(19) DANMARK

(10) **DK/EP 2501888 T3**

Patent- og Varemærkestyrelsen

(12) Oversættelse af europæisk patentskrift

---

(51) Int.Cl.: ***E 06 B 3/673 (2006.01)***

(45) Oversættelsen bekendtgjort den: **2017-08-28**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2017-05-03**

(86) Europæisk ansøgning nr.: **10784474.8**

(86) Europæisk indleveringsdag: **2010-11-17**

(87) Den europæiske ansøgnings publiceringsdag: **2012-09-26**

(86) International ansøgning nr.: **EP2010067633**

(87) Internationalt publikationsnr.: **WO2011061208**

(30) Prioritet: **2009-11-18 BE 200900707** **2010-02-01 BE 201000050**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **AGC Glass Europe, Avenue Jean Monnet 4, 1348 Louvain-la-Neuve, Belgien**

(72) Opfinder: **BOUESNARD, Olivier, AGC Glass Europe, R&D Centre, Rue de l'Aurore 2, B-6040 Jumet, Belgien**
CLOSSET, François, AGC Glass Europe, R&D Centre, Rue de l'Aurore 2, B-6040 Jumet, Belgien

(74) Fuldmægtig i Danmark: **RWS Group, Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Bucks SL9 9FG, Storbritannien**

(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF EN ISOLERENDE RUDE**

(56) Fremdragne publikationer:
US-A- 5 227 206
US-A1- 2001 001 042

Description

Technical field of the invention

The present invention relates to a process for manufacturing a thermally insulating glazing unit, such as a vacuum-insulated glazing unit. The present invention also relates to the glazing unit thus obtained.

Background of the invention

Generally, a vacuum-insulated glazing unit is composed of a minimum of two glass panels separated by an empty space with a thickness of between 100 µm and 800 µm. The tightness is obtained by a leaktight peripheral seal. In order to obtain superinsulation performances (transmission coefficient per unit area $U < 0.6\ W/m^2K$), the vacuum level between the glass panels has to be of the order of 10^{-3} mbar or less, and generally at least one of the two glass panels has to be covered with a low-e layer having an emissivity ideally of less than 0.05.

Various seal technologies exist, each having certain drawbacks. A first type of seal (the most widespread) is a seal based on a solder glass, the melting point of which is lower than that of the glass of the glass panels of the glazing unit. The use of this type of seal limits the choice of low-e layers to those which are not degraded by the thermal cycle required to employ the solder glass, i.e. to that which withstands a temperature which may range up to 350°C. In addition, since this type of solder-glass-based seal is only very slightly deformable, it does not allow the effects of the differential expansions between the interior-side glass panel of the glazing unit and the exterior-side glass panel of the glazing unit, when these are subjected to large temperature differences (for example 40°C), to be absorbed. Quite substantial stresses are therefore generated at the periphery of the glazing unit and may lead to breakage of the glass panels of the glazing unit.

A second type of seal comprises a metal seal, for example a metal strip with a low thickness (< 500 µm) soldered to the periphery of the glazing unit by way of a tie underlayer covered at least partially with a layer of a solderable material, such as a soft tin-alloy solder. One substantial advantage of this second type of seal relative to the first type of seal is that it is able to deform in order to absorb the differential expansions created between the two glass panels. There are various types of tie underlayers on the glass panel.

The patent application WO2006/121954 presents a first exemplary embodiment of a seal of the second type for a vacuum-insulating glazing unit. According to this example, the adhesion layer is deposited on the first glass panel by different processes (physical vapour deposition (PVD), chemical vapour deposition (CVD) and cold spray). The major drawback of CVD and PVD depositions is that they are relatively expensive and complex to carry out.

For its part, cold spray deposition is also expensive and complex to carry out and may additionally damage the glass substrate on which it is carried out. This is because such a deposition may produce cracks on the glass substrate, resulting in leakages and a loss in the vacuum level inside the glazing unit, not making it possible to maintain a sufficiently low vacuum level (~ 10^{-3} mbar) throughout the lifetime of the vacuum-insulated glazing unit (generally at least 10 years).

