



(51) International Patent Classification:

B32B 7/02 (2006.01) **B32B 27/30** (2006.01)
B32B 7/12 (2006.01) **B32B 27/36** (2006.01)
B32B 27/08 (2006.01) **C08J 7/04** (2006.01)

(21) International Application Number:

PCT/EP2017/074434

(22) International Filing Date:

27 September 2017 (27.09.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201711026027 21 July 2017 (21.07.2017) IN

(71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.**
[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).(72) Inventors: **DHANABALAN, Anantharaman**; Block B5,
Plot No. 81 to 85, Chikkadunnasandra Villagem, Anekal
Taluk, Bangalore 562125 (IN). **PATHAM, Bhaskar**; Block
B5, Plot No. 81 to 85, Chikkadunnasandra Village, Anekal

Taluk Off Sarjapura-Attibele State Highway, Bangalore
562125 (IN). **NATARAJAN, Sekarapandian**; Block B5,
Plot No. 81 to 85, Chikkadunnasandra Village, Anekal
Taluk Off Sarjapura-Attibele State Highway, Bangalore
562125 (IN). **UIKEY, Dhiraj**; Block B5, Plot No. 81 to
85, Chikkadunnasandra Village, Anekal Taluk Off Sarjapu-
ra-Attibele State Highway, Bangalore 562125 (IN).

(74) Agent: **SABIC INTELLECTUAL PROPERTY
GROUP**; P.O. Box 3008, 6160 GA GELEEN (NL).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(54) Title: LAMINATE FOR USE IN GLAZING APPLICATIONS, GLAZING PRODUCT COMPRISING SUCH LAMINATE,
VEHICLE COMPRISING SUCH GLAZING PRODUCT AND METHOD OF FABRICATING SUCH LAMINATE

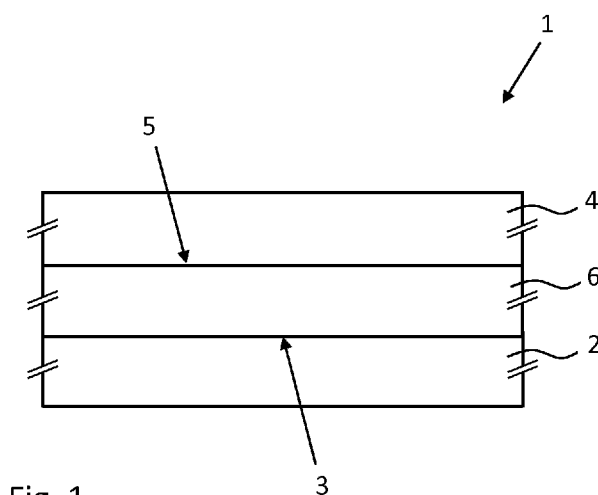


Fig. 1

(57) Abstract: The invention relates to a laminate (1) for use in glazing applications comprising an polymeric substrate (2) that is optically transparent and has a first surface (3) that is selectively enriched with siloxane segments, the polymeric substrate being one of a PMMA-based substrate and a PC-based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer. The laminate further comprises a silicon-based inorganic layer (4) that is optically transparent and has a second surface (5) that is one of directly connected with the first surface of the polymeric substrate and connected with the first surface of the polymeric substrate via one adhesion enhancing layer (6) that is arranged between the first surface of the polymeric substrate and the second surface of the silicon-based inorganic layer. The invention also relates to a glazing product (11) comprising such a laminate, a vehicle (12) comprising such a glazing product and a method of fabricating such a laminate.



(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

LAMINATE FOR USE IN GLAZING APPLICATIONS, GLAZING PRODUCT
COMPRISING SUCH LAMINATE, VEHICLE COMPRISING SUCH GLAZING
PRODUCT AND METHOD OF FABRICATING SUCH LAMINATE

5 FIELD OF THE INVENTION

The present invention relates to a laminate for glazing applications in for example the automotive and aviation industries. The invention also relates to a glazing product comprising such a laminate and a vehicle comprising such a glazing product. Moreover, the invention relates to a method of fabricating such a laminate.

10

BACKGROUND OF THE INVENTION

Polycarbonate (PC) is known to offer high optical transmissivity and design flexibility. The former in combination with its superior low-temperature impact properties render PC a suitable candidate for replacing glass in glazing applications. Automotive glazing is one such application with significant potential for replacing glass with PC for light weighting. The realization of this potential requires improvements of the ultraviolet (UV) weatherability, barrier, and scratch and mar resistance of PC. In known PC-based glazing products, glass-like abrasion resistance is imparted on a surface of a PC substrate through the use of plasma enhanced chemical vapor deposition (PECVD) of an inorganic silicon-based layer, e.g. silicon oxide (SiOx), as top surface.

20

In known PC-based glazing products as described in for example EXATEC LLC patents US 6,797,384 B2 and US 8,361,607 B2, two tie layers are conventionally applied prior to the deposition of the PECVD SiOx layer on the PC substrate. This is done because the inorganic SiOx does not adhere well directly onto the organic PC substrate. A first acrylic-based tie layer, hereinafter also indicated as an acrylic-based primer layer, is applied to improve the adhesion of a wet silicone coating onto the PC substrate. A second tie layer based on a silicone wet coating composition, hereinafter indicated as a silicone hard coat, is applied to enable a robust adhesion of the PECVD SiOx layer.

25

In the way described above, PC-based glazing products known in the art involve organic-inorganic laminates comprising at least four layers and at least three associated interfaces to achieve glass-like surface properties. Fabrication or application of each of the at least four layers is associated with processing infrastructure costs as well as potential rejects associated with formation of each layer, which may adversely affect the overall efficiency of the manufacturing process. Each interface further presents a potential site for failure, thus potentially reducing the reliability of the final product.

30

35

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a laminate for glazing applications that pre-empts, or at least reduces, at least one of the abovementioned and/or other disadvantages associated with PC-based glazing products that are known in the art.

5 These disadvantages may also apply to other polymeric resins that may replace conventional glass, such as poly methyl methacrylate (PMMA). It is also an object to provide a glazing product comprising a laminate according to the invention, a vehicle comprising such glazing product and a method of fabricating a laminate according to the invention.

10 Aspects of the present invention are set out in the accompanying independent and dependent claims. Features from the dependent claims may be combined with features from the independent claims as appropriate and not merely as explicitly set out in the claims.

At least one of the abovementioned objects is achieved by a first aspect of the
15 present invention that provides a laminate for use in glazing applications comprising a polymeric substrate that is optically transparent and has a first surface that is selectively enriched with siloxane segments, the polymeric substrate being one of a poly methyl methacrylate (PMMA) based substrate, and a polycarbonate (PC) based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-
20 siloxane copolymer. The laminate further comprises a silicon-based inorganic layer that is optically transparent and has a second surface that is directly connected with the first surface of the polymeric substrate or connected with the first surface of the polymeric substrate via one adhesion enhancing layer that is arranged between the first surface of the polymeric substrate and the second surface of the silicon-based inorganic layer.

25 The skilled person will appreciate that in the context of this application the term polymeric substrate can be used to refer to a PC-based polymeric substrate, a PMMA-based polymeric substrate, a plastic substrate or a thermoplastic substrate. In the case of a PC-based polymeric substrate, siloxane segments in the PC-siloxane copolymers or blends of PC with PC-siloxane copolymers yield an improved adherence of the
30 second surface of the silicon-based inorganic layer to the first surface of the polymeric substrate that is selectively enriched with the siloxane segments. In another embodiment of the laminate according to the invention, the entire first surface of the polymeric substrate is enriched with siloxane segments. Analogously, in the case of a PMMA-based polymeric substrate, siloxane segments in an acrylate-siloxane
35 copolymer yield an improved adherence of the second surface of the silicon-based inorganic layer to the first surface of the polymeric substrate.

The second surface of the silicon-based inorganic layer and the first surface of the polymeric substrate are facing towards each other and can be in direct contact with each other such that an interface is formed. However, it is also possible that the second surface of the silicon-based inorganic layer is associated with the first surface of the polymeric substrate via one adhesion-enhancing layer that is arranged between the first surface of the polymeric substrate and the second surface of the silicon-based inorganic layer. The adhesion-enhancing layer is a hybrid primer layer, including both organic and inorganic segments, such as one of an oligomeric PC-siloxane primer layer and an oligomeric acrylate-siloxane primer layer.

The laminate enables the omission of at least one of a primer layer and a silicone hard coat layer known from laminates comprised in the state of the art. Consequently, the laminate comprises a reduced number of layers compared to laminates comprised in the state of the art. In this way, the reliability of the laminate having glass like abrasion resistance and barrier properties can be improved. Consequently, the production yield of laminates can be improved.

In an embodiment of the laminate according to the invention, the PC-siloxane copolymer based substrate has a siloxane content ranging from 0.5 wt.% to 10 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$.

The amount and length of the siloxane polymer segments incorporated within the PC-siloxane copolymer substrate are optimized to minimally impact the optical transmissivity of the substrate compared to pure PC. The presence of the siloxane polymer segments incorporated within the PC-siloxane copolymer substrate in turn improves the chemical compatibility of this substrate to a silicone hard coat layer to the extent that the use of any intermediate acrylic-based tie (primer) layer is eliminated. The siloxane content of the PC-siloxane copolymer based substrate ranges from 0.5 wt.% to 10 wt.%, preferably from 1 wt.% to 7 wt.%, and more preferably from 2 wt.% to 5 wt.%. The siloxane segment sizes in the PC-siloxane copolymer based substrate vary from 3 to 20 d-units, preferably from 5 to 15 d-units, and more preferably between 7 to 12 d-units.

In an embodiment of the laminate according to the invention, the substrate based on a blend of PC with PC-siloxane copolymer has a siloxane content in the copolymer ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$.

The amount and length of the siloxane polymer segments incorporated within the polymeric substrate comprising a blend of PC with PC-siloxane copolymer are optimized so as to minimally affect the optical transmissivity of the substrate compared

to pure PC. The presence of the siloxane polymer segments incorporated within the polymeric substrate comprising a blend of PC with PC-siloxane copolymer in turn improves the chemical compatibility of this substrate to a silicone hard coat layer to the extent that the use of any intermediate acrylic-based tie (primer) layer is eliminated.

5 The substrate based on the blend of PC with PC-siloxane copolymer has a siloxane content in the copolymer ranging from 10 wt.% to 80 wt.%, preferably from 15 wt.% to 25 wt.%, and more preferably from 18 wt.% to 22 wt.%. The loadings of the PC-siloxane copolymer in such blends is to be chosen so as to result in an effective siloxane content in the blend ranging from 0.5 wt.% to 10 wt.%, preferably from 1 wt.%
10 to 7 wt.%, and more preferably from 2 wt.% to 5 wt.%. The siloxane segment sizes in the PC-siloxane copolymer vary from 3 to 20 d-units, preferably from 5 to 15 d-units, and more preferably between 7 to 12 d-units.

 In an embodiment of the laminate according to the invention, the adhesion-enhancing layer is one of a hybrid primer layer, such as an oligomeric PC-siloxane
15 primer layer or an oligomeric acrylate-siloxane primer layer, and a silicone hardcoat layer. The adhesion-enhancing layer enables a robust adhesion of the silicon-based inorganic layer to the polymeric substrate. The silicone hardcoat layer can be prepared and applied as described in detail in US 8,940,397 B2, column 16, lines 1-43.

 In an embodiment of the laminate according to the invention, the silicone hardcoat
20 layer comprises ultraviolet (UV) reflecting and/or absorbing additives that prevent UV radiation to reach the underlying polymeric substrate. In this way optimal weatherability of the substrate can be ensured rendering the laminate suitable for out-door applications.

 In an embodiment of the laminate according to the invention, the polymeric
25 substrate is a PC-based substrate and the primer layer is a first composition comprising an oligomeric PC-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 95 wt.%.

