PATENT SPECIFICATION

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(54) GLAZING STRUCTURES AND METHOD OF PRODUCING THE SAME

(71) We, LIBBEY-OWENS-FORD COMPANY, a Corporation organized under the laws of the State of Ohio, United States of America, of 811 Madison Avenue, City of Toledo, County of Lucas, and State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates primarily to the production of transparent structures that include abrasion and weather resistant coatings on plastic sheets. More particularly it has to do with sun roofs, windshields and other automotive glazings embodying such coated sheets and with procedures for incorporating improved coatings of this character into multilayer glazing units to serve as the inboard surface thereof.

The desirability of coating relatively soft plastic materials with a harder, more scratch resistant layer has been recognized for many years and a considerable number of patents have issued on the subject. Similarly, the potential advantages of including sheets or layers of plastic coated in this way in automotive glazings, and with the coating providing the inboard surface of the glazing, have been appreciated. However, to date, no commercially feasible structure of this character capable of meeting the stringent requirements for use in automotive sight openings has been found.

A complete multilayer glazing unit as contemplated by this invention includes essentially, a substrate and a protective cover supported by and over what would otherwise be an exposed surface of the substrate. The substrate may be primarily of glass and take such varied forms as the conventional laminated safety glass structures currently required in automobile windshields in the United States or the single sheet tempered glass glazing units commonly employed in automobile windows and backlights. On the other hand the substrate may be primarily of plastic in the form of a single plastic sheet or of a multilayer plastic structure. Similarly, the protective cover for the substrate will be a multiple layer plastic structure which presents an exposed surface of a fully cured organopolysiloxane compound reinforced with silica.

One object of the invention is to provide an automotive glazing unit that is dimensionally, functionally and optically comparable to its commercially accepted standard glass counter-part, but that will appreciably reduce the number and severity of lacerative injuries to persons thrown against or otherwise brought into contact with the glazing under impact conditions while at the same time, exhibiting improved ability to decelerate movement of a person thrown against it without exceeding tolerable deceleration limits and increased penetration resistance at both high and low temperatures.

Another object, when employing a primarily glass substrate, is to materially reduce the amount of flying glass and of resultant and personal injury to car occupants, from collisions with birds or with objects thrown from overpasses or elsewhere outside the vehicle.

Still another and indeed the primary object of this invention, is to incorporate materials in and employ procedures for, producing such glazing units that will ensure that the resulting units meet the exacting standards of appearance, safety, utility and commercial practicability required in present-day automobiles.

To understand the problems that have rendered these objects heretofore unattainable, it must be appreciated that, although a layer of any one of a large number of plastic materials secured to the inside surface of a conventional glass window or windshield with practically any adhesive, will afford occupants of the automobile some protection from lacerative injuries, such structures can be expected to create more problems than they solve.

For example, while there are any number of adhesives and adhesion promoters available for securing plastics to glass, many of these create serious problems when employed in automotive glazings.

Similarly, plastic sheetings that are otherwise acceptable for use as protective coverings may be susceptible to "denting" or "marking" with any relative sharp or pointed implement and to overcome this, as well as the marring situations incident to normal wear and possible abuse, requires not only finding a functionally acceptable plastic, but also being able to employ it in a thickness that will give the indentation resistance necessary to minimize marking.

Another problem arises from the fact that glass-plastic structures must not only include an adequate protective cover or laceration shield over the glass, but must also be capable of surviving the so-called cold test. This is an accepted procedure in the auto industry for determining the thermomechanical stability of laminated structures and involves subjecting them to a temperature of approximately −65°F. until they come to equilibrium. During the test, the difference in coefficient of expansion between the glass and plastic will either rupture the bond between them or cause patches to spall off the glass surface of any unit that lacks the necessary stability.

A further problem is to ensure that the multilayer glazing that includes the protective cover, attains an acceptable Severity Index. The Severity Index is a factor that has become identified with relative safety of the windshields as determined by impact tests using a test dummy or a head form equipped with suitable accelerometers and is discussed more fully in our prior Patent No. 1 433 532.