The patent U.S. Pat. No. 5,227,206 (cf. column 1, lines 60-65) presents a second exemplary embodiment of a seal of the second type for a vacuum-insulated glazing unit. According to this example, the adhesion layer is a copper layer deposited by a low velocity flame spraying process. The main drawback of this underlayer is its porosity (US 5 227 206; cf. section between columns 1 and 2). This type of deposition does not make it possible to obtain a tightness sufficient for the maintenance of a sufficiently low vacuum level (~ 10^{-3} mbar) during the lifetime of the vacuum-insulated glazing unit (generally at least 10 years).

Summary of the invention

One aspect of the present invention proposes to employ, in a tightness seal of metal type, e.g. a metal strip, for an insulating glazing unit (i.e., for a double or triple glazing unit, for example for a vacuum-insulated glazing unit), an adhesion layer deposited by virtue of the HVOF (high velocity oxy/fuel spraying) process. This is because it has been observed, surprisingly, that such a deposition technique makes it possible to obtain an adhesion layer exhibiting a material density sufficient to guarantee a tightness sufficient for the maintenance of a satisfactory vacuum level (< 10^{-3} mbar) over the conventional lifetime of the vacuum-insulated glazing units (10 years). One advantage of some embodiments of the present invention is a good adhesion to the glass panel. Another advantage of certain embodiments of the present invention is that the deposition is carried out without damaging the glass panel. Another advantage of certain embodiments of the present invention is that they are implemented in a simple way at reasonable costs (for example, lower in cost and complexity than the CVD and PVD depositions).

Another advantage of certain embodiments of the present invention is that they make it possible to obtain greater densities than those obtained by standard flame spraying processes. Said densities are comparable to that of the sprayed metal. Despite the high energy provided to the metal particles by the combination of the combustion and of the high spraying velocity (supersonic), it has been observed, surprisingly, that the substrate is not damaged by the deposition (no cracking observed during analysis with an optical microscope).

The pressure inside a vacuum-insulated glazing unit is preferably less than 10^{-3} mbar in order for the latter to retain its energy superinsulation properties for a useful period of time. Consequently, the rise in pressure acceptable during the lifetime of the product is preferably at most of the same order of magnitude. Some embodiments of the present invention make it possible to retain a vacuum of less than 10^{-4} to 10^{-3} mbar inside a glazing unit for 10 years.

In a first aspect, the present invention relates to a process for manufacturing at least one portion of a tightness seal ensuring gas tightness between at least a first and a second glass panel in a glazing unit, the process comprising the following steps:

depositing a first adhesion layer on a first peripheral zone of the first panel and a second adhesion layer on a second peripheral zone of the second panel;

soldering a first metal seal element to the first adhesion layer; and

soldering a second metal seal element or said first metal seal element to the second adhesion layer;

in which the first and second adhesion layers are deposited with an HVOF (high-velocity oxy/fuel spraying) process.

In the case of a vacuum-insulated glazing unit, the vacuum may be produced in the leaktight cavity delimited by the tightness seal by means, for example, of an appropriate suction system connected to the cavity.

In embodiments of the manufacturing process according to the invention, the process may furthermore comprise a step of depositing a metal solder layer on at least some of at least one of the adhesion layers. In embodiments of the manufacturing process according to the invention, at least one of the seal-element solder joints is a solder joint obtained by melting said metal solder layer. The presence of a metal solder layer facilitates the soldering.

In embodiments of said manufacturing process according to the invention, at least one of said soldering steps may be a step of ultrasonic or induction soldering. Ultrasonic soldering has the advantage of not necessarily requiring a metal solder layer.

In embodiments of said manufacturing process according to the invention, one of said glass panels may be provided with a thermal insulation layer. This makes it possible to render the glazing unit even more insulating.

In embodiments of said manufacturing process according to the invention, the glazing unit may be a vacuum-insulated glazing unit. This makes it possible to render the glazing unit super insulating ($U < 0.6\ W/m^2K$).

In embodiments of said manufacturing process according to the invention, a first metal seal element may be soldered to the first adhesion layer and a second metal seal element may be soldered to the second adhesion layer; the manufacturing process may furthermore comprise soldering the first seal element to the second seal element. This makes it possible to carry out the steps of soldering the first seal element and the second seal element in an atmosphere at atmospheric pressure. Only the final step of soldering the seal elements together then has to be carried out under vacuum in order to obtain a vacuum-insulated glazing unit.

