Convention Application for a Patent

30456/84

We, SAINT-GOBAIN VITRAGE,
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hereby apply for the grant of a Patent
for an invention entitled "LAMINATED SAFETY PANE"

which is described in the accompanying complete specification.

This application is a Convention application and is based on the application numbered 8311507 for a patent or similar protection made in France on 11th July, 1983.

Our address for service is: CALLINAN & NEWTON, Patent Attorneys, of 48-50 Bridge Road, Richmond, State of Victoria, Australia.

Dated this 10th day of July, 1984.

SAINT-GOBAIN VITRAGE
By our Patent Attorneys:
CALLINAN AND ASSOCIATES
Short Title: LAMINATED GLASS

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Complete Spec: 17/10

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Application No: AU-A30456/84

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Actual Invention: 1. A laminated pane comprising a glass sheet and a transparent layer of plastics material, characterised in that the layer of transparent plastics material has properties of absorption of energy and internal protection defined by a resistance to scratching greater than 20 grams measured with the Erichsen type 413 apparatus and a resistance to abrasion according to European standard EN3 such that the difference in hardness is less than 4%.

3. Laminated pane according to one of Claims 1 to 2, characterised in that the layer of plastics material is formed essentially of a polyurethane obtained by reactive casting continuously on a flat horizontal support of a reaction mixture of an isocyanate component and a polyol component, the isocyanate component comprising at least one aliphatic or cycloaliphatic diisocyanate or a polyisocyanate prepolymer, this component having a viscosity measured at 40°C less than about 5000 centipoises, the polyol component comprising at least one long polyol which is difunctional of molecular weight from 500 to 4000 and at least one short diol as a chain lengthening agent.
COMPLETE SPECIFICATION
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Complete Specification for the invention entitled: "LAMINATED SAFETY PANE"

The following statement is a full description of this invention, including the best method of performing it known to the applicant.

* The text description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 130 mm in width, on rough white paper of good quality and it is to be inserted inside this form.
Laminated Safety Pane

The inventor relates to a new laminated pane comprising a glass sheet and a single layer of plastics material.

Laminated panes known as safety panes are generally composed of two glass sheets and an intermediate layer having the property of absorbing energy, generally of polyvinylbutyral. One of the disadvantages of this type of laminated pane when it is used as a windscreen for a vehicle, is that in the case of impact of the head of the occupant of the vehicle with the pane the edges of the internal glass sheet which is broken may cause lacerations and other injuries. This is why it has been suggested for example in French Patent Publication 2 187 719 and 2 251 608 to apply to this glass sheet inside the vehicle a sheet of plastics material formed essentially of a thermohardening polyurethane which has anti-laceration properties. Further, this sheet of plastics material is self-healing, that is to say it is of a material in which superficial damage or local impressions disappear rapidly, the speed of disappearance being a function of the nature of the damage and the temperature of the plastics material.

It has also been suggested for example in French Patent Publication 2 398 606 to provide a laminated pane comprising a glass sheet, a thermoplastics layer having properties of absorption of energy and a self-healing coating layer resistant to scratches formed essentially of a thermohardening polyurethane. In this type of pane each of the layers fulfills a particular function, the thermoplastics layer fulfilling essentially the function of absorbing energy but being insufficiently resistant to abrasion or other exterior effects and the coating layer fulfilling the function of protection of the layer absorbing energy but not having itself good properties of energy absorption.
It has already been suggested for example in Patents Publications US-3 509 015 and US-3 808 077 to provide laminated panes comprising a glass sheet and a single layer of plastics material having properties of absorption of energy. This type of pane has not apparently given entire satisfaction, probably because of an insufficient resistance to abrasion and scratching of the layer of plastics material used as the external layer.

It is known in a general way that a structure of a laminated pane comprising a single layer of plastics material having simultaneously the properties of absorbing energy and a good resistance to scratching and to attack by exterior agents was unlikely to be satisfactory. In fact, for a man in the art there exists a certain incompatibility between the functions of absorbing energy and resistance to scratching for a single layer. For the layer to have properties of absorption of energy it is believed that it has to have an essentially thermoplastic character. On the other hand, for the layer to have a good resistance to scratching it is believed that it has to have an essentially thermohardening character with a cross-linked structure. These mechanical properties associated with thermoplastic or thermohardening characteristics are described for example in French Patent Publication 2398606 and European Patent Publication 0054191.