 In this way, the first surface of the PC-based polymeric substrate comprising one of PC, PC-siloxane copolymers and blends of PC with PC-siloxane copolymers, has a
30 selectively enriched siloxane content. As a result, thereof at least one of the acrylate tie layer and silicone hardcoat layer can be omitted. The PC segments of the oligomeric copolymer tether to the first surface of the PC-based substrate while the siloxane segments of the oligomeric copolymer provide tethers for the second surface of the silicon-based inorganic layer. In this manner, a single oligomeric copolymer layer
35 serves the functionality of the conventionally used acrylic-based tie layer and the silicone hardcoat composition. As a result, material and infrastructure costs associated with an additional acrylate tie layer and / or silicone hardcoat application step can be

reduced. Additionally, the probability of defects and interfacial failures associated with the acrylate tie layer and / or silicone hardcoat layer, and the associated process challenges can be discarded.

5 The oligomeric PC-siloxane copolymer of the first composition of the primer layer has an oligomeric chain length of at most 100. Specifically, incorporating an oligomeric PC-siloxane copolymer in which the siloxane segment lengths range from 3 to 45 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, with 1 or 2 such segments incorporated, and the bisphenol PC segment lengths range between 5 to 20 monomer units.

10 The oligomeric PC-siloxane copolymer has a siloxane content ranging from 5 wt.% to 95 wt.%, preferably from 10 wt.% to 90 wt.%, and more preferably from 25 wt.% to 85 wt.%. The high content of siloxane in the first composition of the primer layer for PC-based substrates facilitates an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments in the first surface of the PC-based
15 substrate through Van der Waals bonds.

In an embodiment of the laminate according to the invention, the first composition of the primer layer comprises UV reflecting and/or absorbing additives. As such, UV weatherability is imparted to the laminate according to the invention.

In an embodiment of the laminate according to the invention, the primer layer is a
20 second composition comprising an oligomeric acrylate-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 90 wt.%. In this way, the first surface of the polymeric substrate has a selectively enriched siloxane content. As a result, thereof at least one of the acrylate tie layer and silicone hardcoat layer can be omitted. In case the laminate has a PMMA-based or PC-
25 based polymeric substrate, the acrylate segments of the oligomeric copolymer tether to the first surface of the PMMA-based or PC-based substrate while the siloxane segments of the oligomeric acrylate-siloxane copolymer provide tethers for the second surface of the silicon-based inorganic layer. In this manner, a single oligomeric copolymer layer serves the functionality of the conventionally used acrylic-based primer
30 and the silicone hardcoat composition. As a result, material and infrastructure costs associated with an additional acrylate tie layer and / or silicone hardcoat application step can be reduced. Additionally, the probability of defects and interfacial failures associated with the acrylate tie layer and / or silicone hardcoat layer, and the associated process challenges can be discarded. The oligomeric acrylate-siloxane
35 copolymer of the second composition of the organic primer layer has an oligomeric chain length of at most 100. Specifically, incorporating an oligomeric siloxane-acrylate copolymer in which the siloxane segment lengths range from 3 to 45 d units, wherein

the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, with 1 or 2 such segments incorporated, and the acrylate segment lengths range between 5 to 20 monomer units. The oligomeric acrylate-siloxane copolymer has a siloxane content ranging from 5 wt.% to 90 wt.%, preferably from 10 wt.% to 85 wt.%, and more preferably from 20 wt.% to 80 wt.%. The high content of siloxane in the second composition of the primer layer facilitates an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments in the first surface of the PC- or PMMA based substrate through Van der Waals bonds.

In an embodiment of the laminate according to the invention, the second composition of the primer layer comprises UV reflecting and/or absorbing additives. In this way, UV weatherability is imparted to the laminate according to the invention.

In an embodiment of the laminate according to the invention, the polymeric substrate is a PC-based substrate that comprises a first additive comprising oligomeric PC-siloxane copolymer having an overall molecular weight ranging from 1500 to 12000, a surface energy ranging from 1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%. Using oligomeric PC-siloxane copolymer additives / master-batches having an optimal siloxane content and composition, and using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface (skin region) of the PC-based polymeric substrate during the injection molding step in which the polymeric substrate is fabricated. By enriching the siloxane content at the first surface of the PC-based substrate, the second surface of the silicon-based inorganic coating layer, e.g. PECVD SiO_x , will have an improved adhesion to the first surface of the PC-based substrate. On the one hand, this is due to the low overall molecular weight of the oligomeric PC-siloxane copolymer that ranges from 1500 to 12000, preferably from 2000 to 9000, and more preferably from 3000 to 4500 in comparison with pure PC. Additionally or alternatively, this is due to chemical modification of the siloxane segments so as to render them with low surface energy ranging from 1 mN/m to 30 mN/m, and preferably from 15 mN/m to 25 mN/m. The siloxane content of the oligomeric PC-siloxane copolymer ranges from 5 wt.% to 90 wt.%, and preferably from 25 wt.% to 85 wt.%. High concentrations of siloxane at the first surface of the PC-based polymeric substrate facilitate an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments in the first surface of the PC substrate through Van der Waals bonds. As a result of the above, the present invention provides a laminate that does not need to comprise both the acrylic-based primer and the silicone hardcoat layer known in the art.

In an embodiment of the laminate according to the invention, the polymeric substrate is a PMMA-based substrate that comprises a second additive comprising oligomeric acrylate-siloxane copolymer having an overall molecular weight ranging from 800 to 9000, a surface energy ranging from 0.1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%. Using oligomeric acrylate-siloxane copolymer additives / master-batches having an optimal siloxane content and composition, and using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface (skin region) of the PMMA-based polymeric substrate during the injection molding step in which the polymeric substrate is fabricated. This will enrich the siloxane content at the first surface of the PMMA-based substrate and it is envisaged that this leads to an improved adhesion of the second surface of the silicon-based inorganic coating layer, e.g. PECVD SiOx, to the first surface of the PMMA-based substrate. On the one hand, this is due to the low overall molecular weight of the oligomeric acrylate-siloxane copolymer that ranges from 800 to 9000, preferably from 1300 to 7500, and more preferably from 1600 to 2750 in comparison with pure PMMA. Additionally or alternatively, this is due to chemical modification of the siloxane segments so as to render them with low surface energy ranging from 0.1 mN/m to 30 mN/m, and preferably from 9 mN/m to 20 mN/m. The siloxane content of the oligomeric acrylate-siloxane copolymer ranges from 5 wt.% to 90 wt.%, and preferably from 20 wt.% to 80 wt.%. High concentrations of siloxane at the first surface of the PMMA-based polymeric substrate facilitate an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments in the first surface of the PMMA substrate through Van der Waals bonds. As a result of the above, the present invention provides a laminate that does not need to comprise both the acrylic-based primer and the silicone hardcoat layer known in the art.

In an embodiment of the laminate according to the invention, an oxide-based inorganic coating layer having UV reflecting and/or absorbing properties is provided either between the first surface of the polymeric substrate and the second surface of the silicon-based inorganic layer or on a third surface of the silicon-based inorganic layer that is arranged opposite to the second surface of the silicon-based inorganic layer. This coating enables application of the laminate not only for in-door applications but also in weatherable applications. Non-limiting examples of the oxide-based inorganic coating layer are based on ZnO and CeO₂.

In an embodiment of the laminate according to the invention, the silicon-based inorganic layer comprises PECVD silicon oxide, SiOx. By using PECVD SiOx, it is

possible to also coat curved substrates. SiOx provides the laminate with glass-like abrasion resistance and barrier properties, weatherability and wear resistance.

According to a second aspect of the present invention there is provided a glazing product comprising a laminate according to the invention. Non-limiting examples of glazing products in which laminates can be envisaged comprise automotive glazing panels, aerospace glazing panels, architectural glazing for building and construction and eyewear.

According to a third aspect of the present invention, there is provided a vehicle comprising a glazing product according to the invention. Non-limiting examples of vehicles in which laminates can be envisaged, comprise cars, trucks, caravans, trailers, busses, trains, trams, metros, yachts, ships, airplanes, helicopters. When applying the laminate in one of the vehicles mentioned above, the skilled person will appreciate that it is advantageous to arrange the laminate in such a way that the optically transparent silicon-based inorganic layer, e.g. PECVD SiOx, is facing towards the environment outside the vehicle because of the glass-like abrasion resistance and barrier properties, weatherability and wear resistance this layer provides to the laminate. Consequently, the optically transparent polymeric substrate of the laminate is facing towards the environment inside the vehicle. Additionally, a further optically transparent silicon-based inorganic layer, e.g. PECVD SiOx, may be facing towards an interior of the vehicle, i.e. a surface of the polymeric substrate opposite of the first surface may be selectively enriched with siloxane segments and may comprise a silicon-based inorganic layer that is optically transparent and has a second surface that is directly connected with the first surface of the polymeric substrate or connected with the first surface of the polymeric substrate via one adhesion enhancing layer that is arranged between the first surface of the polymeric substrate and the second surface of the silicon-based inorganic layer. As such, the polymeric substrate has an inorganic layer on both surfaces.

According to a fourth aspect of the present invention, there is provided a method of fabricating a laminate for use in glazing applications according to the invention. The method comprising at least one of blending, injection molding, injection-compression molding, multi-shot (or multi-component or multi material) injection compression molding, in-mold coating, in-mold painting, flow-coating, coextrusion, laminating, plasticizing, calendaring, coating and plasma-enhanced chemical vapor deposition. Siloxane segments improve adherence of the silicon-based inorganic layer to the polymeric substrate. As a result, the application of at least one of an acrylic-based primer and a silicone hardcoat layer known from laminates comprised in the state of the art can be omitted. Consequently, the method can provide a laminate that

comprises a reduced number of layers compared to laminates comprised in the state of the art. The method enables the fabrication of laminates having glass like abrasion resistance and barrier properties. Moreover, the method has both an improved robustness and yield, which results in laminates having an improved reliability.

5 In an embodiment of the method according to the invention, an polymeric substrate of the laminate is fabricated by blending PC with a masterbatch of a PC-siloxane copolymer having a siloxane content ranging from 10 wt.% to 80 wt. % and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula -
[Si(CH₃)₂O]-. The PC-siloxane copolymer masterbatch contains high concentrations of
10 siloxane segments with the siloxane content in the copolymer ranging from 10 wt.% to 80 wt.%, preferably from 15 wt.% to 25 wt.%, and more preferably from 18 wt.% to 22 wt.%. The loadings of the PC-siloxane copolymer is to be chosen so as to result in an effective siloxane content in the blend of PC with PC-siloxane copolymer ranging from 0.5 wt.% to 10 wt.%, preferably from 1 wt.% to 7 wt.%, and more preferably from 2
15 wt.% to 5 wt.%. The siloxane concentration in the masterbatch is diluted to the desired final concentration through blending with pure PC while ensuring minimal reduction to its optical transmissivity while improving the compatibility of the polymeric substrate to a silicone hardcoat layer to the extent that the need for any intermediate acrylic-based tie (primer) layer is eliminated. The siloxane segment sizes in the PC-siloxane
20 copolymer vary from 3 to 20 d-units, preferably from 5 to 15 d-units, and more preferably between 7 to 12 d-units.

According to this non-limiting embodiment of the method according to the invention, a laminate can be fabricated that comprises a siloxane-rich and hardcoat-compatible polymeric substrate that does not need to be treated with any acrylic-based tie (primer)
25 layer to improve the adhesion of an optically transparent silicon-based inorganic protection layer.

In an embodiment of the method according to the invention, an polymeric substrate of the laminate is fabricated using a two-step injection-compression molding (2K-ICM) process, wherein in a first injection molding step a PC-siloxane copolymer is molded,
30 the PC-siloxane copolymer having a siloxane content ranging from 1 wt.% to 7 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula -[Si(CH₃)₂O]-, and wherein in a second injection-compression molding step a masterbatch of a PC-siloxane copolymer is molded, the masterbatch having a siloxane content ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to
35 20 d-units.

According to this non-limiting embodiment of the method according to the invention, a laminate can be fabricated using a 2K-ICM process. The first injection-molding step

(IM) is carried out to achieve the bulk of the optically transparent polymeric substrate of the laminate according to the invention. The second injection-compression molding (ICM) step is carried out to selectively enrich the first surface of the optically transparent polymeric substrate with siloxane segments. By selectively enriching the first surface of the polymeric substrate, the compatibility of the first surface of the polymeric substrate with the silicone hardcoat layer is improved.