Still another problem and one of the most serious and most important from the optics standpoint, is that of providing acceptable resistance to weathering and wear. This problem arises with a plastic cover or shield on a glass substrate because, inherently, plastic is softer than glass. Also, many plastics are quite easily and adversely affected by atomspheric conditions, so that their use in a protective cover will result in vision through the glazing unit becoming obscure after only a few weeks exposure. Since, at the same time, the cover will also be subjected to the sort of scratching, abrasion and marring which all automotive glazings encounter in any normal use, it can be understood why exposed surfaces of plastic have heretofore been generally considered unacceptable in automotive glazings.

Nevertheless, the present invention makes it possible to provide acceptable and commercially feasible automobile glazings that have incorporated into their structures, a protective cover or shield over the inboard glass surface that, in addition to inhibiting lacerative injuries, will not be adversely affected by exposure to the atmosphere; is unaffected by extreme cold; is clearly transparent and practically color-free; does not adversely affect the Severity Index of the complete structure; and is highly resistive to marking, scratching and abrasion.

In the accompanying drawings:

Figure 1 is a perspective view of the front end of an automobile equipped with a sun roof, windshield and side lights, all produced in accordance with the glass substrate phase of this invention;

Figure 2 is a traverse, sectional view through the sun roof of the automobile, taken substantially along the line 2—2 in Figure 1;

Figure 3 is a vertical, sectional view through the windshield, taken substantially along the line 3—3 of Figure 1; and

Figure 4 is a fragmentary sectional view, on a enlarged scale, taken substantially along the line 4—4 in Figure 3, and illustrates the structure of the protective cover that is bonded to the inboard glass surface of the substrate.

According to the present invention, there is provided a transparent, temperature stable glazing structure consisting essentially of a transparent substrate with a protective shield thereover that comprises a layer of a relatively soft and extensible plastic having one surface bonded to a surface of said substrate, a carrying sheet in the form of a thin layer of indentation resistant plastic having one surface bonded to the free surface of said layer of relatively soft and extensible plastic, and an abrasion resistant coating on and rightly adhered to the opposite surface of said carrying sheet, said abrasion resistant coating comprising a fully cured, silica reinforced, organopolysiloxane compound.

Also, according to this invention there is provided a method of producing a transparent, temperature stable, multilayer structure, comprising the steps of treating a clean surface of a carrying sheet of penetration resistant plastic to promote adhesion, coating said treated surface with a solution of a silica reinforced organopolysiloxane compound containing from 12 to 18 percent resin solids, and incorporating said coated carrying sheet into said structure by bonding one surface of a layer of a relatively soft and extensible plastic to the uncoated surface of said carrying sheet and the opposite surface of said soft and extensible layer to a surface of a transparent substrate.

As illustrated in Figure 1, a windshield 10, sun roof 11 and side windows 12 made according to the present invention can be mounted in an automobile 13 and will appear like ordinary automotive glazings of conventional construction. Thus, as shown in Figs. 2 and 3 by way of example, the glass substrate of the multilayer, glass-plastic sun roof 11 may consist of a single sheet of tempered glass 14, while the primarily glass substrate of the windshield 10 may be conventional laminated safety glass comprising two sheets of glass 15 and 16 bonded together under heat and pressure by an interposed layer 17 of plastic.

In the illustrated embodiment of the windshield 10, the plastic interlayer 17 of the laminated glass is a .030 inch thick sheet of the high penetration resistant polyvinyl butyral disclosed in U.S. Patent No. 3,231,461, while the glass sheets 15 and 16 are sheets of float glass in thicknesses between .085 inch and .110 inch, bonded to the interlayer 17 with the "bath surfaces out", as described in U.S. Patent No. 3,708,386.

Similarly, in the sun roof embodiment, the single glass sheet 14 is of semitempered or partially heat-treated, float glass approximately .100 inch thick and with its "bath" surface to the outside. Also, the glass in the sun roof is preferably tinted, colored, rendered phototropic or otherwise provided with means for filtering light.

Although some specific glass types and thicknesses have been set forth above, the glass substrate of the glazing structures may be in sheets or layers that vary from approximately .040 inch up to 1/8 inch and beyond in thickness and any plastic interlayers within these glass parts may be in thicknesses between .015 inch and .060 inch. For this reason it may also be necessary or desirable to somewhat vary the thickness and/or make-up of the plastic in the protective cover 18 carried by the substrate and which, as shown in Figures 2 to 4, may be a multiple layer structure and is bonded to the inboard glass surface of the substrate.