In embodiments of said manufacturing process according to the invention, said peripheral zones may be heated to a temperature of 150°C or more, preferably 200°C or more and more preferably 250°C or more, before the deposition of said adhesion layers. This makes it possible to improve the adhesion of the adhesion layer to the glass panel.

In embodiments of said manufacturing process according to the invention, said adhesion layers may have a thickness of 1 to 100 µm, preferably of 1 to 30 µm and more preferably of 5 to 15 µm. Such thicknesses prevent the layer from peeling while making possible sufficient thickness to allow the layer to perform its functions.

Advantageously, said adhesion layers may have a roughness Ra of 1 to 5 µm, preferably of 2 to 3 µm. This makes possible good adhesion of the metal solder layer to the adhesion layer.

Advantageously, at least one of the adhesion layers may be exposed to a reducing flame before undergoing said soldering. This makes it possible to reduce the creation of oxide and thus to improve the wettability of the deposited layer for the subsequent operations.

Advantageously, said adhesion layers may be formed from an adhesion material selected from the group composed of copper and its alloys, of aluminium and its alloys, of iron and its alloys, of platinum and its alloys, of nickel and its alloys, of gold and its alloys, of silver and its alloys, of titanium and its alloys, and of tin or its alloys.

In an embodiment in accordance with the invention, said adhesion layers may be formed from an adhesion material having a thermal expansion coefficient of 3 to 23 × 10^{-6} K^{-1}, preferably from 4 to 18 × 10^{-6} K^{-1} and more preferably from 5 to 16 × 10^{-6} K^{-1}. This makes it possible to avoid problems of differential expansion between the glass panel and the adhesion material.

Advantageously, the manufacturing process may furthermore comprise a step of exposing at least one of said adhesion layers to a brazing flux before said soldering and/or before said deposition of a metal solder layer. This makes it possible to dissolve the oxides present at the surface. For example, in the case of an adhesion layer made of copper, the flux used may be a flux sold by Castolin under the reference 157NC.

Advantageously, the manufacturing process may furthermore comprise a step of cleaning the surplus brazing flux after said soldering and/or after said deposition of a metal solder layer.

This prevents deterioration of the seal and limits the degassing after placing under vacuum.

Advantageously, at least one of said metal seal elements may have a metal solder layer before said soldering to one of said adhesion layers. This facilitates the brazing.

In embodiments of the manufacturing process according to the invention, the following steps may be carried out:

depositing, in an atmosphere at atmospheric pressure, a first adhesion layer on a first peripheral zone of the first panel and a second adhesion layer on a second peripheral zone of the second panel;

soldering, in an atmosphere at atmospheric pressure, a first metal seal element to the first adhesion layer;

soldering, in an atmosphere at atmospheric pressure, a second metal seal element that is distinct from the first metal seal element to the second adhesion layer; and

soldering, in an atmosphere at lower pressure and preferably under vacuum, the first metal seal element to the second metal seal element.

This is economically advantageous in comparison with a process carried out entirely under vacuum.

Advantageously, said metal seal elements may comprise at least one material selected from copper and its alloys, aluminium and its alloys, and iron and its alloys.

In embodiments of said manufacturing process, said metal seal elements and/or the adhesion material may be made of an iron alloy comprising the following metals: iron (53-55 wt%, for example 53.5 wt%), nickel (28-30%, for example 29 wt%) and cobalt (16-18%, for example 17 wt%), such as Kovar®. This is advantageous as this type of alloy has a thermal expansion coefficient similar to glass.

In other embodiments of said manufacturing process, said metal seal elements and/or the adhesion material may be made of an iron alloy comprising the following metals: iron (50-55 wt%, for example 52 wt%), nickel (45-50%, for example 48 wt%), such as Alloy 48. This is advantageous as this type of alloy has a thermal expansion coefficient similar to glass.

Advantageously, the thickness of the seal elements is between 50 µm and 1000 µm, preferably between 100 µm and 500 µm and preferably between 150 µm and 300 µm. It is possible, for example, to use a thickness of 200 µm.