The selective surface enrichment of the polymeric substrate with siloxane segments through 2K-ICM-based over-molding is also expected to result in an polymeric substrate with low birefringence and residual stresses, improved compatibility of the PC-based bulk layer (first shot) with the PC-siloxane copolymer masterbatch (second shot), and overall better performance in terms of establishment of the silicone hardcoat on the polymeric substrate.

The composition of the masterbatch (second shot) and the length of siloxane segments in the masterbatch, as well as the thickness of the second shot surface layer in 2K-ICM is optimized so as to minimally impact the optical transmissivity of the substrate compared to pure PC or optically transparent PC-siloxane copolymers. The thickness of first shot (IM) can range from 1 to 8 mm, and preferably between 3 to 5 mm. The thickness of the second shot (ICM) can range between 0.5 to 1 mm and more preferably between 0.6 to 0.8 mm. The thickness of the polymeric substrate may range from 1.5 to 9 mm, preferably 3.6 to 5.8 mm. Further, the incorporation of the PC-siloxane copolymer masterbatch as the second shot (ICM) also ensures a uniformly distributed and optically thin layer of the siloxane-containing layer, thereby ensuring retention of the good optical transmissivity offered by the PC-based bulk layer (first shot).

In an embodiment of the method according to the invention, the masterbatch of the PC-siloxane copolymer is enriched with UV reflecting and/or absorbing additives in the second injection-compression molding step. In this way, the method enables the fabrication of a laminate comprising a polymeric substrate having optimal weatherability.

In an embodiment of the method according to the invention, an polymeric substrate of the laminate is fabricated by blending one of polycarbonate (PC) and poly-methyl methacrylate (PMMA) with a masterbatch of an acrylate-siloxane copolymer having a siloxane content ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$.

The acrylate-siloxane copolymer masterbatch contains high concentrations of siloxane segments with the siloxane content in the copolymer ranging from 10 wt.% to 80 wt.%, preferably from 15 wt.% to 25 wt.%, and more preferably from 18 wt.% to 22

wt.%. The loadings of the acrylate-siloxane copolymer is to be chosen so as to result in an effective siloxane content in the blend of PC or PMMA with acrylate-siloxane copolymer ranging from 0.5 wt.% to 10 wt.%, preferably from 1 wt.% to 7 wt.%, and more preferably from 2 wt.% to 5 wt.%. The siloxane concentration in the masterbatch
5 is diluted to the desired final concentration through blending with either pure PC or pure PMMA while ensuring minimal reduction to its optical transmissivity while improving the compatibility of the polymeric substrate to a silicone hardcoat layer to the extent that the need for any intermediate acrylic-based tie (primer) layer is eliminated. The siloxane segment sizes in the acrylate-siloxane copolymer vary from 3 to 20 d-units,
10 preferably from 5 to 15 d-units, and more preferably between 7 to 12 d-units.

According to this non-limiting embodiment of the method according to the invention, a laminate can be fabricated that comprises a siloxane-rich and hardcoat-compatible polymeric substrate that does not need to be treated with any acrylic-based tie (primer) layer to improve the adhesion of an optically transparent silicon-based inorganic
15 protection layer.

In an embodiment of the method according to the invention, an polymeric substrate of the laminate is fabricated using a 2K-ICM process, wherein in a first injection molding step either pure PC or pure PMMA or a PC-siloxane copolymer is molded, the PC-siloxane copolymer having a siloxane content ranging from 1 wt.% to 7 wt.% and
20 siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, and wherein in a second injection-compression molding step a masterbatch of an acrylate-siloxane copolymer is molded, the masterbatch having a siloxane content ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units.

25 According to this non-limiting embodiment of the method according to the invention, a laminate can be fabricated using a 2K-ICM process. The first injection-molding step is carried out to achieve the bulk of the optically transparent polymeric substrate of the laminate according to the invention. The second injection-compression molding step is carried out to selectively enrich the first surface of the optically transparent polymeric
30 substrate with siloxane segments. By selectively enriching the first surface of the polymeric substrate, the compatibility of the first surface of the polymeric substrate with the silicone hardcoat layer is improved.

The selective surface enrichment of the polymeric substrate with siloxane segments through ICM-based over-molding is also expected to result in an polymeric substrate
35 with low birefringence and residual stresses, improved compatibility of the PC or PMMA or PC-siloxane copolymer bulk layer (first shot) with the acrylate-siloxane masterbatch (second shot), and overall better performance in terms of establishment of

the silicone hardcoat on the polymeric substrate. The composition of the masterbatch (second shot) and the length of siloxane segments in the masterbatch, as well as the thickness of the second shot surface layer in ICM is optimized so as to minimally impact the optical transmissivity of the substrate compared to pure PC or pure PMMA or optically transparent PC-siloxane copolymers. The thickness of first shot (IM) can range from 1 to 8 mm, and preferably between 3 to 5 mm. The thickness of the second shot (ICM) can range between 0.5 to 1 mm and more preferably between 0.6 to 0.8 mm. The thickness of the polymeric substrate may range from 1.5 to 9 mm, preferably 3.6 to 5.8 mm. Further, the incorporation of the acrylate-siloxane copolymer masterbatch as the second shot ICM also ensures a uniformly distributed and optically thin layer of the siloxane-containing layer, thereby ensuring retention of the good optical transmissivity offered by the PC-based or PMMA-based bulk layer (first shot).

In an embodiment of the method according to the invention, the masterbatch of the acrylate-siloxane copolymer is enriched with UV reflecting and/or absorbing additives in the second injection-compression molding step. In this way, the method enables the fabrication of a laminate comprising a polymeric substrate having optimal weatherability.

In an embodiment of the method according to the invention, flow-coating is used to provide a first surface of the polymeric substrate of the laminate with an primer layer that comprises a first composition comprising an oligomeric PC-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 95 wt.%, and wherein the first composition employed for flow-coating has an intrinsic viscosity ranging from 0.5 mPa-s to 25 mPa-s.

In this way, the first surface of the PC-based polymeric substrate comprising one of PC, PC-siloxane copolymers and blends of PC with PC-siloxane copolymers, has a selectively enriched siloxane content. As a result, thereof the silicone hardcoat layer can be omitted. The PC segments of the oligomeric copolymer tether to the first surface of the PC-based substrate while the siloxane segments of the oligomeric copolymer provide tethers for the second surface of the silicon-based inorganic layer. In this manner, a single oligomeric copolymer layer serves the functionality of the conventionally used acrylic tie layer and the silicone hardcoat composition. As a result, material and infrastructure costs associated with an additional acrylic tie layer and / or silicone hardcoat application step can be reduced. Additionally, the probability of defects and interfacial failures associated with at least one of the acrylic tie layer and silicone hardcoat layer, and the associated process challenges can be discarded.

The oligomeric PC-siloxane copolymer of the first composition of the primer layer has an oligomeric chain length of at most 100. Specifically, incorporating an oligomeric

PC-siloxane copolymer in which the siloxane segment lengths range from 3 to 45 d units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, with 1 or 2 such segments incorporated, and the PC segment lengths range between 5 to 20 monomer units.

The oligomeric PC-siloxane copolymer has a siloxane content ranging from 5 wt.%
5 to 95 wt.%, preferably from 10 wt.% to 90 wt.%, and more preferably from 25 wt.% to 85 wt.%. To achieve the primer composition, the oligomeric PC-siloxane copolymer is dissolved or dispersed in a volatile organic solvent mixture containing two or more of chloroform, dichloromethane, toluene, xylene, hexane, isopropanol, n-butanol, isobutanol, and methyl-isobutyl ketone. The volatile solvent mixture is employed to
10 make the primer composition amenable for application using flow-coating. The concentration of the oligomeric PC-siloxane copolymer within the primer ranges from 5 wt.% to 50 wt.%, and more preferably from 10 wt.% to 25 wt.% so as to achieve viscosities ranging from 0.5 mPa-s to 25 mPa-s. The primer is applied through flow-coating, followed by a flash-out stage to remove the volatile solvent mixtures. In this
15 way, the first primer layer that is achieved on the first surface of the PC-based polymeric substrate has an effective siloxane content ranging from 25 wt.% to 85 wt.%. The high content of siloxane in the first composition of the primer layer for PC-based substrates facilitates an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments in the first surface of the PC substrate
20 through Van der Waals bonds.

The low intrinsic viscosity of the first composition of the organic primer layer, ranging from 0.5 mPa-s to 25 mPa-s, allows easy spreading and interdiffusion of the first composition into the polymeric substrate, leading to effective surface treatment.

In an embodiment of the method according to the invention, flow-coating is used to
25 provide a first surface of the polymeric substrate of the laminate with an primer layer that comprises a second composition comprising an oligomeric acrylate-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 90 wt.%, and wherein the second composition employed for flow-coating has an intrinsic viscosity ranging from 0.5 mPa-s to 25 mPa-s.

30 In this way, the first surface of the polymeric substrate has a selectively enriched siloxane content. As a result, thereof the silicone hardcoat layer can be omitted. In case the laminate has a PMMA-based or PC-based polymeric substrate, the acrylate segments of the oligomeric copolymer tether to the first surface of the PMMA-based or PC-based substrate while the siloxane segments of the oligomeric acrylate-siloxane
35 copolymer provide tethers for the second surface of the silicon-based inorganic layer. In this manner, a single oligomeric copolymer layer serves the functionality of the conventionally used acrylic-based primer and the silicone hardcoat composition. As a

result, material and infrastructure costs associated with an additional acrylic tie layer and / or silicone hardcoat application step can be reduced. Additionally, the probability of defects and interfacial failures associated with at least one of the acrylic tie layer and silicone hardcoat layer, and the associated process challenges can be discarded.

- 5 The oligomeric acrylate-siloxane copolymer of the second composition of the organic primer layer has an oligomeric chain length of at most 100. Specifically, incorporating an oligomeric siloxane-acrylate copolymer in which the siloxane segment lengths range from 3 to 45 d units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, with 1 or 2 such segments incorporated, and the acrylate segment lengths range
10 between 5 to 20 monomer units.

 The oligomeric acrylate-siloxane copolymer has a siloxane content ranging from 5 wt.% to 90 wt.%, preferably from 10 wt.% to 85 wt.%, and more preferably from 20 wt.% to 80 wt.%. To achieve the primer composition, the oligomeric acrylate-siloxane copolymer is dissolved or dispersed in a volatile organic solvent mixture containing two
15 or more of chloroform, dichloromethane, toluene, xylene, hexane, isopropanol, n-butanol, isobutanol, and methyl-isobutyl ketone. The volatile solvent mixture is employed to make the primer composition amenable for application using flow-coating. The concentration of the oligomeric acrylate-siloxane copolymer within the primer ranges from 5 wt.% to 50 wt.%, and more preferably from 10 wt.% to 25 wt.% so as to
20 achieve viscosities ranging from 0.5 mPa-s to 25 mPa-s. The primer is applied through flow-coating, followed by a flash-out stage to remove the volatile solvent mixtures. In this way, the first primer layer that is achieved on the first surface of the PMMA-based or PC-based polymeric substrate has an effective siloxane content ranging from 20 wt.% to 80 wt.%. The high content of siloxane in the second composition of the organic
25 primer layer facilitates an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments in the first surface of the PMMA- or PC-based substrate through Van der Waals bonds.

 The low intrinsic viscosity of the second composition of the organic primer layer, ranging from 0.5 mPa-s to 25 mPa-s, allows easy spreading and interdiffusion of the
30 second composition into the polymeric substrate, leading to effective surface treatment. In an exemplary embodiment of the method according to the invention, an polymeric substrate of the laminate having a first surface that is provided with an primer layer having a first composition is fabricated using a two-step injection-compression molding process, wherein in a first injection molding step a PC-siloxane copolymer is molded,
35 the PC-siloxane copolymer having a siloxane content ranging from 1 wt.% to 7 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, and wherein in a second injection-compression molding step a

first composition comprising an oligomeric PC-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 95 wt.% is molded, and wherein the first composition has an intrinsic viscosity ranging from 0.5 mPa-s to 25 mPa-s.

5 The PC-siloxane copolymer contains high concentrations of siloxane segments with the siloxane content in the copolymer ranging from 1 wt.% to 7 wt.%, preferably from 2 wt.% to 5 wt.%. The siloxane segment sizes in the PC-siloxane copolymer vary from 3 to 20 d-units, preferably from 5 to 15 d-units, and more preferably between 7 to 12 d-units.