As explained above, among the important considerations for the glazing structure of this invention is that it be capable of acting to decelerate and resist penetration by a human head or other object thrown against it while, at the same time, presenting an exposed surface capable of effectively withstanding atmospheric exposure and the wear to which the inboard side of every automotive glazing is subjected during normal continuing usage.

As will be seen most clearly in Fig. 4, the shield or cover 18 is a multilayer structure and the thickness of its layers as indicated there are best for incorporation into a windshield glazing that includes a laminated glass substrate, such as has been described in connection with Fig. 3. More particularly, this shield 18 comprises an approximately 15 mil (.015 inch) thick layer 19 of a relatively soft, extensible plastic material such as polyvinyl butyral, adhered to the inboard surface of the inboard glass sheet 16 an approximately 7 mil (.007 inch) thick layer 20 of a higher modulus, indentation resistant plastic such as a polyethylene terephthalate of the character sold by E. I. du Pont de Nemours & Co. under their registered trademark "Mylar" or by Celanese Corporation of America under their registered trademark "Celanar"; and an approximately .110 ml (.00011 inch) thick coating or layer 21 of a harder and abrasion resistant material which can be described generically as a cured, organopolysiloxane compound reinforced with silica and more specifically as a fully cured, silica reinforced methyl siloxane such as produced by Dow Corning Corporation as their "C-resin" (registered trademark).

It is evident from this that the separate materials of which the glazing structures of this invention are composed may be known and available commercially. However, when these materials as individual components are combined and used in the manner contemplated by this invention and employing the procedure described, surprisingly new, useful and unexpected results are obtained.

For example, in the particular shield structure of Fig. 4, the layer 19 may be said to function primarily as an adhesive, but it also acts to cushion impact and, because of its elasticity and extensibility, to assist in resisting penetration by the head of a driver or passenger that may be thrown against the windshield.

The layer 20 with its greater indentation resistance, functions to protect the softer layer 19 and, by reason of its tensile strength, further contributes to the penetration resistance of the structure while acting as a carrier for the abrasion resistant coating layer 21. Both of the layers 19 and 20 are nonlacerative, even when an impact occurs that is of suffiсent magnitude to penetrate the plastic shield and the layer 21 presents a surface hard enough to resist wear, weathering and other abuse without itself constituting a lacerative hazard.

Still more specifically, the plastic in the layer 20 may be in thicknesses of from 1/2 to 14 mils and, when polyethylene terephthalate is used, adequate adhesion to the layer 19 can be ensured by subjecting it to a surface conditioning treatment, which may be carried out electrically or chemically, but is preferably done by direct contact with a gas flame for a length of time sufficient to alter the surface characteristics but not the bulk properties of the material. However, in lieu of the polyethylene terephthalate, other terephthalate esters and other plastic materials including polyesters, polycarbonates, polyurethanes and acrylics may be employed.

Whatever the materials used in its layers, however, the matter of the overall thickness of the protective multilayer plastic cover or shield 18 is significant.

Thus, the layer 20 of polyethylene terephthalate, as the indentation resistant plastic, that is no more than .0005 inch to .014 inch thick, will ensure the glass-plastic glazing passing the "cold test". However, to provide indentation resistance and avoid marking, the layer 20 alone should be between about 5 and 10 mils thick. At the same time, to ensure adequate balance between penetration resistance and a Severity Index within the acceptable range, the combined thicknesses of the interlayer 17 (of the laminated glass part of the unit) and the adhesive layer 19 of the shield should not exceed .065 inch and the combined thicknesses of layers 17, 19 and 20 should not exceed .075 inch.

In this connection, when the substrate of the glazing is a single glass sheet, as in the window or the sun roof structure of Fig. 2, it is well to increase the thickness of the adhesive layer 19 for example, from the .015 inch preferred with the three-ply laminated glass substrate of Fig. 3, to .030 inch.

