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(71) Applicant: **AGP AMERICA S.A.** [PA/PA]; MMG Tower, piso 23, Avenida paseo del Mar, Ciudad De Panamá. (PA).

(72) Inventor: **MANNHEIM ASTETE, Mario Arturo**; Av. Guillermo Dansey 1996, Cercado de Lima, Lima (PE).

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— *as to the identity of the inventor (Rule 4.17(i))*
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(54) Title: LIGHTWEIGHT AUTOMOTIVE LAMINATE WITH HIGH RESISTANCE TO BREAKAGE

(57) Abstract: Working with the traditional soda lime float glass, there is a limit on how thin an automotive laminate can be while still meeting all of the functional and safety requirements. By using alternate glass compositions and chemical tempering, a thinner lightweight automotive laminate, which meets all requirements, and with high resistance to stone chips, has been produced.

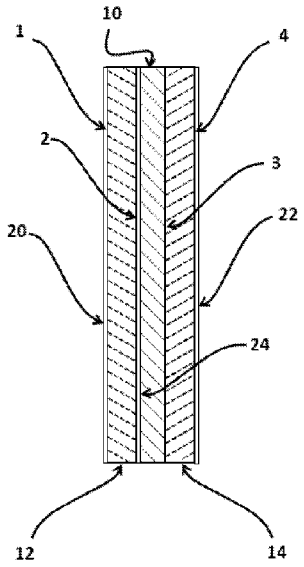


Fig. 2

WO 2018/122769 A1

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LIGHTWEIGHT AUTOMOTIVE LAMINATE WITH HIGH RESISTANCE TO BREAKAGE

Cross-reference to related applications

This application claims the benefits of the filing date of provisional patent application U.S. N° 62/440,453 titled "Lightweight automotive laminate with high resistance to breakage," which was filed on 30 December 2016, by the same inventor of this application. The aforementioned provisional application is incorporated herein as reference, as if it were divulged in the present document.

Field of invention

The present invention relates generally to the field of automotive glass laminate comprising a chemically tempered layer.

Background of the invention

In response to the regulatory requirements for increased automotive fuel efficiency as well as the growing public awareness and demand for environmentally friendly products, automotive original equipment manufacturers, around the world, have been working to improve the efficiency of their vehicles.

One of the key elements of this strategy to improve efficiency has been the concept of light weighting. Often times, more traditional, less expensive, conventional materials and processes are being replaced by innovative new materials and processes which while sometime being more expensive, still have higher utility than the materials and processes being replaced due to their lower weight and the corresponding increase in fuel efficiency. Sometimes, the new materials and processes bring with them added functionality as well in addition to their lighter weight. Vehicle glazing has been no exception.

For many years, the standard automotive windshield had a thickness of 5.4 mm. In more recent years, we have seen the thickness decrease to 4.75 mm. While a reduction of 0.65 mm

may not seem significant, at a density of 2600 kg per cubic meter for the typical standard soda lime float glass, each millimeter that the thickness is reduced, decreases the weight by 2.6 kg per square meter. The weight of a typical 1.2 square meter windshield going from 5.4 mm to 4.75 mm is reduced by a little over 2 kg. On a vehicle with a total of 6 square meters of glass, a 1 mm reduction on all of the windows translates into a savings of 15.6 kg.

In addition to the weight saved by reducing the glazing thickness, the glazed area of vehicles has been steadily increasing and in the process displacing other heavier materials for further savings. The popular large glass panoramic roofs are just one example of this trend.

However there are limits as to have thin the glazing can be with an annealed soda lime glass construction. The windshield must have sufficient strength to hold up under the stress induced by wind load. With the trend towards increasing the size of windshields in particular, even more strength is needed. Glass is also becoming a structural element in more and more vehicles. The glazing now contributes to the stiffness and strength of the car. Fixed glass, once bonded with a relatively soft curing poly-urethane, is being mounted with higher modulus adhesives. As a result, the glass, once isolated by rubber gaskets and soft butyl adhesives, is now much more subject to loading from the bumps in the road and vehicle torsion.