10 The oligomeric PC-siloxane copolymer has a siloxane content ranging from 5 wt.% to 95 wt.%, preferably from 10 wt.% to 90 wt.%, and more preferably from 25 wt.% to 85 wt.%. In this way, the first composition of the organic primer layer that is employed for treating the first surface of the PC-based polymeric substrate has a siloxane content ranging from 25% to 85%. The oligomeric PC-siloxane copolymer has an oligomeric
15 chain length of at most 100. Specifically, incorporating an oligomeric PC-siloxane copolymer in which the siloxane segment lengths range from 3 to 45 d units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, with 1 or 2 such segments incorporated, and the PC segment lengths range between 5 to 20 monomer units.

 In this way, a polymeric substrate can be achieved that has a first surface that is
20 selectively enriched with siloxane segments to improve the compatibility with the silicon-based inorganic layer, which for example is PECVD SiOx. The second compression step associated with the primer layer that comprises a first composition comprising oligomeric PC-siloxane copolymer allows an intimate surface contact of the primer layer with the bulk substrate and also allows the formation of an optically thin
25 layer of the primer layer to ensure minimal reduction of the optical transmissivity of the bulk substrate.

 Furthermore, it is noted that using an oligomeric PC-siloxane copolymer primer in the second stage ICM step, or alternatively an in-mold coating or painting step, can result in an even thinner top layer as it would be possible to reduce the thickness of the
30 top layer to 0.1 mm instead of 0.5 mm with the masterbatch. This is due to the lower viscosity of the oligomeric PC-siloxane copolymer compared to the masterbatch.

 Moreover, it is noted that in contrast to using an oligomeric PC-siloxane copolymer primer for flow-coating, using a primer for ICM step in 2K-ICM does not require the application of any solvents for viscosity reduction. The skilled person will appreciate
35 that adhesion between two layers in 2K-ICM is achieved via heat-sealing instead of solvent etching, as is the case in flow-coating.

In another specific embodiment of the method according to the present invention, the first composition comprising oligomeric PC-siloxane copolymer is used as an in-mold coating during injection molding of the bulk substrate. In yet another specific embodiment of the method according to the present invention, the first composition
5 comprising oligomeric PC-siloxane copolymer is used as an in-mold decoration surface film during injection molding of the bulk substrate.

In an exemplary embodiment of the method according to the invention, an polymeric substrate of the laminate having a first surface that is provided with an organic layer having a second composition is fabricated using a two-step injection-
10 compression molding process, wherein in a first injection molding step either pure PC or pure PMMA or a PC-siloxane copolymer is molded, the PC-siloxane copolymer having a siloxane content ranging from 1 wt.% to 7 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{[Si(CH}_3\text{)}_2\text{O]}-$, and wherein in a second injection-compression molding step a second composition
15 comprising an oligomeric acrylate-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 90 wt.%, and wherein the second composition has an intrinsic viscosity ranging from 0.5 mPa-s to 25 mPa-s.

The PC-siloxane copolymer contains high concentrations of siloxane segments with
20 the siloxane content in the copolymer ranging from 1 wt.% to 7 wt.%, preferably from 2 wt.% to 5 wt.%. The siloxane segment sizes in the PC-siloxane copolymer vary from 3 to 20 d-units, preferably from 5 to 15 d-units, and more preferably between 7 to 12 d-units.

The oligomeric acrylate-siloxane copolymer has an oligomeric chain length of at
25 most 100. Specifically, incorporating an oligomeric siloxane-acrylate copolymer in which the siloxane segment lengths range from 3 to 45 d units, wherein the d-unit has the formula $-\text{[Si(CH}_3\text{)}_2\text{O]}-$, with 1 or 2 such segments incorporated, and the acrylate segment lengths range between 5 to 20 monomer units. The oligomeric acrylate-siloxane copolymer has a siloxane content ranging from 5 wt.% to 90 wt.%, preferably
30 from 10 wt.% to 85 wt.%, and more preferably from 20 wt.% to 80 wt.%. In this way, the primer layer comprising the second composition that is employed for treating the first surface of the PMMA-based or PC-based polymeric substrate has a siloxane content ranging from 25% to 85%.

In this way, a polymeric substrate can be achieved that has a first surface that is
35 selectively enriched with siloxane segments to improve the compatibility with the silicon-based inorganic layer, e.g. PECVD SiOx. The second compression step associated with the primer layer that comprises the second composition comprising

oligomeric acrylate-siloxane copolymer allows an intimate surface contact of the primer layer with the bulk substrate and also allows the formation of an optically thin layer of the primer layer to ensure minimal reduction of the optical transmissivity of the bulk substrate.

5 Furthermore, it is noted that using an oligomeric siloxane-acrylate copolymer primer in the second stage ICM step, or alternatively an in-mold coating or painting step, can result in an even thinner top layer as it would be possible to reduce the thickness of the top layer to 0.1 mm instead of 0.5 mm with the masterbatch. This is due to the lower viscosity of the oligomeric siloxane-acrylate copolymer compared to the masterbatch.

10 Moreover, it is noted that in contrast to using an oligomeric siloxane-acrylate copolymer primer for flow-coating, using a primer for ICM step in 2K-ICM does not require the application of any solvents for viscosity reduction.

In another specific embodiment of the method according to the present invention, the second composition comprising oligomeric acrylate-siloxane copolymer is used as
15 an in-mold coating during injection molding of the bulk substrate. In another specific embodiment of the method according to the present invention, the second composition comprising oligomeric acrylate-siloxane copolymer is used as an in-mold decoration surface film during injection molding of the bulk substrate.

In an embodiment of the method according to the invention, a PC-based polymeric
20 substrate of the laminate comprising a PC-siloxane copolymer having a siloxane content ranging from 0.5 wt.% to 10 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, is plasticized with oligomeric PC-siloxane copolymer having an overall molecular weight ranging from 1500 to 12000, a surface energy ranging from 1 mN/m to 30 mN/m, and a siloxane
25 content ranging from 5 wt.% to 90 wt.%.

During molding of the PC-based polymeric substrate using oligomeric PC-siloxane copolymer having an optimal siloxane content and composition, and using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface (skin region) of the PC-based polymeric substrate. In this way,
30 the siloxane content at the first surface of the PC-based substrate will be enriched and it is envisaged that this leads to an improved adhesion of the second surface of the silicon-based inorganic coating layer, e.g. PECVD SiO_x, to the first surface of the PC-based substrate. On the one hand, this is due to the low overall molecular weight of the oligomeric PC-siloxane copolymer that ranges from 1500 to 12000, preferably from
35 2000 to 9000, and more preferably from 3000 to 4500 in comparison with pure PC. Additionally or alternatively, this is due to chemical modification of the siloxane segments so as to render them with low surface energy ranging from 1 mN/m to 30

mN/m, and preferably from 15 mN/m to 25 mN/m. The siloxane content of the oligomeric PC-siloxane copolymer ranges from 5 wt.% to 90 wt.%, and preferably from 25 wt.% to 85 wt.%. High concentrations of siloxane at the first surface of the PC-based polymeric substrate facilitate an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments through Van der Waals bonds. As a result of the above, the present invention provides a laminate that does not need to comprise both the acrylate-based primer and the silicone hardcoat layer known in the art.

In an embodiment of the method according to the invention, a PMMA-based polymeric substrate of the laminate is blended with oligomeric acrylate-siloxane copolymer having an overall molecular weight ranging from 800 to 9000, a surface energy ranging from 0.1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%.

During blending the PMMA-based polymeric substrate using oligomeric acrylate-siloxane copolymer having an optimal siloxane content and composition, and using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface (skin region) of the PMMA-based polymeric substrate. In this way, the siloxane content at the first surface of the PMMA-based substrate will be enriched and it is envisaged that this leads to an improved adhesion of the second surface of the silicon-based inorganic coating layer, e.g. PECVD SiO_x, to the first surface of the PMMA-based substrate. On the one hand, this is due to the low overall molecular weight of the oligomeric acrylate-siloxane copolymer that ranges from 800 to 9000, preferably from 1300 to 7500, and more preferably from 1600 to 2750 in comparison with pure PMMA. Additionally or alternatively, this is due to chemical modification of the siloxane segments so as to render them with low surface energy ranging from 0.1 mN/m to 30 mN/m, and preferably from 9 mN/m to 20 mN/m. The siloxane content of the oligomeric acrylate-siloxane copolymer ranges from 5 wt.% to 90 wt.%, and preferably from 20 wt.% to 80 wt.%. High concentrations of siloxane at the first surface of the PMMA-based polymeric substrate facilitate an improved adhesion of the second surface of the silicon-based inorganic layer and the siloxane segments through Van der Waals bonds. As a result of the above, the present invention provides a laminate that does not need to comprise the silicone hardcoat layer known in the art.

In an embodiment of the method according to the invention, the method further comprises the step of applying an oxide-based inorganic coating layer having UV reflecting and/or absorbing properties either between a first surface of the polymeric substrate of the laminate and a second surface of a silicon-based inorganic layer of the

lamine or to at least a third surface of the silicon-based inorganic layer that is arranged opposite to the second surface of the silicon-based inorganic layer. This coating enables application of the lamine not only for in-door applications but also in weatherable applications. Non-limiting examples of the oxide-based inorganic coating layer are based on ZnO and CeO₂.

In an embodiment of the method according to the invention, the method further comprises the step of covering the lamine with a silicon-based inorganic layer comprising SiO_x using PECVD. By using PECVD SiO_x, it is possible to also coat curved substrates. SiO_x provides the lamine with glass-like abrasion resistance and barrier properties, weatherability and wear resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages of the invention will become apparent from the description of the invention by way of exemplary and non-limiting embodiments of a lamine for use in glazing applications according to the invention, a method of fabricating such lamine, a glazing product comprising such lamine, and a vehicle comprising such glazing product.

The person skilled in the art will appreciate that the described embodiments of the lamine, the method, the glazing product and the vehicle are exemplary in nature only and not to be construed as limiting the scope of protection in any way. The person skilled in the art will realize that alternatives and equivalent embodiments of the lamine, the method, the glazing product, and the vehicle can be conceived and reduced to practice without departing from the scope of protection of the present invention. Reference will be made to the figures on the accompanying drawing sheets. The figures are schematic in nature and therefore not necessarily drawn to scale. Furthermore, equal reference numerals denote equal or similar parts. On the attached drawing sheets,

figure 1 shows a cross-sectional view of a first exemplary, non-limiting embodiment of a lamine according to the invention comprising an adhesion-enhancing layer that is a silicone hardcoat layer;

figure 2a shows a cross-sectional view of a second exemplary, non-limiting embodiment of a lamine according to the invention comprising a PC-based substrate that is provided with an adhesion enhancing layer at its first surface, the adhesion enhancing layer being an organic primer layer comprising a first composition;

figure 2b shows a cross-sectional view of the second exemplary, non-limiting embodiment of the lamine according to the invention comprising an polymeric substrate that is one of a PC-based substrate and a PMMA-based substrate, the

polymeric substrate being provided with an adhesion enhancing layer at its first surface, the adhesion enhancing layer being an organic primer layer comprising a second composition;

figure 3a shows a cross-sectional view of a third exemplary, non-limiting embodiment of a laminate according to the invention that is free of any adhesion enhancing intermediate layer;

figure 3b shows a cross-sectional view of the third exemplary, non-limiting embodiment of the laminate according to the invention that is provided with an oxide-based inorganic coating layer that is arranged between a first surface of the polymeric substrate and a second surface of a silicon-based inorganic layer of the laminate;

figure 3c shows a cross-sectional view of the third exemplary, non-limiting embodiment of the laminate according to the invention that is provided with an oxide-based inorganic coating layer that is arranged on a third surface of the silicon-based inorganic layer of the laminate;

figure 4 shows a perspective view of a first exemplary, non-limiting embodiment of a glazing product comprising a laminate according to the invention; and

figure 5 shows a perspective view of a first exemplary, non-limiting embodiment of a vehicle comprising a glazing product according to the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

Embodiment 1: Laminate free of acrylic-based tie layer

Figure 1 schematically shows a cross-sectional view of a first exemplary, non-limiting embodiment of a laminate 1 according to the invention. The laminate 1 comprises an optically transparent polymeric substrate 2 that that can be either a PMMA-based substrate, or a PC-based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer. The laminate 1 has a high light transmissivity, stability to ultraviolet (UV) light, and glass-like high scratch and mar resistance. These properties render the laminate 1 suitable for use in glazing applications. The optically transparent polymeric substrate is transparent to at least light visible to the human eye, wherein the transmittance of visible light is above 30%. The transparent polymeric substrate may be combined with an opaque polymeric substrate, wherein opaque is defined as having a visible light transmittance of up to 30%. Both the transparent and the opaque polymeric substrates can be provided with a coating arrangement as described herein. The transparent and opaque polymeric substrates may comprise similar materials, or dissimilar materials.