In producing the glazing units of the invention, it has been found practicable to coat the layer of indentation resistant plastic 20 of the protective shield with the harder, abrasion resistant layer or coating 21 and so utilize the layer 20 as a carrying sheet prior to incorporating it with the abrasion resistant layer 21 thereon, into either a single glass layer structure such as the sun roof panel of Fig. 2 or the windshield structure of Fig. 3 as the protective cover or shield 18.

The abrasion resistance of the fully cured, silica reinforced organopolysiloxane compound of the layer 21 of this invention was found to exceed that of any material previously considered for the purpose. It was obtained from Dow Corning Corporation as their "C-Resin" and as such, was furnished in a 22.5 percent resin solids solution.

However, while a coating of the so obtained resin solution, flow coated onto an untreated polyethylene glycol terephthalate carrying sheet, appeared clear and bright, it exhibited a lack of adhesion to the polyester, as judged by the 40 ounce tape test and a decided tendency to craze. Nevertheless, by the procedures described in the following examples, various kinds of indentation resistant plastic materials were flow coated with the silica reinforced, organopolysiloxane compound in a manner that successfully prepared them for incorporation, as the protective cover or laceration shield, into commercially practicable multilayer, glass-plastic automotive glazing units.

Example I

Sheets of polyethylene terephthalate biaxially stretched but with no surface treatment, were cleaned with isopropanol, air dried, primed by flow coating with a solution of 1/2 percent beta-(3,4 epoxy cyclohexyl) ethyl trimethoxysilane in butanol, air dried and then heated for 30 minutes at 120°C. A silica reinforced organopolysiloxane compound (Dow Corning's "C-resin"), was diluted with butanol to 15 percent solids, flow coated over the so treated sheets at 30 percent relative hudimity and then air dried and cured for 4 hours at 120°C.

Example II

Sheets of polyethylene terephthalate were coated as in Example I, except that the cleaned and dried sheets were primed by flow coating with 1/2 percent gamma-glycidoxypropyltrimethoxysilane in butanol, air dried and then heated for 30 minutes at 120°C.

Example III

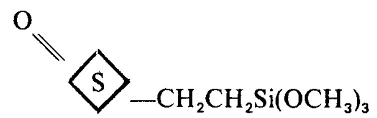
Sheets of polyethylene terephthalate were processed as in Example I except that the cleaned and dried sheets were primed with 1/2 percent gamma-aminopropyl triethoxysilane in a butanol solution. The solvent was allowed to air dry and then the sheet was overcoated with a 1 percent solution of "Acryloid AT-50" (registered trademark), a member of a family of thermosetting acrylic resins made by Rohm and Haas, in 50 percent butanol and 50 percent cellosolve before applying the final resin coating.

The primers of Examples I and II may be represented by the generic formula:

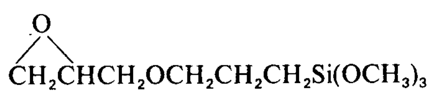
$$R{-}Si{-}(OCH_3)_3$$

where R is an aliphatic organic radical containing an epoxide group.

The primer of Example I may be represented by the specific formula:



and the primer of Example II by the specific formula:



The primer system of Example III is a specific member of a family of primers that can be represented by a silane in conjuction with a thermosetting acrylic resin.

The coatings on the sheets of Examples I through III passed the 40 ounce tape test before and after being incorporated into multilayer units in accordance with the invention and the abrasion resistance of the coatings were determined on the Taber Abrader before and after exposure in the Weather-Ometer for over 500 hours facing the light with the following results:

		Percent Haze		
Example I	Original	100 Rev.	200 Rev.	300 Rev.
Unexposed	1.9	2.7	4.2	4.0
Exposed	1.3	2.5	4.1	5.2

		Percent Haze		
Example II	Original	100 Rev.	200 Rev.	300 Rev.
Unexposed	1.0	2.6	3.3	3.0
Exposed	1.6	2.0	3.0	4.6

		Percent Haze		
Example III	Original	100 Rev.	200 Rev.	300 Rev.
Unexposed	1.4	2.0	2.5	4.0
Exposed	1.5	2.1	2.8	4.1

The Taber abrasion test is described in ASTM Test D-1044-56. Specifically, for the instant purpose, a 500 gram load was applied to the CS-10F wheels and the percent of haze in the track of the test was determined after 100, 200 and 300 revolutions, respectively.