There has now been found a single layer of plastics material which, in a laminated pane structure in which it is associated with a glass sheet fulfills the function of absorbing energy, protection against fragments of glass and which also has a good resistance to abrasion and scratching and to different attacks from exterior agents.

The layer according to the invention is formed in a process which is continuous by reactive casting on a flat horizontal support from which it may be detached, of a
reaction mixture of an isocyanate component and a component having active hydrogens, notably a polyol component, the isocyanate component comprising at least one aliphatic diisocyanate or a cycloaliphatic diisocyanate or a diisocyanate prepolymer, this component having a viscosity measured at 40°C less than about 5000 centipoises and the polyol component comprising at least one long polyol which is difunctional of molecular weight from 500 to 4000 and at least one short diol as a chain lengthening agent.

By reactive casting is meant casting in the form of a layer or film of a liquid mixture of components in the monomeric or prepolymeric state followed by polymerisation of this mixture by heating. This reactive casting which forms the layer having good mechanical and optical properties will be described more completely in the following description.

The proportions of components of the polyurethane are chosen to obtain preferably a balanced stoichiometric system, that is to say the ratio of equivalent NCO groups provided by the diisocyanate component to equivalent OH groups provided by the polyol component, that is to say the long polyol or polyols and the short diols is of the order of 1. When the ratio NCO/OH is less than 1, the more it decreases the more the desired mechanical properties for this application become less satisfactory. When all the components of the polyurethane are difunctional the lower limit of the NCO/OH ratio for obtaining satisfactory mechanical properties is about 0.9. When one of the components at least is trifunctional this low limit may be lowered to about 0.8. When the ratio NCO/OH is greater than 1, the more it increases and the greater become certain mechanical properties of the layer obtained by reactive casting, for example the layer becoming more rigid, but given the higher cost of the isocyanate component with respect of that of the polyol component,
the choice of a ratio NCO/OH substantially equal to 1 is a good compromise between the properties obtained and the cost.

The proportions between the long polyol and the short diol may vary as a function of the desired properties as indicated in the following, the number of OH group equivalents due to the short diol however representing generally from 20 to 70% of the total group equivalents of the mixture forming the polyol component in the case where the ratio of OH groups is of the order of 1. When the proportion of short diol is increased, the layer is hardened and its modulus is generally increased.

Suitable diisocyanates which may be used in the invention are chosen especially from the difunctional aliphatic isocyanates following: hexamethylenediisocyanate (HMDI), 2,2,4-trimethyl 1,6-hexanediisocyanate (TMDI), bis 4-isocyanatocyclohexylmethane (Hylene W) bis 3-methyl-4-isocyanatocyclohexylmethane, 2,2 bis (4-isocyanatocyclohexyl) propane, 3-isocyanatomethyl-3,5,5 trimethylcyclohexyl-isocyanate (IPDI), m-xylenediisocyanate (XDI), m-and p-tetramethylyxylenedi-isocyanate (m- and p-TMXDI), trans-cyclohexane-1,4 diisocyanate (CHDI), and 1,3-(diisocyanatomethyl)-cyclohexane (hydrogenated XDI).

IPDI is preferably used especially for reasons of cost.

According to one of the aspect of the invention there is used an isocyanate component containing urea functions. These urea functions improve certain mechanical properties of the layer. The content of the urea may be up to about 10% of the total weight of the isocyanate component having urea functions. Preferably the content of the urea is from 5 to 7% by weight of the total of said component. For the reason mentioned previously there is
preferably used 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate comprising urea functions (IPDI and derivatives thereof).

The long polyols which are suitable are chosen from polyether diols and polyester diols of molecular weight 500 to 4000; the polyester diols being products of esterification of a diacid such as adipic acid, succinic acid, palmitic acid, azelaic acid, sebacic acid, orthophthalic acid and a diol such as ethyleneglycol, propanediol -1,3, butanediol -1,4, hexanediol -1,6, and polyether diols of general formula

\[ H \left[ \begin{array}{c} \text{O} \\ (\text{CH}_2)_n \end{array} \right] m \text{ OH} \]

where \( n \) = 2 to 6; \( m \) is such that the molecular weight is situated in the range 500 to 4000, or polyether diols of general formula:

\[ H \left[ \begin{array}{c} \text{CH}_3 \\ \text{OCH} - \text{CH}_2 \end{array} \right] m \text{ OH} \]

where \( m \) is such that the molecular weight is also situated in the range 500 to 4000. It is also possible to use polycaprolactonediols.