The polymeric substrate 2 has a first surface 3 that is selectively enriched with siloxane segments, either partially or entirely. The siloxane segments may be uniformly distributed. The first surface 3 of the polymeric substrate is provided with a coating system that comprises an optically transparent silicon-based inorganic layer 4 as a top or capping layer. The silicon-based inorganic layer 4 can comprise plasma-enhanced chemical-vapor deposited (PECVD) silica, e.g. silicon oxide (SiO_x). The silicon-based inorganic layer 4 provides the laminate 1 with glass-like abrasion resistance and barrier properties. The silicon-based inorganic layer 4 has a second surface 5 that faces towards the first surface 3 of the polymeric substrate 2. According to the first embodiment of the laminate 1 shown in figure 1, the second surface 5 of the silicon-based inorganic layer 4 is associated with the first surface 3 of the polymeric substrate 2 via an adhesion-enhancing layer 6 of the coating system that is provided on the first surface 3. The adhesion-enhancing layer 6 forms an interface with both the first surface 3 of the polymeric substrate 2 and the second surface 5 of the silicon-based inorganic layer 4. In the embodiment of the laminate 1 shown in figure 1, the adhesion-enhancing layer 6 is a silicone hardcoat layer that enables optimal adhesion between the polymeric substrate 2 and the silicon-based inorganic capping layer 4. The silicone hardcoat layer can be prepared and applied as described in detail in US 8,940,397 B2, column 16, lines 1-43.

The adhesion-enhancing layer 6 can comprise a silicone coating composition comprising at least one of silicone resin, curing catalyst and solvent. Furthermore, the adhesion-enhancing layer 6 can comprise UV reflecting and/or absorbing additives. In this way, optimal weatherability of the substrate 2 can be ensured rendering the laminate 1 suitable for out-door applications.

The chemistry and functionalization of the polymeric substrate 2 are suitably tailored to enable direct application of the silicone hardcoat layer to the first surface 3 of the polymeric substrate 2 without the use of an acrylic-based primer known in the state of the art. By avoiding the use of a known acrylic-based primer, it is possible to reduce the number of intermediate tie layers as compared to the state of the art without compromising on the desired functionality. The skilled person will appreciate that by reducing the number of tie layers used, productivity and part quality can be improved. Furthermore, it is expected that in this way material and infrastructure costs associated with the application of the known acrylic-based primer layer can be reduced. Moreover, it is expected that the probability of defects and interfacial failures associated with the known acrylic-based primer layer, and the associated process challenges can be discarded.

The amount and length of the siloxane polymer segments incorporated within the PC-siloxane copolymer substrate 2 are optimized so as to minimally impact the optical transmissivity of the substrate 2 compared to pure PC. The presence of the siloxane polymer segments incorporated within the PC-siloxane copolymer substrate 2 in turn improves the chemical compatibility of the substrate 2 to the intermediate or silicone
5 hardcoat layer to the extent that the use of any intermediate acrylic-based tie (primer) layer as known in the art is eliminated.

The PC-based polymeric substrate 2 shown in figure 1 may be fabricated using a two-step injection-compression molding process (2K-ICM). In a first injection-molding
10 step, a PC or PC-siloxane copolymer is molded. In this way, the bulk of the optically transparent polymeric substrate 2 of the laminate 1 can be achieved. In a second injection-compression molding step, a masterbatch of a PC-siloxane copolymer is molded. By carrying out the second injection-compression, molding step the first surface 3 of the optically transparent polymeric substrate 2 can be selectively enriched
15 with siloxane segments. In this way, the compatibility of the first surface 3 of the polymeric substrate 2 with the silicone hardcoat layer can be improved.

The selective enrichment of the first surface 3 of the polymeric substrate 2 with siloxane segments through ICM-based over-molding is also expected to result in an polymeric substrate 2 with low birefringence and residual stresses, improved
20 compatibility of the PC-based bulk layer (first shot) with the PC-siloxane copolymer masterbatch (second shot), and overall better performance in terms of establishment of the silicone hardcoat layer on the polymeric substrate 2.

In the second injection-compression, molding step the masterbatch of the PC-siloxane copolymer can be enriched with UV-stabilizing and/or UV-resistant additives.
25 In this way, a laminate 1 can be fabricated that comprises a polymeric substrate 2 having optimal weatherability.

Accordingly, the present invention provides a way of fabricating a laminate 1 that comprises a siloxane-rich and hardcoat-compatible PC-based substrate 2 that does not need to be treated with any acrylic-based tie (primer) layer as known in the art to
30 improve the adhesion of an optically transparent silicon-based inorganic protection layer 4.

Alternatively, the polymeric substrate 2 of the laminate 1 can be fabricated by blending one of PC and PMMA with a masterbatch of an acrylate-siloxane copolymer having high concentrations of siloxane segments with the siloxane content in the
35 copolymer. The siloxane concentration in the masterbatch is diluted to the desired final concentration through blending with either pure PC or pure PMMA while ensuring that both its optical transmissivity is minimally reduced and the compatibility of the

polymeric substrate 2 with the silicone hardcoat layer is improved to the extent that the need for any intermediate acrylic-based tie layer as known in the art is eliminated.

Furthermore, the polymeric substrate 2 of laminate 1 may be manufactured using a 2K-ICM molding a first injection-molding step either pure PC or pure PMMA or a PC-siloxane copolymer. In this way, the bulk of the optically transparent polymeric substrate 2 of the laminate 1 can be achieved. In a second injection-compression, molding step a masterbatch of an acrylate-siloxane copolymer is molded. The second injection-compression molding step is carried out to selectively enrich the first surface 3 of the optically transparent polymeric substrate 2 with siloxane segments. In this way, the compatibility of the first surface 3 of the polymeric substrate 2 with the silicone hardcoat layer can be improved.

The selective surface enrichment of the polymeric substrate 2 with siloxane segments through ICM-based over-molding is also expected to result in an polymeric substrate 2 with low birefringence and residual stresses, improved compatibility of the PC or PMMA or PC-siloxane copolymer bulk layer (first shot) with the acrylate-siloxane masterbatch (second shot), and overall better performance in terms of establishment of the silicone hardcoat layer on the polymeric substrate 2.

In the second injection-compression, molding step the masterbatch of the acrylate-siloxane copolymer can be enriched with UV-stabilizing and/or UV-resistant additives. In this way, a laminate 1 can be fabricated that comprises an polymeric substrate 2 having optimal weatherability.

Accordingly, the present invention provides a way of fabricating a laminate 1 that comprises a siloxane-rich and hardcoat-compatible PC-based or PMMA-based polymeric substrate 2 that does not need to be treated with any acrylic-based tie (primer) layer as known in the art to improve the adhesion of an optically transparent silicon-based inorganic protection layer 4.

Embodiment 2: Laminate free of silicone hardcoat layer

Figure 2a schematically shows a cross-sectional view of a second exemplary, non-limiting embodiment of a laminate 1 having a high light transmissivity, stability to ultraviolet (UV) light, and glass-like high scratch and mar resistance. These properties render the laminate 1 suitable for use in glazing applications. The laminate 1 shown in figure 2a comprises a PC-based substrate 2 that comprises one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer. The polymeric substrate 2 has a first surface 3 that is selectively enriched with siloxane segments. Preferably, the entire first surface 3 is enriched with siloxane segments. The siloxane segments can be uniformly distributed. The first surface 3 is provided with an adhesion-enhancing layer

that in the embodiment of the laminate shown in figure 2a is a primer layer comprising a first composition 7.

The first surface 3 of the PC-based polymeric substrate 2 shown in figure 2a is provided with a coating system that comprises an optically transparent silicon-based inorganic layer 4 as a top or capping layer. The silicon-based inorganic layer 4 can comprise plasma-enhanced chemical-vapor deposited (PECVD) silica, e.g. silicon oxide (SiOx). The silicon-based inorganic layer 4 provides the laminate 1 with glass-like abrasion resistance and barrier properties. The silicon-based inorganic layer 4 has a second surface 5 that faces towards the first surface 3 of the polymeric substrate 2.

According to the second embodiment of the laminate 1 shown in figure 2a, the second surface 5 of the silicon-based inorganic layer 4 is connected with the first surface 3 of the polymeric substrate 2 via a primer layer having a first composition 7 that is provided on the first surface 3. The primer layer forms interfaces with the first surface 3 of the polymeric substrate 2 and the second surface 5 of the silicon-based inorganic layer 4.

The first composition 7 of the primer layer can comprise an oligomeric PC-siloxane copolymer comprising high siloxane concentrations in order to enable an improved adhesion of the second surface 5 of the silicon-based inorganic layer 4 and the siloxane segments through Van der Waals bonds. Furthermore, the first composition 7 can comprise UV reflecting and/or absorbing additives. In this way, optimal weatherability of the substrate 2 can be ensured rendering the laminate 1 suitable for out-door applications.

By using an oligomeric PC-siloxane copolymer primer instead of aqueous acrylate-based primers conventionally employed in laminates known in the art, the first surface 3 of the substrate 2 can be selectively enriched with siloxane segments. This results in an adequate compatibility between the polymeric substrate 2 and the inorganic silicon-based layer 4 so as to eliminate the need for the silicone polymer composition based hardcoat layer that is routinely employed in laminate structures known in the art.

The PC segments of the oligomeric copolymer tether to the PC based substrate while the siloxane segments of the oligomeric copolymer provide tethers for the silicon-based inorganic layer 4. In this manner, a single oligomeric copolymer primer layer serves the functionality of the acrylic-based primer and the silicone hardcoat formulations known in the art. By avoiding the use of a known silicone hardcoat layer, the second embodiment of the laminate 1 makes it possible to reduce the number of intermediate tie layers as compared to the state of the art without compromising on the desired functionality. The skilled person will appreciate that by reducing the number of tie layers used, productivity and part quality can be improved. Furthermore, it is expected that in this way material and infrastructure costs associated with the

application of the known silicone hardcoat layer can be reduced. Moreover, it is expected that the probability of defects and interfacial failures associated with the known silicone hardcoat layer, and the associated process challenges can be discarded.

5 The first composition 7 can be applied to the first surface 3 of the PC-based polymeric substrate 2 by using flow-coating. The first composition 7 has a low intrinsic viscosity ranging from 0.5 mPa-s to 25 mPa-s which allows easy spreading and interdiffusion of the first composition into the PC-based polymeric substrate 2, leading to an effective surface treatment.

10 The PC-based polymeric substrate 2 of the laminate 1 having a first surface 3 that is provided with the first composition 7 may be fabricated using a two-step injection-compression molding process (2K-ICM). In a first injection molding step a PC-siloxane copolymer is molded. In a second injection-compression molding step a first composition comprising an oligomeric PC-siloxane copolymer is used.

15 Based on the above, the present invention provides ways to achieve a PC-based polymeric substrate 2 that has a first surface 3 that is selectively enriched with siloxane segments to improve the compatibility with the silicon-based inorganic layer 4, which for example is PECVD SiOx. The second compression step associated with the first composition comprising oligomeric PC-siloxane copolymer allows an intimate surface
20 contact of the primer layer with the bulk substrate and also allows the formation of an optically thin layer of the primer layer to ensure minimal reduction of the optical transmissivity of the bulk substrate.