Today, windshields with a 2.1 mm outer ply or layer **12**, a 1.6 mm inner ply or layer **14** and a 0.76 mm plastic interlayer **10** totaling just under 4.5 mm in total thickness are becoming common (Figure 1). This may be close to the limit of what can be done with conventional annealed soda lime glass.

Annealed glass is glass that has been slowly cooled from the bending temperature through the glass transition range. This is done to relieve stress in the glass. Annealed glass breaks into large shards with sharp edges. In a laminate, two layers **12**, **14** of annealed glass are glued together using a layer of thermo plastic **10** situated between the major faces **2**, **3** of said glass layers (Figure 1). If the laminated glass should break, the plastic interlayer **10** holds the shards of glass together, helping to maintain the structural integrity of the glass. The shards of broken glass tend to interlock much like the pieces of a jigsaw puzzle. A vehicle with a broken windshield can still be operated, often for an extended period if the damage is not in

the vision zones or too extensive. On impact, the plastic interlayer **10** also helps to prevent penetration by the occupant in the event of a collision or by objects striking the laminate from the exterior of the vehicle.

To make a thinner windshield, the glass needs to be stronger. Two processes can be used to increase the strength of glass. They are heat treating, in which the temperature of hot glass is rapidly cooled and chemical tempering which achieves the same effect through a chemical treatment.

Heat strengthened, full temper soda lime float glass, with a compressive strength in the range of at least 70 MPa, can be used in all vehicle positions other than the windshield. Heat strengthened (tempered) glass has a layer of high compression on the outside surfaces of the glass, balanced by tension on the inside of the glass which is produced by the rapid cooling of the hot softened glass. When tempered glass breaks, the tension and compression are no longer in balance and the glass breaks into small beads with dull edges. Tempered glass is much stronger than annealed laminated glass. The thickness limits of the typical automotive heat strengthening process are in the 3.2mm to 3.6 mm range. This is due to the rapid heat transfer that is required. It is not possible to achieve the high surface compression needed with thinner glass using the typical blower type low pressure air quenching systems.

Glass can also be chemically tempered. In this process, ions in and near the outside surface of the glass are exchanged with ions from the bath that are larger. This places the outer layer of glass in compression. Compressive strengths of up to 1,000 MPa are possible.

Chemical tempering is performed by immersing the glass in a bath of molten potassium nitrate. During the process, potassium ions replace ions of smaller elements in the glass surface creating a compression layer. The tempered strength is a function of the time that the glass is treated, the temperature of the bath, and the glass composition. The strength correlates to the depth of the compression layer. Typical parameters for chemical tempering are treatment at a temperature ranging from 350 °C to 475 °C for a period from 2 to 24 hours.

Unlike heat tempered glass, chemically tempered glass breaks into shards rather than the small bead typical of heat treated glass. This property allows for its use in windshields.

However, in standard windshield glass thicknesses of 2.0 mm or greater, chemically strengthened glass would actually be too strong. In the event of a crash and a head impact, the windshield must break, absorbing the energy of the impact rather than the head of the occupant. Therefore, depending upon the tempered strength, thicknesses of 1.0 mm or less must be used in windshields.

In the bullet resistant glazing market, two glass compositions commonly used are borosilicate glass and aluminosilicate glass.

Borosilicate glass is a type of glass that contains boric oxide. It has a low coefficient of thermal expansion and a high resistance to corrosive chemical. It is commonly used to make light bulbs, laboratory glassware, and cooking utensils.

Aluminosilicate glass is made with aluminum oxide. It is even more resistant to chemicals than borosilicate glass and it can withstand higher temperatures. Chemically tempered Aluminosilicate glass is widely used for displays on smart phones and other electronic devices.