Advantageously, said process of high-velocity oxy/fuel spraying type may comprise the following steps:

- in a spraying apparatus comprising first, second and third inlets, each leading to a combustion chamber, and one outlet, injecting under pressure a fuel (for example kerosene or propylene) and oxygen via said first inlet;

- injecting the adhesion material into said second inlet;

- combusting (combustion may be ignited automatically or manually with a spark or a flame) said fuel and said oxygen in order to melt the adhesion material in the combustion chamber;

- injecting a pressurized gas (for example argon, compressed air, and the like) via said third inlet in order to allow said molten adhesion material to be sprayed at supersonic speed out of said apparatus via said outlet; and

- orienting the outlet of said apparatus towards one of said peripheral zones, thus allowing one of said adhesion layers to be formed.

Advantageously, the angle between the axis of said outlet and said glass panel may be from 45° to 90°, preferably from 70° to 90°, more preferably from 75° to 90° and even more preferably from 80 to 90°.

For example, an angle of 90° allows a denser deposited layer to be obtained, whereas, with an angle of 45°, the deposited layer will be rougher (and the masking will also be more effective).

In embodiments of the invention, the distance measured in the extension of the axis of said outlet between said outlet and the glass panel may be from 10 to 30 cm, preferably from 15 to 25 cm and more preferably from 17 to 23 cm.

Thus, it is advantageous to provide a sufficient distance in order to avoid providing the glass with too much energy (which risks resulting in the breaking thereof, and in excess oxidation of the deposited layer) and in order to obtain a fairly wide metallized zone.

In embodiments of the invention, said apparatus and the glass panel may be moved one relative to the other during the formation of said adhesion layers at a speed of 5 to 30 m/min, preferably at a speed of 5 to 20 m/min, more preferably at a speed of 5 to 15 m/min and even more preferably at a speed of 7 to 13 m/min.

Thus, such speeds are compatible with a glass conveying and allow a good adhesion layer thickness to be maintained.

Advantageously, the pressure of the oxygen may be from 4 to 10 bar, preferably from 5 to 9 bar and more preferably from 6 to 8 bar.

Thus, such pressures allow the combustion mixtures to be correctly prepared and the supersonic speeds to be achieved.

Advantageously, said fuel may be selected from the group formed of methane, ethane, propane, butane, natural gas, propylene, hydrogen, kerosene or acetylene.

Advantageously, said fuel may be propylene.

Advantageously, the pressure of said fuel may be from 2 to 10 bar, preferably from 3 to 8 bar and more preferably from 4 to 6 bar.

Advantageously, said compressed air may be injected with a pressure of 2 to 10 bar, preferably of 3 to 9 bar, more preferably of 4 to 8 bar and most preferably of 5 to 7 bar.

Advantageously, the adhesion material may be injected in a carrier gas and the pressure of said carrier gas is from 2 to 8 bar, preferably from 2 to 6 bar and more preferably from 3 to 5 bar.

Another aspect of the present invention relates to a glazing unit obtained by any embodiment of the manufacturing process according to the present invention.

Brief description of the figures

Fig. 1 shows a diagram illustrating the high-velocity oxy/fuel spraying step according to an embodiment of the present invention.

Fig. 2 shows a diagram illustrating a triple glazing unit obtained via an embodiment of a process according to the present invention.

Fig. 3 shows, in perspective, the diagram of a double glazing unit obtained via an embodiment of a process according to the present invention.

Fig. 4 shows a diagram illustrating a double glazing unit obtained via an embodiment of a process according to the present invention.

Fig. 5 illustrates a process for manufacturing a tightness seal according to an embodiment of the present invention.

Fig. 6 shows the diagram of a glazing unit obtained according to an embodiment of a process for manufacturing a tightness seal according to the present invention.

Fig. 7 shows the diagrams of two glazing units obtained according to two different embodiments of a process for manufacturing a tightness seal according to the present invention.

Fig. 8 illustrates an embodiment of a process for manufacturing a tightness seal according to the present invention.

Description of the invention

The present invention will be described with reference to specific embodiments and with reference to certain drawings where the invention is not limited by this and is limited only by the claims. In the drawings, the relative size and dimensions of certain elements may be exaggerated and not be drawn to scale for reasons of illustration.

Furthermore, the terms first, second, third and the like in the description and in the claims are used to distinguish between similar elements and not necessarily to describe a sequence, whether temporal, spatial, for classification purposes or other. It is clearly understood that the terms thus used are interchangeable under appropriate circumstances and that the embodiments of the invention described here are capable of taking effect in other sequences than those described or illustrated here.