 Alternatively, the laminate 1 according to the second embodiment of the present invention can comprise an optically transparent polymeric substrate 2 that is one of a
25 PMMA-based substrate and a PC-based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer. In such a case, the first surface 3 of the substrate 2 can be provided with a primer layer comprising a second composition 8 that can comprise an oligomeric acrylate-siloxane copolymer comprising high siloxane concentrations in order to enable an improved adhesion of
30 the silicon-based inorganic layer 4 and the siloxane segments through Van der Waals bonds. As shown in the schematic cross-sectional view of the laminate 1 of figure 2b, the second composition 8 forms interfaces with the first surface 3 of the polymeric substrate 2 and the second surface 5 of the silicon-based inorganic layer 4. Furthermore, the second composition 8 can comprise UV reflecting and/or absorbing.
35 In this way, optimal weatherability of the substrate 2 can be ensured rendering the laminate 1 suitable for out-door applications. By using an oligomeric acrylate-siloxane copolymer primer instead of aqueous acrylic-based primers conventionally employed in

laminates known in the art, the first surface 3 of the substrate 2 can be selectively enriched with siloxane segments. This results in an adequate compatibility between the polymeric substrate 2 and the inorganic silicon-based layer 4 so as to eliminate the need for the silicone polymer composition based hardcoat layer that is routinely employed in laminate structures known in the art. The acrylate segments of the oligomeric copolymer tether to the PMMA-based or PC-based polymeric substrate 2 while the siloxane segments of the oligomeric copolymer provide tethers for the silicon-based inorganic layer 4. In this manner, a single oligomeric copolymer primer layer serves the functionality of the acrylic-based primer and the silicone hardcoat formulations known in the art. By avoiding the use of a known silicone hardcoat layer, the second embodiment of the laminate 1 makes it possible to reduce the number of intermediate tie layers as compared to the state of the art without compromising on the desired functionality. The skilled person will appreciate that by reducing the number of tie layers used, productivity and part quality can be improved. Furthermore, it is expected that in this way material and infrastructure costs associated with the application of the known silicone hardcoat layer can be reduced. Moreover, it is expected that the probability of defects and interfacial failures associated with the known silicone hardcoat layer, and the associated process challenges can be discarded.

According to an exemplary embodiment of the method according to the invention, the second composition 8 comprising oligomeric acrylate-siloxane copolymer can be applied to the first surface 3 of the PMMA-based or PC-based polymeric substrate 2 by using flow-coating.

According to another exemplary embodiment of the method according to the invention, the PMMA-based or PC-based polymeric substrate 2 of the laminate 1 having a first surface 3 that is provided with the second composition 8 can be fabricated using a two-step injection-compression molding process (2K-ICM). In a first injection-molding step, either pure PC or pure PMMA or a PC-siloxane copolymer is molded. In a second injection-compression molding step a second composition comprising an oligomeric acrylate-siloxane copolymer is used.

Additionally or alternatively, the second composition comprising oligomeric acrylate-siloxane copolymer is used as an in-mold coating during injection molding of the bulk substrate. Moreover, the second composition comprising oligomeric acrylate-siloxane copolymer may be used as an in-mold decoration surface film during injection molding of the bulk substrate.

Based on the above, the present invention provides ways to achieve a PC-based or PMMA-based polymeric substrate 2 that has a first surface 3 that is selectively

enriched with siloxane segments to improve the compatibility with the silicon-based inorganic layer 4, which for example is PECVD SiOx. The second compression step associated with the second composition 8 comprising oligomeric acrylate-siloxane copolymer allows an intimate surface contact of the organic primer layer with the bulk substrate and also allows the formation of an optically thin layer of the organic primer layer to ensure minimal reduction of the optical transmissivity of the bulk substrate.

Embodiment 3: Laminate free of both acrylic-based tie layer and silicone hardcoat layer

Figure 3a schematically shows a cross-sectional view of a third exemplary, non-limiting embodiment of a laminate 1. The laminate 1 comprises an optically transparent polymeric substrate 2 that is one of a PMMA-based substrate and a PC-based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer. The laminate 1 has a high light transmissivity, stability to ultraviolet (UV) light, and glass-like high scratch and mar resistance. These properties render the laminate 1 suitable for use in glazing applications.

The polymeric substrate 2 has a first surface 3 that is selectively enriched with siloxane segments. Preferably, the entire first surface 3 is enriched with siloxane segments. The siloxane segments can be uniformly distributed. As shown in figure 3a, the first surface 3 is provided with an optically transparent silicon-based inorganic layer 4 as a top or capping layer, such as plasma-enhanced chemical-vapor deposited (PECVD) silica, e.g. silicon oxide (SiOx). The silicon-based inorganic layer 4 provides the laminate 1 with glass-like abrasion resistance and barrier properties. The silicon-based inorganic layer 4 has a second surface 5 that faces towards the first surface 3 of the polymeric substrate 2. According to the third embodiment of the laminate 1 shown in figure 3a, the second surface 5 of the silicon-based inorganic layer 4 is connected with the first surface 3 of the polymeric substrate 2 without using any adhesion enhancing or intermediate layer that is provided on the first surface 3. The second surface 5 of the silicon-based inorganic layer 4 forms an interface with low-surface-energy and low molecular weight oligomeric PC-siloxane copolymer additives within the polymeric substrate 2 that provide high siloxane concentrations at the first surface 3. In this way, an optimal adhesion can be achieved between the organic polymeric substrate 2 and the silicon-based inorganic layer 4. The use of low-surface-energy and low molecular weight PC-siloxane copolymer additives within the formulation of the substrate 2 allows selective segregation of the siloxane rich moieties from the bulk of the substrate 2 during injection molding to enrich the first surface 3 selectively with siloxane segments. Such selective enrichment of the first surface 3 of the substrate 2 with siloxane segments results in adequate compatibility between the polymeric

substrate 2 and the silicon-based inorganic layer 4. Consequently, the laminate 1 according to the third non-limiting embodiment as shown in figure 3a is free of both an acrylic-based primer layer and a silicone hardcoat layer that are known from the art. Accordingly, process challenges associated with the use of such acrylic-based primer and silicone hardcoat layers can be avoided. Hence, it is expected that the laminate 1 according to the third embodiment can be cost effective and easily implementable.

Using oligomeric PC-siloxane copolymer additives / master-batches having an optimal siloxane content and composition, and using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface 3 (skin region) of the PC-based polymeric substrate 2 during an injection molding step in which the polymeric substrate 2 is fabricated. This will enrich the siloxane content at the first surface 3 of the PC-based substrate 2 and it is envisaged that this leads to an improved adhesion of the second surface 5 of the silicon-based inorganic coating layer 4 to the first surface 3 of the PC-based substrate 2. High concentrations of siloxane at the first surface 3 of the PC-based polymeric substrate 2 facilitate an improved adhesion of the second surface 5 of the silicon-based inorganic layer 4 and the siloxane segments through Van der Waals bonds. As a result of the above, the present invention provides a laminate 1 that does not need to comprise both the acrylic-based primer and the silicone hardcoat layer known in the art. During molding of the PC-based polymeric substrate 2 using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface 3 (skin region) of the PC-based polymeric substrate 2. This will result in the abovementioned benefits of selectively enriching the siloxane content at the first surface 3 of the PC-based substrate 2 and the improved adhesion of the second surface 5 of the silicon-based inorganic coating layer 4 to the first surface 3 of the PC-based substrate 2.

In the event that the laminate 1 as shown in figure 3a comprises a PMMA-based polymeric substrate 2, this substrate can comprise a second organic additive comprising oligomeric acrylate-siloxane copolymer.

Using oligomeric acrylate-siloxane copolymer additives / master-batches having an optimal siloxane content and composition, and using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface 3 (skin region) of the PMMA-based polymeric substrate 2 during an injection molding step in which the polymeric substrate 2 is fabricated. This will enrich the siloxane content at the first surface 3 of the PMMA-based substrate 2 and it is envisaged that this leads to an improved adhesion of the second surface 5 of the silicon-based inorganic coating layer 4 to the first surface 3 of the PMMA-based substrate 2. High concentrations of siloxane at the first surface 3 of the PMMA-based polymeric

substrate 2 facilitate an improved adhesion of the second surface 5 of the silicon-based inorganic layer 4 and the siloxane segments through Van der Waals bonds. As a result of the above, the present invention provides a laminate 1 that does not need to comprise both the acrylic-based primer and the silicone hardcoat layer known in the art.

During molding of the PMMA-based polymeric substrate 2 using optimized process conditions, it is envisaged that these oligomers will preferentially migrate towards the first surface 3 (skin region) of the PMMA-based polymeric substrate 2. This will result in the abovementioned benefits of selectively enriching the siloxane content at the first surface 3 of the PMMA-based substrate 2 and the improved adhesion of the second surface 5 of the silicon-based inorganic coating layer 4 to the first surface 3 of the PMMA-based substrate 2.

According to another embodiment of the method according to the invention, an oxide-based inorganic coating layer 9 having UV reflecting and/or absorbing properties is applied either between a first surface 3 of the polymeric substrate 2 of the laminate 1 and a second surface 5 of a silicon-based inorganic layer 4 of the laminate 1 or to a third surface 10 of the silicon-based inorganic layer 4 that is arranged opposite to the second surface 5 of the silicon-based inorganic layer 4 as is schematically shown in figures 3b and 3c, respectively.

The oxide-based inorganic coating layer 9 enables application of the laminate 1 not only in in-door applications but also in weatherable applications. Non-limiting examples of the oxide-based inorganic coating layer are based on ZnO and CeO₂. The skilled person will appreciate that two processes of this invention are critical for determining the overall glazing part quality and productivity. These include the preparation of the formulation used for the injection molding and the process associated with inorganic coating layer 9.

Figure 4 shows a perspective view of a first exemplary, non-limiting embodiment of a glazing product 11 comprising a laminate 1 according to the invention. The glazing product 11 shown in figure 4 is a front window of a car. The skilled person will appreciate that other non-limiting examples of glazing products in which laminates can be envisaged comprise aerospace glazing panels and eyewear.

Figure 5 shows a perspective view of a first exemplary, non-limiting embodiment of a vehicle 12 comprising a glazing product 11 according to the invention. The vehicle 12 shown in figure 5 is car having at least one glazing panel, in this case the rear window that comprises a laminate 1 according to the invention. When applying the laminate in one of the vehicles mentioned above, the skilled person will appreciate that it is advantageous to arrange the laminate in such a way that the optically transparent

silicon-based inorganic layer, e.g. PECVD SiO_x, is facing towards the environment outside the vehicle because of the glass-like abrasion resistance and barrier properties, weatherability and wear resistance this layer provides to the laminate. Consequently, the optically transparent polymeric substrate of the laminate is facing towards the environment inside the vehicle. Other applications of the glazing product in vehicles may be in a head light, a tail light, a backlite, i.e. rear window, a panoramic roof window, a front window, a quarter window and/or a side window of the vehicle, specifically a passenger car.

The present invention can be summarized as relating to a laminate 1 for use in glazing applications comprising an polymeric substrate 2 that is optically transparent and has a first surface 3 that is selectively enriched with siloxane segments, the polymeric substrate being one of a PMMA-based substrate and a PC-based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer. The laminate further comprises a silicon-based inorganic layer 4 that is optically transparent and has a second surface 5 that is one of directly connected with the first surface of the polymeric substrate and connected with the first surface of the polymeric substrate via one adhesion enhancing layer 6 that is arranged between the first surface of the polymeric substrate and the second surface of the silicon-based inorganic layer. The invention also relates to a glazing product 11 comprising such a laminate, a vehicle 12 comprising such a glazing product and a method of fabricating such a laminate.

It will be clear to a person skilled in the art that the scope of the present invention is not limited to the examples discussed in the foregoing but that several amendments and modifications thereof are possible without deviating from the scope of the present invention as defined by the attached claims. While the present invention has been illustrated and described in detail in the figures and the description, such illustration and description are to be considered illustrative or exemplary only, and not restrictive.

The present invention is not limited to the disclosed embodiments. Variations to the disclosed embodiments can be understood and effected by a person skilled in the art in practicing the claimed invention, from a study of the figures, the description and the attached claims. In the claims, the word "comprising" does not exclude other steps or elements, and the indefinite article "a" or "an" does not exclude a plurality. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage. Any reference numerals in the claims should not be construed as limiting the scope of the present invention.