In an attempt to reduce weight beyond what is possible with soda lime glass, hybrid glazings have been produced using a chemically tempered aluminosilicate layer of thin glass for the inner layer **14** and an annealed soda-lime glass layer for the outer layer **12** (Figure 1). The aluminosilicate, while having the potential for up to 1000 MPa at 0.7 mm thickness, does not hold up well to stone impacts. As a result, it must be used for the inner layer **14**. The soda lime glass outer layer **12** is no stronger or durable than the outer layer of an ordinary windshield. Due to the flexibility of the thin inner layer **14**. However, stone chip resistance in improved by a factor of two. Upon impact, the surface of glass will flex more so than an ordinary windshield, partially absorbing some of the energy of impact.

Another problem faced when transitioning to the thinner soda-lime glass alternatives is that they are typically only available in a clear color. This is in contrast to the hundreds of variations in compositions and coatings that are available in standard windshield thickness soda lime glass. The soda lime variations are primarily targeted at solar load control but also

serve an aesthetic function. Thus we are faced with the loss of the solar performance when designing with thinner glass.

It would be advantageous to be able to produce an even thinner laminate, with greater resistance to breakage and enhanced solar performance.

Description of the Figures

Figure 1 is a conventional laminate cross section according to prior art;
Figure 2 is a laminate cross section with coatings on surfaces 1, 2 and 4 according to the present invention;
Figure 3 is a laminate cross section with laminated film and coatings on surfaces 1 and 4 according to the present invention;
Figure 4 is a laminate cross section with coatings on surfaces 1, 3 and 4 according to the present invention.

Key to the Drawing Numerals

1	Surface one
2	Surface two
3	Surface three
4	Surface four
10	Plastic Interlayer
12	Outer glass layer
14	Inner glass layer
20	Coating
22	Coating
24	Coating
26	Coating
28	Film

Detailed description of the invention

As shown in Figures 1-4, standard terminology is used to describe the configuration of a laminated glazing wherein a normal automotive windshield is comprised of two layers of glass: an outer layer **12** and an inner layer **14**, which are permanently bonded together with a plastic interlayer **10**. The glass surface that is on the outside of the vehicle is referred to as surface one **1**. The opposite face of the outer layer of glass **12** is surface two **2**. The glass surface that is on the inside of the vehicle is referred to as surface four **4**. The opposite face of the inner layer of glass **14** is surface three **3**.

Now referring to Figures 2-4, the laminate of the invention utilizes an inner layer **14** of glass having a thickness of less than or equal to 1 mm, an aluminosilicate composition and chemically tempered with a depth of layer of at least 20 μm. This provides for a flexible yet strong substrate that can provide the support needed to hold up under wind load but yield under occupant impact.

For the outer layer **12**, annealed borosilicate glass, having a thickness equal to or less than 2.1 mm is used. Borosilicate was selected for its extreme hardness and resistance to breakage. Ordinary borosilicate, for the same thickness, is five times as resistance to stone chips as ordinary soda-lime glass. Combined with an aluminosilicate inner layer **14**, the stone resistance is as high as ten times that of soda-lime glass windshields.

With a 0.38 plastic interlayer **10**, a maximum total thickness of 3.48 is achieved. Even thinner compositions are possible. It should also be noted that the density of borosilicate glass is less than that of soda-lime glass. Borosilicate is 12% lighter for an additional weight savings.

Compared to the 4.5 mm windshield discussed earlier, the windshield of this cross section is close to 3 kg lighter per square meter. Going to a 1.6 mm borosilicate outer layer **12** increases the weight savings to 3.6 kg per square meter.