Furthermore, the terms high, low, above, below and the like in the description and in the claims are used for reasons of description and not necessarily to describe relative positions.

It is clearly understood that the terms thus used are interchangeable under appropriate circumstances and that the embodiments of the invention described here are capable of being implemented under other orientations than those described or illustrated here.

It should be pointed out that the term "comprising" used in the claims should not be interpreted as being restricted to the means listed after this term; it does not exclude other elements or steps. It should thus be interpreted as specifying the presence of the elements specified, units, steps or components referred to but does not exclude the presence or the addition of an element, unit, step or component, or group of these. Thus, the scope of the expression "an apparatus comprising the means A and B" should not be limited to apparatuses consisting only of the components A and B. This means that, as regards the present invention, the only relevant components of the apparatus are A and B.

As used here and unless otherwise indicated, the term "at least one portion" is understood to mean that, if the first seal element and the second seal element are not one and the same seal element, the process results in an intermediate, that is to say a seal portion which would ensure its role of seal only after soldering together said first seal element and said second seal element of said seal.

As used here and unless otherwise indicated, the term "gas tightness" is understood to mean the tightness to any gas which might be used in a double glazing unit in order to improve insulation (for example argon) or the tightness to air or any other gas present in the atmosphere (in the case of a vacuum-insulated glazing unit).

As used here and unless otherwise indicated, the term "thermal insulation layer" is understood to mean a layer of metal oxide having an emissivity of less than 0.2, preferably of less than 0.1 and more preferably of less than 0.05. One of the adhesion layers may be deposited on a thermal insulation layer (deposited beforehand on one of the glass panels) which may, for example, be one of the following layers: Planibel G, Planibel top N and Planibel top NT, sold by AGC.

As used here and unless otherwise indicated, the term "reducing flame" relates to a flame obtained when there is insufficient oxygen for incinerating (i.e. splitting of the molecule and oxidizing all its hydrogen and its carbon thereof) all the fuel (e.g., propylene or any other fuel).

As used here and unless otherwise indicated, the term "spacer" relates to one or more elements ensuring a relatively constant distance between two adjacent glass panels.

The HVOF process is a thermal spraying technique where a substrate is covered with a material (in this instance an adhesion material) sprayed by a spraying apparatus. One of the distinguishing features of this spraying method is the relatively high velocity of the particles sprayed. The spraying apparatus is generally known as "spray gun".

The energy necessary for the melting and in part (as the gas injected under pressure also participates in the acceleration) for the acceleration of the particles of said adhesion material is obtained during the combustion of a fuel by oxygen. Examples of appropriate fuel are methane, ethane, propane, butane, natural gas, propylene, hydrogen, kerosene or acetylene, among others. Preferably, propylene is used.

In one embodiment of the present invention, the fuel and the oxygen are both injected into the spraying apparatus under high pressure. Furthermore, the flame is accelerated by feeding with compressed gas (argon, air, and the like) and directed into an injection nozzle forming part of the spraying apparatus in order to achieve a supersonic speed at the nozzle outlet. The powder of the adhesion material to be sprayed is itself injected axially into the spraying apparatus.

The layers produced by this type of process are very dense and resistant.

In one embodiment of the present invention, the peripheral zone of the glass panel where the adhesion layer is deposited may first of all be preheated to a temperature of greater than 150°C, preferably of greater than 200°C and even more preferably of greater than 250°C. The use of a preheating improves the adhesion to the glass panel. The preheating may be carried out by any means known to a person skilled in the art, such as, for example, using a flame or infrared lamp.

The adhesion layer is deposited on the periphery of each of the glass panels over a track with a width of several millimetres, for example between 1 and 15 mm.

For the deposition of the adhesion layer, for example, either the glass panel is conveyed below a spraying apparatus side after side, or the spraying apparatus is moving and the glass panel is stationary, or the glass panel is conveyed below a spraying apparatus which is itself moving.

The spraying apparatus used may be a powder HVOF spraying apparatus (such as that sold by GMA under the "Microjet™" commercial reference). It may be equipped with one of the following nozzles, sold by Aircap Microjet - Metallizing Equipment Co. Pvt. Ltd:

- the nozzle having the reference HP-3-A (made of aluminium and with a diameter of 8.4 mm);

- the nozzle having the reference HP-3-B (made of aluminium and with a diameter of 9.4 mm);

- the nozzle having the reference HP-3-C (made of copper and with a diameter of 9.5 mm).