REFERENCE NUMERALS

	1	laminate
	2	optically transparent polymeric substrate
	3	first surface of optically transparent polymeric substrate
5	4	optically transparent silicon-based inorganic layer
	5	second surface of the optically transparent silicon-based inorganic layer
	6	adhesion enhancing layer
	7	first composition of the primer layer
	8	second composition of the primer layer
10	9	oxide-based inorganic coating layer
	10	third surface of the optically transparent silicon-based inorganic layer
	11	glazing product
	12	vehicle

CLAIMS

1. A laminate (1) for use in glazing applications comprising:
- a polymeric substrate (2) that is optically transparent and has a first surface (3) that is selectively enriched with siloxane segments, the polymeric substrate being one of a poly methyl methacrylate (PMMA) based substrate, and a polycarbonate (PC) based substrate comprising one of PC, a PC-siloxane copolymer and a blend of PC with PC-siloxane copolymer; and
 - a silicon-based inorganic layer (4) that is optically transparent and has a second surface (5) that is one of
 - directly connected with the first surface (3) of the polymeric substrate (2); and
 - connected with the first surface (3) of the polymeric substrate (2) via one adhesion enhancing layer (6) that is arranged between the first surface (3) of the polymeric substrate (2) and the second surface (5) of the silicon-based inorganic layer (4).
2. The laminate (1) according to claim 1, wherein the PC-siloxane copolymer based substrate has a siloxane content ranging from 0.5 wt.% to 10 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula -[Si(CH₃)₂O]-.
3. The laminate (1) according to claim 1, wherein the substrate based on the blend of PC with PC-siloxane copolymer has a siloxane content in the copolymer ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula -[Si(CH₃)₂O]-.
4. The laminate (1) according to any one of claims 1 to 3, wherein the adhesion-enhancing layer (6) is one of a silicone hardcoat layer and a primer layer.
5. The laminate (1) according to claim 4, wherein the silicone hardcoat layer comprises UV reflecting and/or absorbing additives.
6. The laminate (1) according to claim 4, wherein the polymeric substrate (2) is a PC-based substrate and the primer layer is a first composition (7) comprising an oligomeric PC-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 95 wt.%.
7. The laminate (1) according to claim 6, wherein the first composition (7) comprises UV reflecting and/or absorbing additives.
8. The laminate (1) according to claim 4, wherein the primer layer is a second composition (8) comprising an oligomeric acrylate-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 90 wt.%.

9. The laminate (1) according to claim 8, wherein the second composition (8) comprises UV reflecting and/or absorbing additives.

10. The laminate (1) according to any one of claims 1 to 3, wherein the polymeric substrate (2) is a PC-based substrate that comprises a first additive
5 comprising oligomeric PC-siloxane copolymer having an overall molecular weight ranging from 1500 to 12000, a surface energy ranging from 1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%.

11. The laminate (1) according to any one of claims 1 to 3, wherein the polymeric substrate (2) is a PMMA-based substrate that comprises a second additive
10 comprising oligomeric acrylate-siloxane copolymer having an overall molecular weight ranging from 800 to 9000, a surface energy ranging from 0.1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%.

12. The laminate (1) according to any one of claims 1 to 11, wherein the silicon-based inorganic layer (4) comprises PECVD silicon oxide, SiOx.

13. A glazing product (11) comprising a laminate (1) according to any one of
15 claims 1 to 12.

14. A vehicle (12) comprising a glazing product (11) according to claim 13.

15. A method of fabricating a laminate (1) for use in glazing applications according to any one of claims 1 to 12, comprising at least one of blending, injection
20 molding, injection-compression molding, multi-component or multi-shot injection compression molding, solvent based flow-coating, coextrusion, laminating, plasticizing, calendaring, coating and plasma-enhanced chemical vapor deposition.

16. The method according to claim 15, wherein an polymeric substrate (2) of the laminate (1) is fabricated by blending PC with a masterbatch of a PC-siloxane
25 copolymer having a siloxane content ranging from 10 wt.% to 80 wt. % and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula -
[Si(CH₃)₂O]-.

17. The method according to claim 15, wherein an polymeric substrate (2) of the laminate (1) is fabricated using a two-step injection-compression molding process,
30 wherein in a first injection molding step a PC-siloxane copolymer is molded, the PC-siloxane copolymer having a siloxane content ranging from 1 wt.% to 7 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula -[Si(CH₃)₂O]-, and wherein in a second injection-compression molding step a masterbatch of a PC-siloxane copolymer is molded, the masterbatch having a siloxane
35 content ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units.

18. The method according to claim 17, wherein in the second injection-compression molding step the masterbatch of the PC-siloxane copolymer is enriched with UV-stabilizing additives.

19. The method according to claim 15, wherein an polymeric substrate (2) of the laminate (1) is fabricated by blending one of polycarbonate (PC) and poly methyl methacrylate (PMMA) with a masterbatch of an acrylate-siloxane copolymer having a siloxane content ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$.

20. The method according to claim 15, wherein an polymeric substrate (2) of the laminate (1) is fabricated using a two-step injection-compression molding process, wherein in a first injection molding step either pure PC or pure PMMA or a PC-siloxane copolymer is molded, the PC-siloxane copolymer having a siloxane content ranging from 1 wt.% to 7 wt.% and siloxane segment sizes varying from 3 to 20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$; and wherein in a second injection-compression molding step a masterbatch of an acrylate-siloxane copolymer is molded, the masterbatch having a siloxane content ranging from 10 wt.% to 80 wt.% and siloxane segment sizes varying from 3 to 20 d-units.

21. The method according to claim 20, wherein in the second injection-compression molding step the masterbatch of the acrylate-siloxane copolymer is enriched with UV reflecting and/or absorbing additives.

22. The method according to any one of claims 16 to 18, wherein flow-coating is used to provide a first surface (3) of the polymeric substrate (2) of the laminate (1) with an primer layer that comprises a first composition (7) comprising an oligomeric PC-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 95 wt.%, and wherein the first composition (7) employed for flow-coating has an intrinsic viscosity ranging from 0.5 mPa-s to 25mPa-s.

23. The method according to any one of claims 19 to 21, wherein flow-coating is used to provide a first surface (3) of the polymeric substrate (2) of the laminate (1) with an primer layer that comprises a second composition (8) comprising an oligomeric acrylate-siloxane copolymer having an oligomeric chain length of at most 100 and a siloxane content ranging from 5 wt.% to 90 wt.%, and wherein the second composition employed for flow-coating has an intrinsic viscosity ranging from 0.5 mPa-s to 25 mPa-s.

24. The method according to claim 15, wherein a PC-based polymeric substrate (2) of the laminate (1) comprises a PC-siloxane copolymer having a siloxane content ranging from 0.5 wt.% to 10 wt.% and siloxane segment sizes varying from 3 to

20 d-units, wherein the d-unit has the formula $-\text{Si}(\text{CH}_3)_2\text{O}-$, is plasticized with oligomeric PC-siloxane copolymer having an overall molecular weight ranging from 1500 to 12000, a surface energy ranging from 1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%.

- 5 25. The method according to claim 15, wherein a PMMA-based polymeric substrate (2) of the laminate (1) is plasticized with oligomeric acrylate-siloxane copolymer having an overall molecular weight ranging from 800 to 9000, a surface energy ranging from 0.1 mN/m to 30 mN/m, and a siloxane content ranging from 5 wt.% to 90 wt.%.
- 10 26. The method according to any one of claims 15 to 25, further comprising the step of covering the laminate (1) with a silicon-based inorganic layer (4) comprising SiO_x using PECVD.