There is used preferably a polytetramethyleneglycol (\( n = 4 \)) of molecular weight also equal to about 1000.

The lengthening agents for chains which may be used are the short diols such as ethyleneglycol, propanediol-1,2, propanediol-1,3, butanediol-1,2, -1,3 and -1,4, dimethyl-2,2-propanediol-1,3 (neopentyglycol), pentanediol-1,5, hexanediol-1,6, octanediol-1,8, decanediol-1,10, dodecanediol-1,12, cyclohexanediethanol, bisphenol A, methyl-2 pentanediol-2,4, methyl-3 pentanediol-2,4, ethyl-2 hexane-diol-1,3, trimethyl-2,2,4-pentanediol-1,3, diethylene-glycol, triethyleneglycol, tetraethyleneglycol, butyne-2-diol-1,4, and substituted
and/or etherified decynediol, hydroquinone-bis-hydroxyethylether, bisphenol A etherified by two or four propylene oxide groups and dimethylolpropionic acid. In general the shorter the diol the harder the layer.

There is preferably used butanediol-1,4 which is a good compromise to obtain a layer which is neither too hard nor too soft which is desired for this type of application.

One of the characteristics of the layer according to the invention is that it is obtained by reactive casting on a flat horizontal support, this reactive casting being already described in French Patent Publication 2 442 128 for obtaining a layer of thermohardening polyurethane from a mixture of trifunctional components providing in surprising manner, according to the invention, in the case of difunctional starting components, a layer which is not entirely thermoplastic when the group NCO/OH ratio is substantially equal to or greater than 1.

Reactive casting implies a rapid polymerisation reaction so that the layer may be formed in a time compatible with industrial manufacture. This requires a higher temperature, of the order of about 100 to 140°C, the temperature at which the secondary reactions of branching which are produced creating for example allophanate groups or biurets between the polyurethane chains, such as:

\[
\begin{align*}
- R &- NH - CO - O - R' - O - \\
OCN &- R - NCO \\
- R &- NH - CO - O - R' - O - \\
\end{align*}
\]

\[
\begin{align*}
- R &- N - CO - O - R' - O - \\
&\text{allophanate} \\
\end{align*}
\]

\[
\begin{align*}
- R &- N - CO - R' - O - \\
\end{align*}
\]
In these operating conditions, even with difunctional components, when the NCO/OH ratio is substantially equal to or greater than 1, as indicated before, the product obtained is not completely thermoplastic; in fact it is infusible and insoluble in the majority of solvents for polyurethanes such as tetrahydrofuran and dimethylformamide. This does not present any disadvantage when the layer is already formed; on the contrary, advantage is taken of the improved mechanical properties for the layer especially regarding the stress at the start of flow $y$, the stress at rupture $R$, elongation at rupture $R$, and resistance to the start of tearing $R_a$, the resistance to scratching measured in the ERIKSEN test as described below, or the resistance to abrasion, in comparison with an equivalent system polymerised at low temperature when only a linear polycondensation is produced.

When the NCO/OH ratio is less than 1 and of the order of 0.8 to 0.9, a reticulation of the type described above is produced only to an insignificant extent.
In one embodiment of the layer of polyurethane according to the invention, the polyol component may contain a small proportion of at least one polyol of functionality greater than two and especially the monomeric aliphatic triols such as glycerol, trimethylolpropane, triols having polyether chains and polycaprolactone triols, the molecular weight of these triols generally being from 90 to 1000, and mixed polyether/polyester polyols of functionality greater than 2, for example of functionality from 2 to 3. The addition of a polyol of functionality greater than 2 gives supplementary bridging connections between the polyurethane chains and may thus increase the cohesion of the layer.