For example, the HP-3-C nozzle is used, which nozzle is an open and short nozzle ideal for the spraying of low-melting-point metals.

Fig. 1 shows a spraying apparatus 6 spraying a jet 7 containing an adhesion material. Spraying is carried out over a peripheral zone of a glass panel 5, thus forming an adhesion layer 3. The jet 7 and the glass panel 5 form an angle α. The distance measured in the extension of the axis of the outlet of the spraying apparatus 6 between said outlet and the glass panel is indicated by the letter d.

In order to obtain a functional adhesion layer for an insulating glazing unit (for example vacuum-insulated glazing unit) seal, the following deposition parameters are preferably used: as regards the geometrical parameters (see Fig. 1), the angle α between the axis of the outlet of the spraying apparatus 6 and the glass panel 5 may be from 45 to 90°, preferably from 70° to 90°, more preferably from 75° to 90° and ideally from 80° to 90°. The distance d measured in the extension of the axis of said outlet between said outlet (the bushing) of the spraying apparatus 6 and the surface of the glass panel 5 may be from 10 to 30 cm, preferably from 15 to 25 cm, more preferably from 17 to 23 cm and ideally in the vicinity of 20 cm. The relative velocity between the glass panel 5 and the spraying apparatus 6 may be from 5 to 30 m/min, preferably from 5 to 20 m/min, more preferably from 5 to 15 m/min and even more preferably from 7 to 13 m/min, and ideally in the vicinity of 10 m/min.

For the flame parameters, the oxygen pressure may be from 4 to 10 bar, preferably from 5 to 9 bar, more preferably from 6 to 8 bar and ideally in the vicinity of 7 bar. The preferred fuel is propylene. The pressure of the fuel is preferably from 2 to 10 bar, preferably from 3 to 8 bar, more preferably from 4 to 6 bar and ideally in the vicinity of 5 bar. The compressed air may be injected with a pressure located between 2 and 10 bar, preferably from 3 to 9 bar, more preferably from 4 to 8 bar and most preferably from 5 to 7 bar and ideally in the vicinity of

6 bar. The powder is injected with a carrier gas (for example argon); the pressure of the latter may, for example, be between 2 to 8 bar, preferably from 2 to 6 bar, more preferably from 3 to 5 bar and ideally in the vicinity of 4 bar.

The mean thickness of the adhesion layers 3 deposited is preferably from 1 to 100 µm, preferably from 1 to 30 µm and more preferably from 5 to 15 µm.

Ideally, the mean thickness lies between 5 and 15 µm (measurements carried out with a profilometer sold by Veeco under the "DekTak® 6M" commercial reference). If the deposited layers 3 are too thick, the layer 3 may peel during the deposition. Another parameter of the adhesion layer 3 deposited is its roughness. Its roughness is preferably such as to allow good adhesion of the optional tinning layer 9 (see Fig. 5). The roughness (Ra) obtained, measured with a roughness metre of Talysurf™ type, preferably lies between 1 and 5 µm and is ideally of the order of 2 to 3 µm.

The roughness Ra is defined here as being the mean separation, or arithmetic mean of the distances between successive peaks and hollows of the surface.

An optional passage under a reducing flame directly after deposition of the adhesion layer makes it possible to prevent the creation of too much oxide and thus to improve the wettability of the deposited layer for the subsequent operations.

Different metals may be sprayed onto the glass panel. For example, the adhesion material may be selected from the group consisting of copper and its alloys (for example with titanium and/or chromium), aluminium and its alloys, iron and its alloys (such as Fe-Ni alloys: e.g. iron (50-55 wt%, for example 52 wt%), nickel (45-50%, for example 48 wt%), such as Alloy 48), iron alloys comprising the following metals: iron (53-55 wt%, for example 53.5 wt%), nickel (28-30%, for example 29 wt%) and cobalt (16-18%, for example 17 wt%), and Kovar®, platinum and its alloys, nickel and its alloys; gold and its alloys, silver and its alloys, gallium arsenide, and tin or its alloys, this list not being exhaustive.