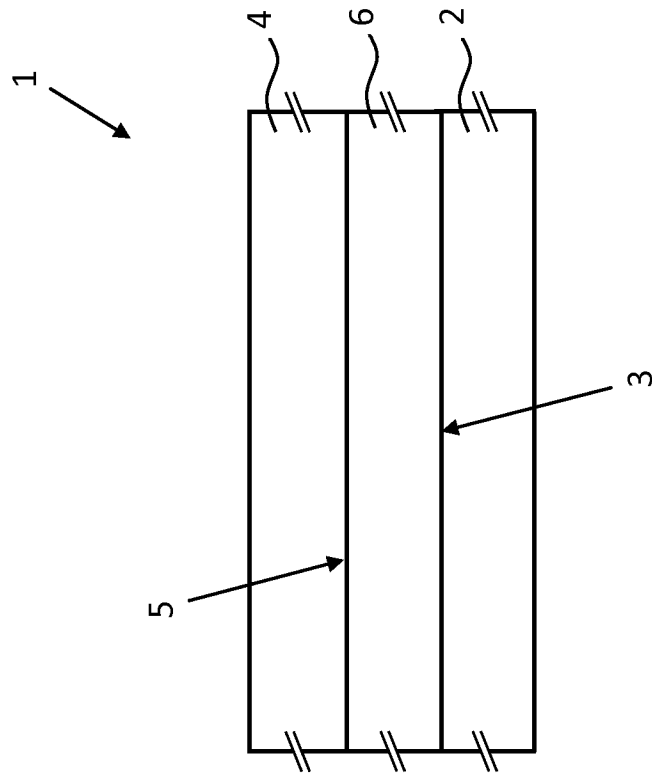


Fig. 1

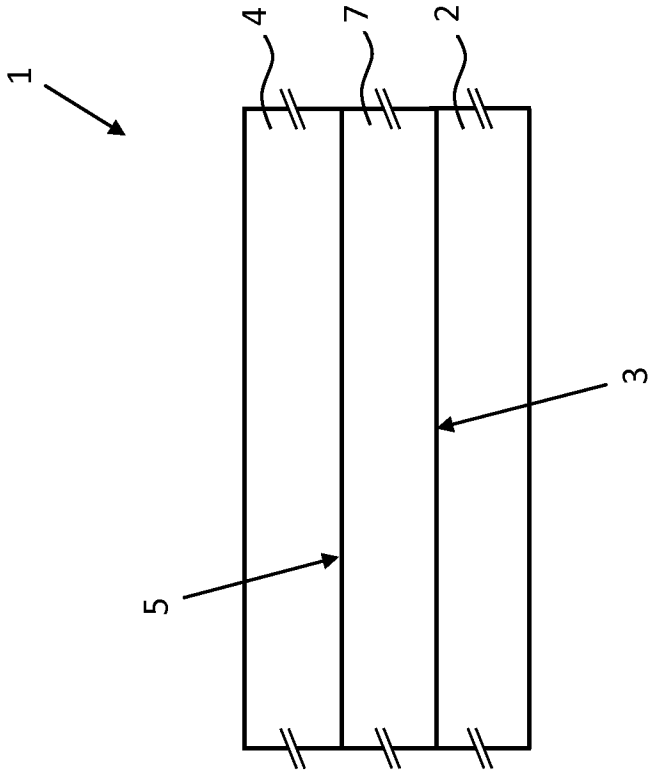


Fig. 2a

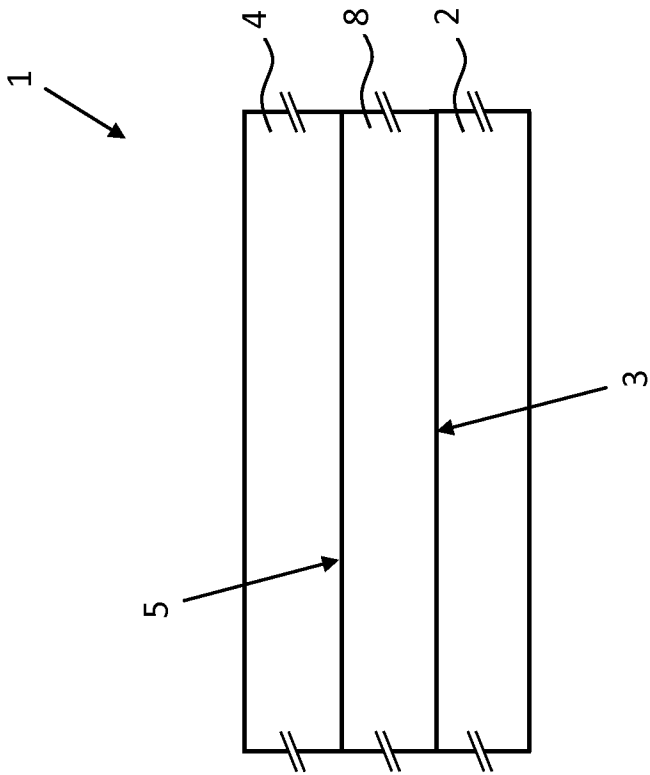


Fig. 2b

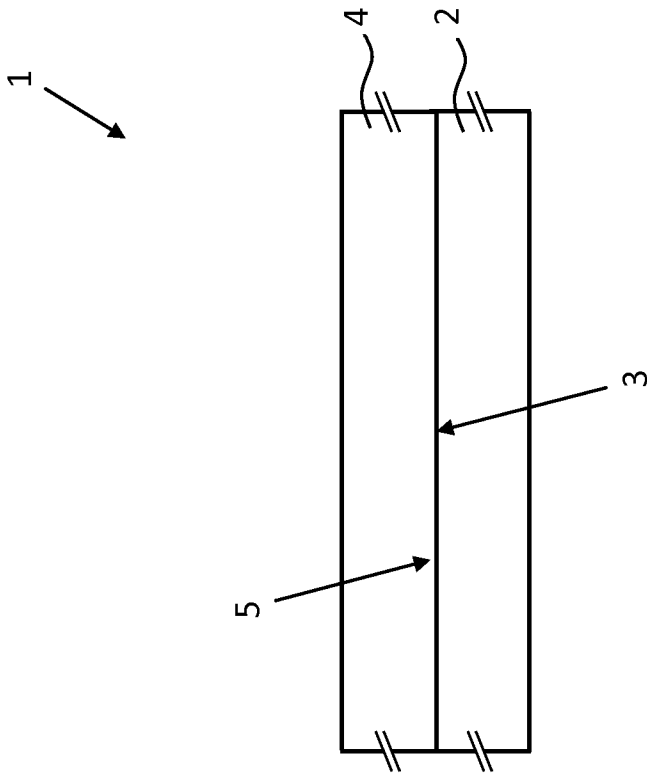


Fig. 3a

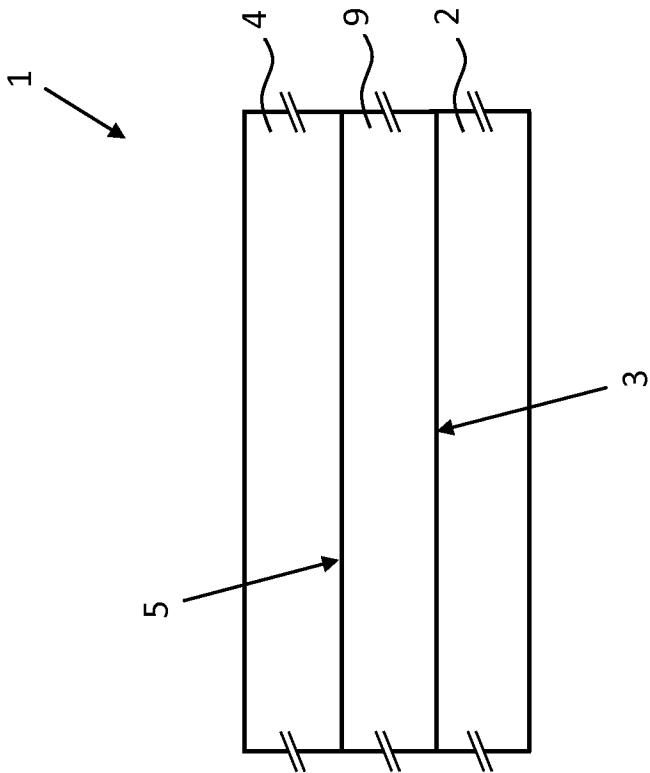


Fig. 3b

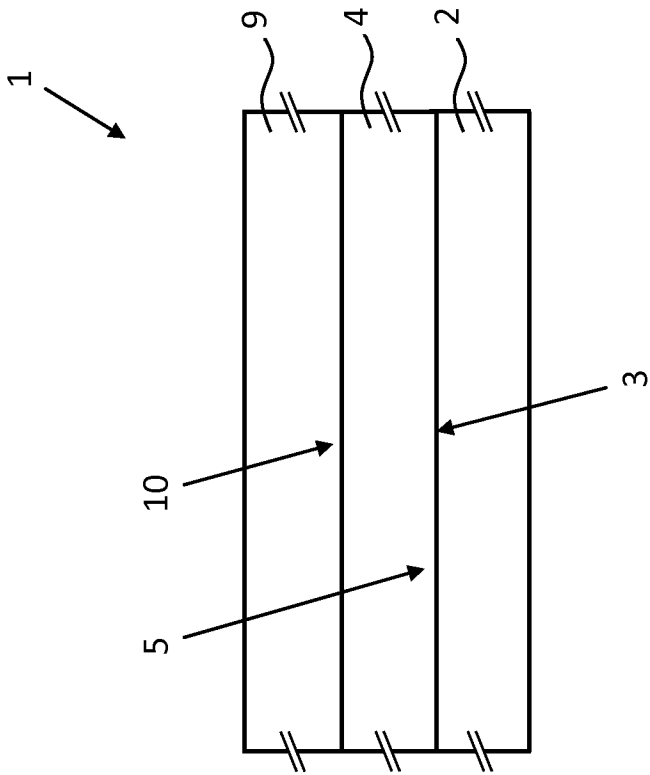


Fig. 3c

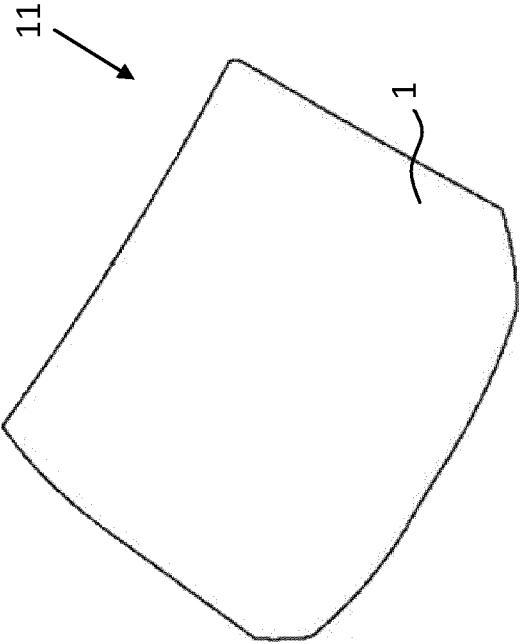


Fig. 4

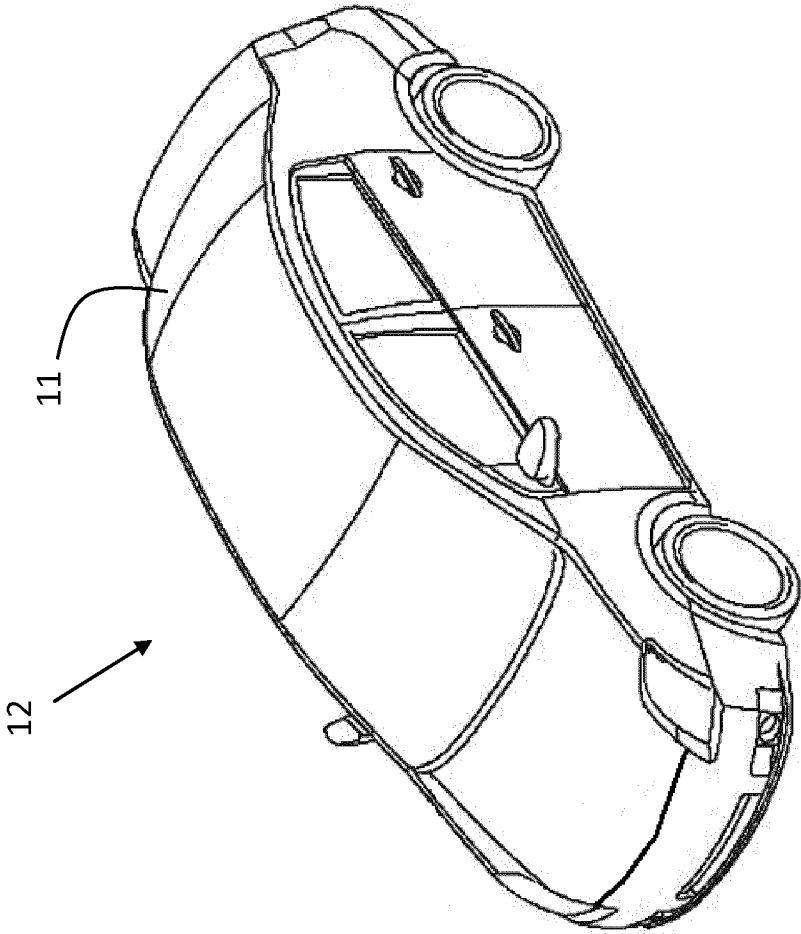


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/074434

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B7/02 B32B7/12 B32B27/08 B32B27/30 B32B27/36
C08J7/04

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 201359 29 August 2013 (2013-08-29) Thomson Scientific, London, GB; AN 2013-M79667 XP002779177, -& JP 2013 166807 A (FUJI KASEI KK) 29 August 2013 (2013-08-29)	1-15,26
A	abstract paragraphs [0001] - [0004], [0008] - [0014], [0017], [0028], [0032], [0034], [0036] examples 1-4, 6-9; table 1 claims 1-3, 6, 8 ----- -/--	16-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

16 March 2018

Date of mailing of the international search report

06/04/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Vandoolaeghe, P

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/074434

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/219803 A1 (MALLESHA HONNAIAH [IN] ET AL) 30 August 2012 (2012-08-30) cited in the application paragraphs [0001] - [0003], [0006] - [0008], [0019], [0046], [0049], [0050], [0052] examples 1, 9; tables 1-4, 7, 8 claims 1, 12, 14-17, 19, 20, 25, 27, 28 -----	1,12-15, 26
X	US 4 842 941 A (DEVINS JOHN C [US] ET AL) 27 June 1989 (1989-06-27) column 1, lines 9-21 column 2, lines 15-26 column 3, line 53 - column 4, line 21 column 4, lines 51-57 examples 7, 8, 16-25; tables I-V claims 1, 2 -----	1,12-15, 26
X	US 2006/204746 A1 (LI CHENGTAO [US] ET AL) 14 September 2006 (2006-09-14) paragraphs [0003], [0005] - [0010], [0025], [0026], [0029] - [0031] figure 1 claims 1-5, 7, 11-14, 44, 46, 47, 50-52 -----	1,4, 12-15,26 2,3, 5-11, 16-25
A	US 2014/058023 A1 (WAN SHUN [CN] ET AL) 27 February 2014 (2014-02-27) paragraphs [0005] - [0012], [0074], [0148] claim 1 -----	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/074434

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2013166807 A	29-08-2013	JP 5939825 B2 JP 2013166807 A	22-06-2016 29-08-2013
US 2012219803 A1	30-08-2012	BR 112013021992 A2 CN 103492502 A EP 2681285 A1 ES 2591008 T3 JP 6026440 B2 JP 2014511421 A KR 20140010084 A TW 201239048 A US 2012219803 A1 WO 2012118741 A1	16-11-2016 01-01-2014 08-01-2014 24-11-2016 16-11-2016 15-05-2014 23-01-2014 01-10-2012 30-08-2012 07-09-2012
US 4842941 A	27-06-1989	DE 3884438 D1 DE 3884438 T2 EP 0285870 A2 JP S644343 A JP H0781023 B2 US 4842941 A	04-11-1993 28-04-1994 12-10-1988 09-01-1989 30-08-1995 27-06-1989
US 2006204746 A1	14-09-2006	CN 101198463 A EP 1879739 A2 JP 2008531338 A KR 20070120508 A KR 20140035503 A US 2006204746 A1 WO 2006121484 A2	11-06-2008 23-01-2008 14-08-2008 24-12-2007 21-03-2014 14-09-2006 16-11-2006
US 2014058023 A1	27-02-2014	CN 104411767 A EP 2888324 A1 KR 20150046239 A US 2014058023 A1 WO 2014030133 A1	11-03-2015 01-07-2015 29-04-2015 27-02-2014 27-02-2014