The proportions of the long polyol, the short diol and possibly the polyol of functionality greater than 2 may vary according to the desired properties. There are generally chosen proportions such that for one hydroxyl equivalent the long polyol represents about 0.3 to 0.45 equivalent, the short diol about 0.2 to 0.7 equivalent and the polyol of functionality greater than 2, about 0 to 0.35 equivalent. In these conditions the layer has the following mechanical characteristics measured according to standards AFNOR/NFT 46.002, 51 034 and 51 108.

- A stress at the start of flow $\sigma^{-y}$ at $-20^\circ$C less than or equal to 3 daN/mm$^2$,
- A stress at rupture $\sigma^{-R}$ at $+40^\circ$C greater than or equal to 2 daN/mm$^2$,
- An elongation at rupture $\varepsilon^{-R}$ at $+20^\circ$C from 250 to 500%,
- A resistance to the start of tearing $R_a$ at $+20^\circ$C greater than or equal to 9 daN/mm thickness,
- A resistance to scratching greater than 20 g measured according to the test described below,
- Resistance to tearing greater than 4%,
- According to the product's material component, example 1.

One triisocyanate is used: 4,4'-diisocyanatodiphenylmethane (MDI 300) and 4,4'-diisocyanatodiphenyl (HMDI) content, catalysts containing an active silicon component and 1,8-cyclododecane diisocyanate. The layer contains additives by reaction with a thickener and by reaction with a catalyst such as dibutyltin dilaurate. The silicone contains 30% piperidyl groups.

Examples of plastics in the form of thin layers.
Resistance to abrasion, with a difference in haze less than 4% measured according to the abrasion test indicated below.

According to one of the aspects of the invention, a part of the polyol component may be replaced by a different product having active hydrogens such as an amine.

According to another embodiment of the layer of plastics material according to the invention, the isocyanate component may contain within limited proportions, for example less than about 15% in NCO equivalents, at least one triisocyanate such as a isocyanate biuret or a triisocyanurate.

To fulfill all the functions which are demanded, the polyurethane layer according to the invention should have a thickness generally greater than 0.4mm and preferably greater than 0.5mm.

The layer according to the invention may contain various additives which generally serve to facilitate manufacture by reactive casting. It may contain a catalyst such as a tin catalyst for example tin dibutyldilaurate, tributyltin oxide, tin octoate, an organomercuric catalyst, for example mercuricphenylester, an amine catalyst such as for example diazabicyclo-(2,2,2)-octane, and 1,8-diazabicyclo (5,4,0)-1 deoene-7. The layer may contain stabilisers such as bis (2,2,6,6-tetramethyl-4-piperidyl)sebacate, and a phenolic antioxidant.

The layer may also contain a spreading agent such as a silicone resin, a fluoroalkyl ester, or an acrylic ester.

Examples of manufacture of laminated panes and the layer of plastics material used for this manufacture are described in the following.
Example 1

To make the layer of plastics material, there is first prepared the polyol component by mixing a polytetramethylene glycol of molecular weight 1000 (for example the product sold commercially under the name Polymeg 1000 by the QUAKER OATS company, with butanediol-1,4, the proportions of the two constituents being such that the polytetra-methyleneglycol contributes 0.37 equivalent of hydroxyl groups whereas the butanediol-1,4 contributes 0.63.

To the polyol component there is added a stabiliser in an amount of 0.5% by weight of the total weight of polyol component and isocyanate component, a spreading agent in an amount of 0.05% by weight calculated in the same way and a dibutyltin dilaurate catalyst in an amount of 0.02% by weight calculated in the same way.

The isocyanate component used is 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (IPDI) having urea functions obtained by partial hydrolysis of IPDI and having a content of NCO groups of about 31.5% by weight.

The components are used in quantities such that the NCO/OH ratio is 1. After degassing under vacuum of the components, the mixture brought to 40°C is cast by means of a casting head such as that described in French Patent Publication 2 347 170 on a movable glass support covered with a separating agent. There is thus formed a layer of homogeneous thickness of about 0.755 mm thickness which is subjected to a polymerisation cycle, that is to say a temperature of 120°C for about 25 minutes.

After polymerisation, the layer is removed from the support of glass and forms a sheet which may be stored or used just after for manufacture of laminated panes.
To make the pane there is assembled a sheet of plastics material with a sheet of 2.6mm thickness of heated glass. The glass may possibly be hardened or tempered. This assembly may be carried out in two stages, a first stage consisting of a preliminary assembly obtained by passage of the elements forming the pane between two rollers of a calendar and it is possible to use for this purpose a device described in European Patent Publication 0015209, and a second stage consisting of putting the laminated product in an autoclave where, for about one hour it is subjected to a pressure of about 10 bars at a temperature of about 130°C. This autoclave cycle may possibly be replaced by a stoving cycle at normal pressure.