This adhesion layer preferably has good tying to the glass panel. This adhesion layer is ideally sufficiently ductile to absorb differential expansions relative to the substrate (glass panel). In order to avoid this type of stress, it is possible to use a material having a thermal expansion coefficient (TEC) which is substantially similar to that of the glass panel (in the vicinity of 9×10^{-6} K^{-1}). For example, a thermal expansion coefficient of 3 to 23×10^{-6} K^{-1} is advantageous, preferably from 4 to 18×10^{-6} K^{-1} and more preferably from 5 to 16×10^{-6} K^{-1}. Kovar® is a particularly advantageous material in the light of its thermal expansion in the vicinity of 5×10^{-6} K^{-1}. Copper, which may also be used, exhibits a thermal expansion of 16×10^{-6} K^{-1}.

Kovar® is an alloy comprising iron (53.5 wt%), nickel (29 wt%), cobalt (17 wt%), manganese (0.3 wt%) and silicon (0.2 wt%). An advantageous material is an iron alloy comprising the following metals: iron (53-55 wt%, for example 53.5 wt%), nickel (28-30%, for example 29 wt%) and cobalt (16-18%, for example 17 wt%).

Different methods may be used to weld the metal seal element to the adhesion layer deposited by HVOF. One possibility is to use a metal solder layer (for example for low temperature brazing). The adhesion layer is covered with a metal solder layer. This step is known as tinning. The metal solder layer may be deposited by curtain coating, by a flame spraying process, by HVOF, with a soldering iron or by electroplating, the list not being exhaustive. It is sometimes advantageous, in order to wet the adhesion layer, to apply a brazing flux in order to dissolve the oxides present at the surface of the layer (by spraying or other method). A brazing flux is a mixture of chemicals allowing good wetting to be ensured by removing the oxides of the layer, by protecting the adhesion layer from oxidation and by lowering the surface tension of the layer. The brazing flux may be in the liquid, pasty, gas or solid form. Preferably, the brazing flux used is liquid. It is preferably suited to the nature of the adhesion material deposited on the glass. A person skilled in the art knows what brazing flux is suited to what material.

In certain embodiments of the present invention, the metal solder layer may have a thickness which may range from a few microns to several hundred microns. The standard alloys for low-temperature (< 300°C) brazing are tin alloys (tin-silver, tin-copper, tin-silver-copper, tin-lead, tin-aluminium, among others).

After tinning, the surplus flux is preferably cleaned off (for example by virtue of washing with water) in order to prevent deterioration of the seal and to limit the degassing after placing under vacuum. The metal seal element is subsequently brazed to the adhesion layer. The brazing may be carried out with local heating with a soldering iron, with or without contribution of material. The heat load (contact time and temperature) experienced by the underlayer is preferably limited in order to avoid damaging it (detachment).

Another possibility is to use brazing by induction, which has the advantage of being carried out without contact with a hot part and uniformly, which reduces the risk of degradation of the adhesion layer. Other local heating methods may also be used for the brazing: local infrared heating, hot air, laser brazing and microwaves, among others. Ultrasonic brazing may also be used. In this case, the first and second solder layers may not be present. The seal element may be brought into direct contact with respectively the first and second adhesion layers. High frequency vibrations are sent to the seal element and to the adhesion layer via a vibrating device, known as sonotrode or soldering head. The soldering takes place by virtue of the heat generated at the interface of the two parts.

For the different soldering methods, it is preferable for the tinning to be brought into intimate contact with the metal seal element. This may be carried out via a sufficient pressure, for this reason ensuring the continuity of the seal.

In order to facilitate the brazing, the seal element may be precovered with a metal solder layer having a thickness which may range from a few microns to approximately a hundred microns, indeed even more (of material identical to or different from the metal solder deposited on the adhesion layer).

In the case of soldering by ultrasound, it is also possible to join the adhesion layer to the metal seal element without a tinning layer.

The process of soldering the metal seal element may be carried out in one or more steps.

In the option of the single-step soldering, the seal element allowing vacuum tightness is provided as a single part and is brazed to the different respective adhesion layers of the different glass panels (for example to the two respective adhesion layers of the two glass panels).