For purposes of comparison, uncoated control samples of the polyethylene terephthalate sheets, of polymethylmethacrylate sheets and of polycarbonate sheets were subjected to this same test with the following results:

	Percent Haze		
	100 Revs.	200 Revs.	300 Revs.
Polyethylene terephthalate	47.0%		
Polymethylmethacrylate	36.5%	36.6%	37.8%
Polycarbonate	40.0%	45.6%	46.0%

In the case of the polyethylene terephthalate, the uncoated control sample was considered worthless for vision after 100 revolutions and the test discontinued.

In additional Examples IV, V and VI, the procedures of Examples I, II and III, respectively, were used in priming and coating .007 inch thick sheets of du Pont's flame treated, uniaxially stretched "Mylar" (polyethylene terephthalate) instead of the biaxially stretched, untreated "Celanar" (polyethylene terephthalate) sheets of Examples I to III. The coated sheets of Examples IV, V and VI were exposed and tested in the manner reported for Examples I, II and III and similar results obtained.

The only significant difference noted between the treated and untreated types of polyethylene terephthalate sheeting is that a silica reinforced organopolysiloxane coating will exhibit initial adherence (as determined by the tape and Taber tests) to the flame treated "Mylar" used in Examples IV, V and VI without the priming step described therein. However, such directly applied coatings lose their adhesive properties after even short exposure in the Weather-Ometer.

Coated sheets, produced as described in Examples I to VI, when bonded to a compatible glass part in the manner described in connection with Figs. 1 to 4, constitute glazing units as contemplated by this invention.

The shield 18 described above for use with a glass substrate can, as well, be used with a plastic substrate where desired.

While a 15 percent solids solution of the coating material is considered best, solutions containing from 12 to 18 percent can be employed. Similarly, butanol is considered the best solvent because it lends desirable coating properties to the solution, but other solvents may be used and various relative humidities below 35 percent with curing times as low as 1-1/2 hours have given acceptable results.

WHAT WE CLAIM IS:—

1. A transparent, temperature stable glazing structure consisting essentially of a transparent substrate with a protective shield thereover that comprises a layer of a relatively soft and extensible plastic having one surface bonded to a surface of said substrate, a carrying sheet in the form of a thin layer of indentation resistant plastic having one surface bonded to the free surface of said layer of relatively soft and extensible plastic, and an abrasion resistant coating on and tightly adhered to the opposite surface of said carrying sheet, said abrasion resistant coating comprising a fully cured, silica reinforced, organopolysiloxane compound.

2. A glazing structure as claimed in Claim 1, characterised by said substrate being a sheet of approximately .100 inch thick float glass, said relatively soft plastic layer being of polyvinyl butyral in a thickness between .015 inch and .030 inch, and said thin indentation resistant plastic layer being of a polyester in a thickness between .005 inch and .014 inch.

3. A glazing structure as claimed in either of claims 1 or 2, characterized by said abrasion resistant coating being composed of a silica reinforced methyl siloxane.

4. A method of producing a transparent, temperature stable, multilayer structure, comprising the steps of treating a clean surface of a carrying sheet of penetration resistant plastic to promote adhesion, coating said treated surface with a solution of silica reinforced organopolysiloxane compound containing from 12 to 18 percent resin solids, and incorporating said coated carrying sheet into said structure by bonding one surface of a layer of a relatively soft and extensible plastic to the uncoated surface of said carrying sheet and the opposite surface of said soft and extensible layer to a surface of a transparent substrate.

5. A method as claimed in claim 4, characterised by said treating of said surface comprising priming the same with a primer selected from a group represented by the generic formula $R—Si—(OCH_3)_3$ where R is an aliphatic organic radical containing an epoxide group, and members of a family of primers represented by a silane in conjunction with a thermosetting acrylic resin.

6. A method as claimed in Claim 5, characterised by said primer being 1/2 percent beta-(3,4-epoxy cyclohexyl) ethyl trimethoxysilane, said silica reinforced

organopolysiloxane solution containing approximately 15 percent solids, and said primed surface being heated before coating.