The pane obtained has an excellent optical quality and a perfect transparency.

The adhesion obtained between the glass sheet and the sheet of plastics material is measured by a peel test described below.

There is cut a strip of 5cm width from the covering layer. The end of the strip is unstuck and there is applied thereto a pulling force perpendicular to the surface of the glass at a pulling speed of 5 cm per minute. The operation is carried out at 20°C. There is noted the pulling force required for unsticking of the strip. Operating in this way there is obtained a pulling force of 10 daN/5cm.

Trials for resistance to shock at different temperatures are carried out on the pane made according to the example.

A first trial for resistance to shock is carried out at +20°C with a steel ball weighing 2.260 kg (heavy ball test) which is allowed to fall onto the central part of a square glass sample of 30.5 cm side, held on a rigid frame. There is determined the approximate height for
which 90% of the samples tested at the chosen temperature resist fall of the ball without the ball passing through.

For the laminated pane according to the example, the value obtained is 12 metres.

Another trial for resistance to shock is carried out with a steel ball of 0.227 kg weight at 38mm diameter. One trial is carried out at a temperature of -20°C. Another trial is carried out at a temperature at +40°C. The values obtained are respectively 12 and 11 metres.

Taking account of European standard R43 which is in force, the desired results are at least 4 metres for the heavy ball, at least 8.5 metres for the light ball at -20°C and at least 9 metres for the light ball at +40°C.

The resistance to scratching is measured by a known scratch test called MAR resistance test which is carried out with an ERICHSEN apparatus, type 413. There is measured the load applied on a diamond head to introduce a persistent scratch on the layer of plastics material assembled with a glass support. The load should be greater than or equal to 20 grams for the layer of plastics material to have the property of being self-healing.

The resistance to scratching measured according to this test, for the pane according to the example is 32 grams.

The resistance to abrasion is measured according to European standard R43. For this purpose, an assembled sample of pane is subjected to abrasion by means of an abrasive mill. After 100 rotations in abrasion, there is measured with a spectrophotometer the difference in haziness between the abraded part and non-abraded part. The difference in haziness (Δhaze) has to be less than 4% for the layer to have anti-abrasive qualities.
A long polyol which is difunctional of molecular weight from 500 to 4000 and at least one short diol as a chain lengthening agent.

The layer according to the example has a difference in haze of 0.94%.

The pane according to the example has all the characteristics which render it suitable for use as a vehicle windscreen.

Example 2

The procedure of Example 1 is followed except that the polyol component is formed of a mixture of polytetramethylene glycol of molecular weight 1000, butanediol 1,4 and polycaproactonetriol (for example the product sold commercially under the name Niax 301 by UNION CARBIDE) in respective proportions such that for one total hydroxyl equivalent, there is used 0.35, 0.45 and 0.20 hydroxyl equivalent.

There is made a layer of 0.70mm thickness. The pane obtained shows mechanical and optical characteristics which are completely satisfactory. The values measured in different tests are as follows:

- an adhesion of 11 daN/5cm, values of 8 metres with a heavy ball, 11 at 11 metres respectively with a light ball at -20°C and +40°C.

- a resistance to scratching of 35 g and a difference in haze on abrasion of 1.2%.

The pane made according to the example is thus suitable for use as a windscreen.

Example 3

The procedure of Example 2 is followed except that the proportions between the different polyols are such that for an equivalent total hydroxyl there is used 0.35, 0.55 and 0.10 hydroxyl equivalent respectively for the long
polyol, the short diol and the triol.

There is formed a layer of 0.66 mm thickness. The values measured in different tests are as follows:

- an adhesion of 11 daN/5 cm, values of 10 metres with the heavy ball, 13.5 and 13.5 metres with the light ball at -20°C and +40°C respectively, a resistance to scratching of 25 g, and a difference in haze on abrasion of 1.2%.

The pane made, according to the example, is thus capable of being used as a windsreen.