The typical stone impact leaves a defect in the glass that is on average 20-30 μm deep. To further improve upon the stone chip resistance a hard coat **20** can be applied to the outside surface **1** of the outer layer **12**. Such coatings are well known in the art. They can be applied by vacuum sputtering, spray coating, dip coating or by any other sufficient means of coating know in the art. A sol-gel is a preferred method as the coating can be easily applied by spray

or dip coating and the coating can be cured during the bending process. The hard coat **20** serves to absorb additional energy from the impact and further limit the depth of the defect preventing failure the glass layer under all but the most severe cases.

To add solar properties, surfaces one **1**, two **2**, three **3** and/or four **4** can be coated with a coating **20**, **22**, **24**, **26** that reflects or absorbs heat or that functions in some combination of the two. Again, any means know in the art can be used such as a vacuum sputtered metallic coating, a pyrolytic, a sol-gel or others. Alternately, a performance film layer **28** (Fig. 3), which reflects or absorbs heat or functions in some combination of the two, can be added to the laminate.

To further increase the utility to the final customer, additional coatings (not shown) can be included on the surface four **4** of the inner layer of glass **14**. This include but are not limited to anti-reflective, easy clean, finger print resistance and self-cleaning. Again, any means know in the art can be used such as a vacuum sputtered metallic coating, a pyrolytic, a sol-gel or others as appropriate for the type of coating selected. Any such coating however, must be done after the glass has been bent and chemically tempered. Most coatings will interfere with or be damaged by the chemical tempering process.

Embodiment 1

Outer layer

Borosilicate glass 2.1 mm with scratch resistance coating on surface 1 and with IR coating on surface 2

Plastic interlayer

0.76 mm PVB

Inner layer

Aluminosilicate glass 0.7 mm with anti-reflective coating, anti-fingerprints and easy to clean on surface 4

Embodiment 2

Outer layer

Borosilicate glass 1.75 mm with scratch resistance coating on surface 1 and with IR coating on surface 2

Plastic interlayer

0.76 mm PVB

Inner layer

Aluminosilicate glass 0.55mm with anti-reflective coating, anti-fingerprints and easy to clean on surface 4

Embodiment 3

Outer layer

Borosilicate glass 1.6 mm with scratch resistance coating on surface1 and with IR coating on surface 2

Plastic interlayer

0.38 mm PVB

Inner layer

Aluminosilicate 0.3mm with anti-reflective coating, anti-fingerprints and easy to clean on surface 4

Embodiment 4

Outer layer

Borosilicate glass 1.75 mm with scratch resistance coating on surface1 and with IR coating on surface 2

Plastic interlayer

0.76 mm PVB

Inner layer

Aluminosilicate 0.55mm with anti-reflective coating, anti-fingerprints and easy to clean on surface 4

The forms of the invention shown and described in this specification represent illustrative preferred embodiments and it is understood that various changes may be made without departing from the spirit of the invention as defined in the following claimed subject matter.

Claims

1. A laminate comprising
    a. Two glass layers, an inner layer and an outer layer;
    b. The inner layer having a thickness of less than or equal to 1 mm
        i. Fabricated from aluminosilicate glass
        ii. And chemically tempered;
    c. The outer layer having a thickness of less than or equal to 2.1 mm
        i. Fabricated from borosilicate glass;
    d. At least one plastic interlayer;
    e. Said at least one plastic interlayer situated between the major faces of said glass layers and serving to bond said glass layers to each other.
2. The laminate of claim 1 further comprising a protective hard coat applied to the outer layer.
3. The laminate of claim 1 further comprising at least one coating selected from the group consisting of heat reflecting coatings and heat absorbing coatings.
4. The laminate of claim 1 further comprising at least one film selected from the group consisting of heat reflecting films and heat absorbing films.
5. The laminate of claim 1 further comprising a coating applied to the surface four of the inner layer, wherein said coating is selected from the group consisting of an anti-reflective coating, an easy to clean coating, a finger print resistance coating and a self-cleaning coating.
6. The laminate of claim 1, wherein the outer layer is chemically tempered.

