). The formulation was applied coated using a # 28 wire-wound coating rod. The coating was allowed to flash off solvent at room temperature and then allowed to sit at room temperature for 24 hours before the application of the clearcoated PET film to the glass (see "Glass Application Procedure", Example 40 below).

**Glass Application Procedure****Example 39**

The coated film of Example 37 was attached to 90 mil thick annealed float glass by (1) spraying the glass surface with a mist of water, (2) laying the coated film onto the wet glass with the ELVANOL® coated side to the glass, and (3) pressing the film onto the glass using a rubber bladed "squeegee", using multiple passes to eliminate all excess water from the interface. The coated film/glass structure was allowed to dry for several days before being tested for scratch resistance and optical properties. The dried structure was very clear and colorless and the film was adequately bonded to the glass.

**Example 40**

The coated film of Example 38 was attached to 90 mil thick annealed float glass according to the procedure of Example 39.

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TABLE 9

Example	Haze (%)	Transmission (%)	Clarity (%)	YID
C3 <sup>1</sup>	2.2*	90.8	98.4	0.55
39	0.9	92.0	98.6	0.52
40	0.6	92.1	98.8	0.70

<sup>1</sup>Uncoated PET/PVA/Glass, not an example of the present invention.

\* The uncoated PET film was abraded by the squeegee and gave a higher haze reading, i.e. no clearcoat to protect from scratching.

10 The film/glass structures of Examples 39 and 40 were subjected to the Taber scratch test, as described above, using scratch loads of 50 and 100 grams. The scratched samples were measured for scratch width using a microscope, and for visibility with the unaided eye. They were then allowed to sit overnight at room temperature and were then re-examined for the scratches. The results are given in

15 TABLE 10:

TABLE 10

Example	Load (grams)	Visibility		Width	
		As Scratched	After 18 hrs (rt)	As Scratched	After 18 hrs (rt)
C3	50	V	V	0.050	0.052
	100	V	V	0.079	0.078
39	50	V	NV	0.070	NV
	100	V	NV	0.085	0.019
40	50	V	NV	0.069	NV
	100	V	V*	0.076	0.042

\*The coating of Ex. 40 is softer than the 39 coating, and the stylus penetrated through it into the underlying PET surface – this made the scratch permanently visible even though some healing of the clearcoat took place with sitting at room temperature.

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**WHAT IS CLAIMED IS:**

1. A glass laminate comprising: a clearcoat/polymer film bilayer wherein the clearcoat is a scratch-resistant coating composition obtained from the combination of components (1) and (2), wherein component (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.
2. The laminate of Claim 1 wherein component (1) is at least one hydroxyl-containing oligomer and component (2) is at least one isocyanate oligomer.
3. The laminate of Claim 2 wherein the laminate comprises at least one layer of glass laminated to at least one layer of a thermoplastic polymer.
4. The laminate of Claim 3 wherein the polymer of the clearcoat/polymer bilayer is laminated to the thermoplastic polymer layer.
5. The laminate of Claim 4 wherein the thermoplastic polymer is either PVB or an ethylene copolymer.
6. The laminate of Claim 5 wherein the thermoplastic polymer is PVB.
7. The laminate of Claim 6 wherein the polymer of the bilayer component is PET.
8. The laminate of Claim 7 wherein at the least one hydroxy-containing oligomers is the reaction product of a multifunctional alcohol with a cyclic monomeric anhydride then further reacted with an epoxide.
9. The laminate of Claim 8 wherein the multifunctional alcohol is selected from the group consisting of: pentaerythritol, hexanediol, trimethylol propane, similar compounds, or mixtures thereof.
10. The laminate of Claim 9 wherein the epoxide is selected from the group consisting of: 1,2-butylene oxide; 2,3-butylene oxide; propylene oxide; ethylene oxide; and similar compounds, or mixtures thereof.
11. The laminate of Claim 10 wherein the hydroxy-containing oligomer is a tetrahydroxy-containing oligomer.