Example 4

The procedure of Example 1 is followed except that polymerisation of the layer is carried out at a temperature of 60°C only for 20 hours.

Trials for resistance to shock give a value with a small ball of -20°C at 6.5 metres which is insufficient.

This example, compared with Example 1 shows the effect of the polymerisation temperature used during reactive casting. In this case this temperature is too low.
fulfilling the function of protection of the layer absorbing energy but not having itself good properties of energy absorption.
The layer according to the invention is formed in a process which is continuous by reactive casting on a flat horizontal support from which it may be detached, of a

The claims defining the invention are as follows:

1. A laminated pane comprising a glass sheet and a transparent layer of plastics material, characterised in that the layer of transparent plastics material has properties of absorption of energy and internal protection defined by a resistance to scratching greater than 20 grams measured with the Erichsen type 413 apparatus and a resistance to abrasion according to European standard R43 such that the difference in haze is less than 4%.

2. Laminated pane according to Claim 1, characterised in that the layer of plastics material has at a thickness of about less than 0.5mm a stress at the start of flow $\sigma_y$ at $-20^\circ C$ less than or equal to 3 daN/mm$^2$, a stress at rupture $\sigma_R$ at $+20^\circ C$ greater than or equal to 2 daN/mm$^2$, a lengthening at rupture $\xi R$ at $+20^\circ C$ from 250 to 500% and a resistance to start of tearing $R_a$ at $+20^\circ C$ greater than or equal to 9 daN/mm.

3. Laminated pane according to one of Claims 1 to 2, characterised in that the layer of plastics material is formed essentially of a polyurethane obtained by reactive casting continuously on a flat horizontal support of a reaction mixture of an isocyanate component and a polyol component, the isocyanate component comprising at least one aliphatic or cycloaliphatic diisocyanate or a diisocyanate prepolymer, this component having a viscosity measured at 40$^\circ C$ less than about 5000 centipoises, the polyol component comprising at least one long polyol which is difunctional of molecular weight from 500 to 4000 and at least one short diol as a chain lengthening agent.
4. Laminated pane according to one of Claims 1 to 3, characterised in that the isocyanate component contains urea functions, the content of the urea being able to reach 10% of the total weight of the isocyanate component, preferably this content of urea being from 5 to 7%.

5. Laminated pane according to one of Claims 1 to 4, characterised in that the isocyanate component comprises 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate.

6. Laminated pane according to one of Claims 1 to 5, characterised in that the isocyanate component and the polyol component are used in such quantities that the ratio of equivalent isocyanate groups to equivalent hydroxyl groups is about 1.

7. Laminated pane according to one of Claims 1 to 6, characterised in that the proportions between the different polyols are chosen such that the number of equivalent hydroxyl groups due to the short diol represents 20 to 70% of the total of the hydroxyl groups.

8. Laminated pane according to one of Claims 1 to 7, characterised in that the isocyanate component is formed essentially of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate having urea groups and in that the polyol component is formed essentially of polytetramethylene glycol and butanediol-1,4.

9. Laminated pane according to one of Claims 1 to 8, characterised in that the polyol component comprises further at least one polyol of functionality greater than 2.

10. Laminated pane according to Claim 9, characterised in that the polyol of a functionality greater than 2 is a polycaprolactonetriol.
11. Laminated pane according to one of Claims 1 to 10, characterised in that for one total hydroxyl equivalent, the long polyol has 0.30 to 0.45 equivalent, the short diol 0.2 to 0.7 equivalent and the polyol of functionality greater than 2 has 0 to 0.35 equivalent.

12. Laminated pane according to Claim 1 to 11, characterised in that the polyurethane layer having properties of absorption of energy and internal protection comprises additives such as a catalyst, spreading agent and a stabiliser.

13. Laminated pane according to one of Claims 1 to 12, characterised in that the layer of transparent plastics material is obtained by a reactive casting using a temperature of polymerisation greater than 80°C.

14. Laminated pane according to one of Claims 1 to 13, characterised in that the isocyanate component further contains at least one triisocyanate.

15. A laminated pane as claimed in claim 1, substantially as described herein with reference to any one of the Examples.

DATED this 10th day of July, 1984.

SAINT-GOBAIN VITRAGE
By our Patent Attorneys:
CALLINAN AND ASSOCIATES