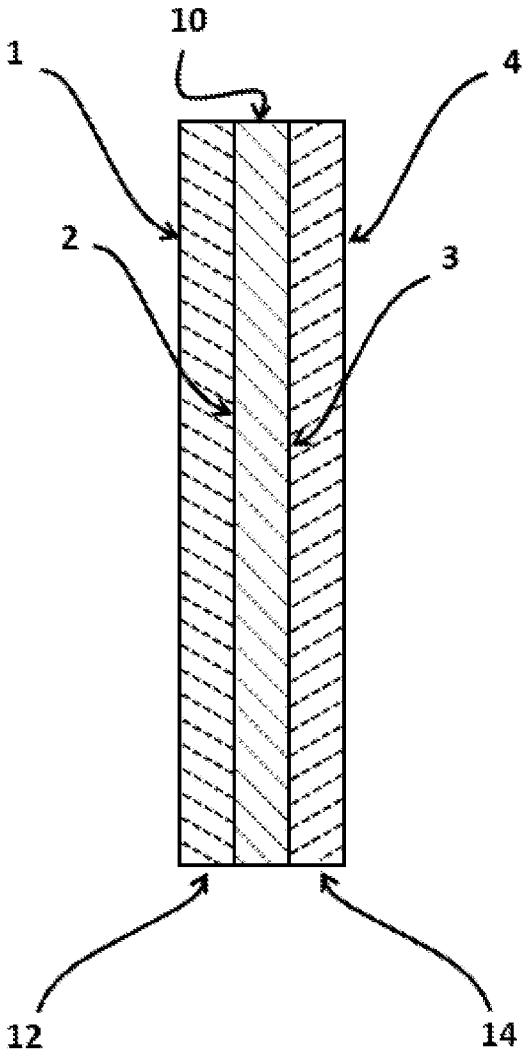


Fig. 1

(PRIOR ART)