7. A method as claimed in claim 6, characterised by said clean surface being primed by flow coating the same with a 1/2 percent solution of said primer in butanol, drying and then heating the dried coating for 30 minutes at 120°C., and by the primed sheet being coated by diluting said solution of silica reinforced organopolysiloxane from a solution having a higher percentage of solids with butanol, and flow coating said diluted solution over the primed sheet at approximately 30 percent relative humidity, drying the coating, and then curing the dried coating for 4 hours at 120°C.

8. A method as claimed in claim 5, characterised by the primer being 1/2 percent gamma-glycidoxypropyltrimethoxysilane.

9. A method as claimed in Claim 4, characterised by said clean surface being treated to promote adhesion with a solution of glacial acetic acid.

10. A transparent, temperature stable glazing structure substantially as described with reference to, and as shown in, the accompanying drawings.

11. A method of producing a transparent, temperature stable, multilayer structure substantially as herein described with reference to the accompanying drawings.

LEWIS W. GOOLD & CO.,
Chartered Patent Agents,
St. Martin's House,
Bull Ring,
Birmingham B5 5EY
Agents for the Applicants.

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1580353 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

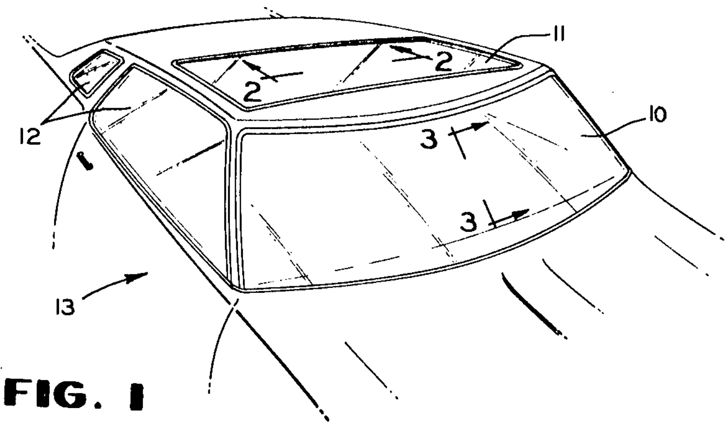

FIG. 1

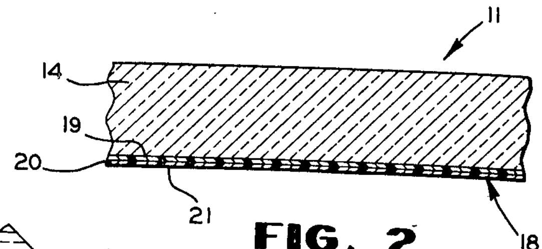

FIG. 2

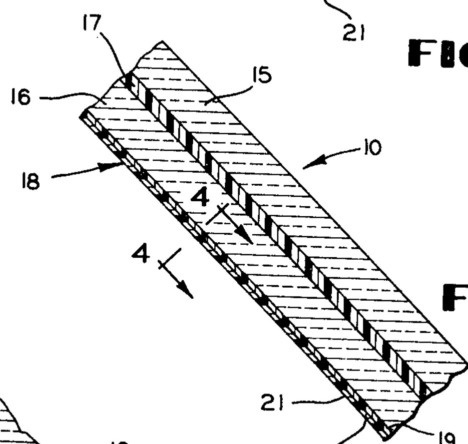

FIG. 3

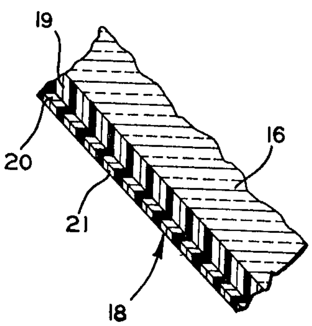

FIG. 4

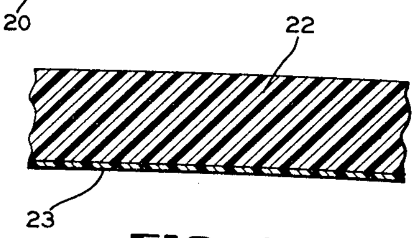

FIG. 5