12. The laminate of Claim 11 wherein the isocyanate oligomer is an isocyanurate trimer of hexamethylene diisocyanate.
13. The laminate of Claim 1 wherein the clearcoat/polymer film bilayer is adhesively bonded to glass without an intervening thermoplastic polymer layer between the glass and the bilayer.
14. The laminate of Claim 13 wherein component (1) is at least one hydroxyl-containing oligomer and component (2) is at least one isocyanate oligomer.
15. The laminate of Claim 14 wherein the polymer of the bilayer component is PET.
16. The laminate of Claim 15 wherein at the least one hydroxy-containing oligomers is the reaction product of a multifunctional alcohol with a cyclic monomeric anhydride then further reacted with an epoxide.
17. The laminate of Claim 16 wherein the multifunctional alcohol is selected from the group consisting of: pentaerythritol, hexanediol, trimethylol propane, similar compounds, or mixtures thereof.
18. The laminate of Claim 17 wherein the epoxide is selected from the group consisting of: 1,2-butylene oxide; 2,3-butylene oxide; propylene oxide; ethylene oxide; and similar compounds, or mixtures thereof.
19. The laminate of Claim 18 wherein the hydroxy-containing oligomer is a tetrahydroxy-containing oligomer.
20. The laminate of Claim 19 wherein the equivalent ratio the hydroxyl oligomer to the isocyanate of oligomer is greater than 0.60 relative.
21. The laminate of Claim 20 wherein the equivalent ratio is in the range of from about 0.70 to about 1.50.
22. The laminate of Claim 21 wherein the equivalent ratio is in the range of from about 0.80 to about 1.40.
23. The laminate of Claim 22 wherein the equivalent ratio is in the range of from about 0.90 to about 1.35.
24. The laminate of Claim 23 wherein the isocyanate oligomer is an isocyanurate trimer of hexamethylene diisocyanate.
25. An article comprising a clearcoat on a polymeric film wherein the clearcoat is the product of the combination of components (1) and (2) combined in an



- equivalent ratio of greater than 0.90, wherein (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.
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26. The article of Claim 25 wherein the polymeric film is a polymer selected from the group consisting of polyurethanes, ethylene/acid copolymers, and PET.
27. The article of Claim 26 wherein the polymeric film is PET.
28. An article comprising a clearcoat on a polymeric film wherein the clearcoat is
- 10 the product of the combination of components (1) and (2) combined in an equivalent ratio in the range of from about 1.10 to about 1.35, wherein (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a
- 15 compound having epoxy functionality, wherein component (1) has a molecular weight in the range of from about 300 to about 3000.
29. The article of Claim 28 wherein component (1) has a molecular weight in the range of from about 400 to about 2,500.
30. The article of Claim 29 wherein component (1) has a molecular weight in the
- 20 range of from about 450 to about 2,000.
31. The article of Claim 30 wherein component (1) has a molecular weight in the range of from about 500 to about 1,500.
32. A process for making a glass laminate article comprising the steps: (a) combining two components, (1) and (2), to obtain a clearcoat composition; (b)
- 25 coating a polymer film by applying the clearcoat composition onto one of at least two surfaces of the polymer film; (c) curing the clearcoat composition on the surface of the polymer film to obtain a cured clearcoat/polymer film bilayer film having at least one surface of the polymer film that is exposed; and (d) laminating the exposed polymer surface of the cured bilayer film to a
- 30 stack comprising at least one layer of glass to obtain a glass laminate; wherein the clearcoat composition is a scratch-resistant coating composition and wherein component (1) comprises an oligomeric compound selected from the

group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.

33. A process for removing defects from the surface of a transparent laminate comprising the step: heating the defective surface of the laminate to at least 70°C, wherein the surface comprises a clearcoat obtained by combining two components, (1) and (2), at an equivalent ratio of at least 0.90 (component (1):component (2)) and wherein component (1) comprises an oligomeric compound selected from the group consisting of oligomeric compounds having either hydroxyl functionality or anhydride functionality, and wherein component (2) is either an isocyanate oligomer or a compound having epoxy functionality.