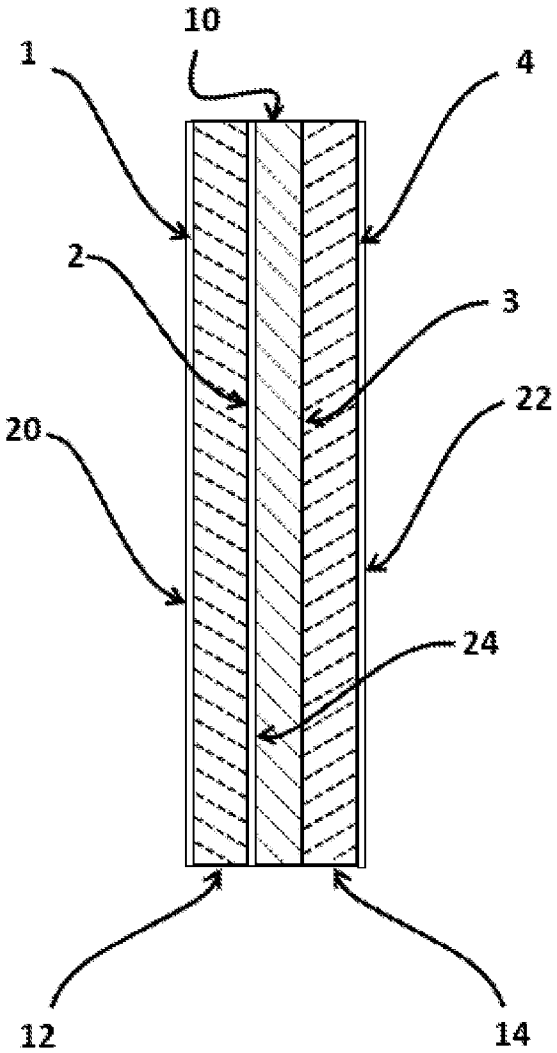


Fig. 2

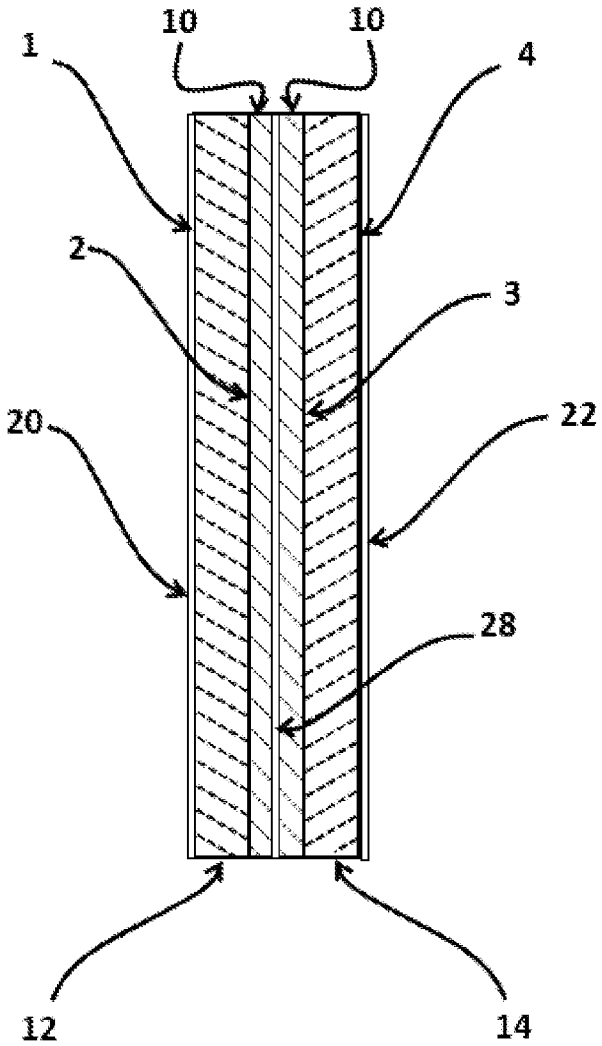


Fig. 3

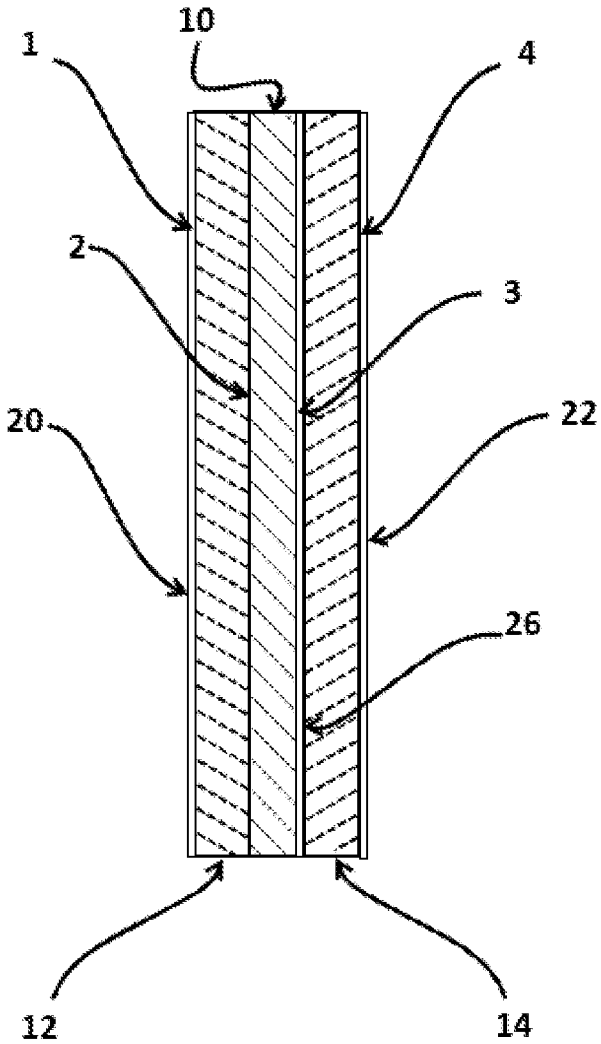


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/058468

A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B17/10 B64C1/14 B60J1/02
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 B64C B60J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/136929 A1 (MEISS JENS [DE] ET AL) 19 May 2016 (2016-05-19) paragraph [0121] - paragraph [0153]; figures 1,3,4,5; examples 5-11 paragraph [0092] - paragraph [0093]	1,6
X	DE 10 2014 213017 A1 (SCHOTT AG [DE]) 7 January 2016 (2016-01-07) paragraph [0097] - paragraph [0101]; claims 1,2,5,6; figure 1; examples 4-9	1,2,4-6
A	US 2016/279904 A1 (SIENERTH SANDRA [DE] ET AL) 29 September 2016 (2016-09-29) paragraph [0014] - paragraph [0023] paragraph [0069] - paragraph [0075]; claims 16,17-19	3,4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
27 March 2018	06/04/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lindner, Thomas

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/058468

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA 2 944 082 A1 (SAINT-GOBAIN GLASS FRANCE [FR]) 22 October 2015 (2015-10-22) page 7, line 4 - line 22; claims; figures 1,2	1-6
A	US 2013/302581 A1 (MANNHEIM ASTETE MARIO ARTURO BENJAMIN [CO] ET AL) 14 November 2013 (2013-11-14) paragraph [0079] - paragraph [0081]; claims; figures 1,7a,7b; examples 1-3	1,6
A	US 2016/257094 A1 (LESTRINGANT CLAIRE [FR] ET AL) 8 September 2016 (2016-09-08) paragraph [0046] - paragraph [0052]; claims; table 1	1,6

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2017/058468

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016136929 A1	19-05-2016	CA 2919071 A1	29-01-2015
		CN 105408107 A	16-03-2016
		DE 102013214422 A1	29-01-2015
		DE 112014003401 A5	19-05-2016
		JP 2016531067 A	06-10-2016
		US 2016136929 A1	19-05-2016
		WO 2015010922 A1	29-01-2015
DE 102014213017 A1	07-01-2016	NONE	
US 2016279904 A1	29-09-2016	CA 2925022 A1	30-04-2015
		CN 105636778 A	01-06-2016
		EA 201690830 A1	31-08-2016
		EP 3060392 A1	31-08-2016
		JP 2016539894 A	22-12-2016
		KR 20160060113 A	27-05-2016
		US 2016279904 A1	29-09-2016
		WO 2015058885 A1	30-04-2015
CA 2944082 A1	22-10-2015	CA 2944082 A1	22-10-2015
		CN 106458743 A	22-02-2017
		EA 201692058 A1	28-02-2017
		EP 3131753 A1	22-02-2017
		JP 2017518246 A	06-07-2017
		KR 20160135280 A	25-11-2016
		US 2017113520 A1	27-04-2017
		WO 2015158464 A1	22-10-2015
US 2013302581 A1	14-11-2013	BR 112014027982 A2	27-06-2017
		CO 6790239 A1	14-11-2013
		EP 2846997 A2	18-03-2015
		PE 19622014 A1	17-12-2014
		US 2013302581 A1	14-11-2013
		US 2016023938 A1	28-01-2016
		WO 2013168125 A2	14-11-2013
		ZA 201409033 B	30-09-2015
US 2016257094 A1	08-09-2016	CA 2926172 A1	30-04-2015
		CN 104755265 A	01-07-2015
		EA 201690771 A1	31-08-2016
		EP 3060397 A1	31-08-2016
		FR 3012072 A1	24-04-2015
		JP 2017500261 A	05-01-2017
		KR 20160077060 A	01-07-2016
		US 2016257094 A1	08-09-2016
		WO 2015059407 A1	30-04-2015