Fig. 3 and 4 show a vacuum-insulated glazing unit comprising two glass panels 5, each being covered over a peripheral zone with an adhesion layer 3. The two panels are assembled in a gastight manner (in this instance ensuring the void 4) via a tightness seal composed of a single metal strip 1 soldered to the adhesion layers 3 by solder joints 2. Fig. 3 also shows spacers 8 ensuring an unvarying distance between the two glass panels 5.

In the option of the multistep soldering (see Fig. 8), the system of strips is composed of several strips 1. A first metal strip 1 is welded to the first glass panel 5 via a solder joint 2. A second metal strip 1 is welded to the second glass panel 5 via another solder joint 2. These two distinct strips 1 are subsequently soldered together via a solder joint 10 in order to obtain the tightness by a standard soldering technique, for example laser soldering. This two-step process may have the advantage of carrying out the sealing of the vacuum-insulated glazing unit under an atmosphere at low pressure, while the brazing of each strip is carried out beforehand at atmospheric pressure.

The seal element is preferably a metal strip. It may be produced by virtue of a non-metal element (for example a material made of plastic) covered with metal (which allows the thermal conduction by the seal to be reduced), and the like. For example, it may be made of copper or copper alloy, aluminium or aluminium alloy, steel or steel alloy, iron or iron alloy (for example made of an iron alloy comprising the following metals: iron (53-55 wt%, for example 53.5 wt%), nickel (28-30%, for example 29 wt%) and cobalt (16-18%, for example 17 wt%), such as Kovar®, or made of an iron alloy comprising the following metals: iron (50-55 wt%, for example 52 wt%) and nickel (45-50%, for example 48 wt%), such as Alloy 48. It may also be a composite of these different materials.

In the case of a vacuum-insulated triple glazing unit (see Fig. 2), a first glass panel 5 is separated from a second glass panel 5 by an empty space 4, this second panel 5 being separated from a third panel 5 by a second empty space 4.

A first adhesion layer 3 is deposited on a first peripheral zone of the first panel 5, a second adhesion layer 3 on a second peripheral zone of the second panel 5 and a third adhesion layer 3 on a third peripheral zone of the third panel 5. A first option is to use just one metal strip 1 welded to each of the adhesion underlayers by means of a solder joint 2. A second option (not illustrated in Fig. 2) is to solder a first strip to the first adhesion layer of the first panel, a second strip to the second adhesion layer of the second panel and a third strip to the third adhesion layer of the third panel. In an atmosphere at lower pressure (for example under vacuum, such as a vacuum of 10^{-3} bar or a higher vacuum), the first strip is subsequently soldered to the second strip to create the empty space between the first glass panel and the second glass panel. The second strip is welded to the third strip to create the void between the second panel and the third panel. Generally, there are several embodiments for manufacturing a tightness seal according to the present invention. Whatever embodiment described above, any glass panel may be provided with an adhesion layer located on an edge comprising the end of the glass panel (situation of Fig. 2-6 and 8), located on the edge face of a glass panel (left-hand situation of Fig. 7) or located close to an edge, not comprising the end of the glass panel but covering a peripheral zone of said glass panel, said zone beginning at a distance of between 0 and 10 cm from said end (right-hand situation of Fig. 7). In the case of a double glazing unit, each adhesion layer may be deposited on its glass panel so as to be oriented towards the inside of the glazing unit (see Fig. 4, bottom panel, Fig. 6, the two panels, and Fig. 7, the two panels forming the right-hand glazing unit), towards the outside of the glazing unit (see Fig. 4, top panel, Fig. 5, the two panels, and Fig. 8, the two panels) or on the edge face of the glass panel. In the case of an exterior panel of a triple glazing unit, each adhesion layer may be deposited on its glass panel so as to be oriented towards the inside of the glazing unit (see Fig. 2, bottom panel), towards the outside of the glazing unit (see Fig. 2, top panel), or on the edge face of the glazing unit (not represented in Fig. 2 but analogous to the situation of Fig. 7). In the case of an interior panel of a triple glazing unit, the adhesion layer may either be deposited on the edge face of the glass panel (situation not represented but analogous to the situation of Fig. 7) or on one of the main surfaces of the glass panel. If it is deposited on one of the main surfaces of the glass panel, the adhesion layer may be present on one or other of said surfaces. In all cases, the following configurations are possible: the adhesion layers of two adjacent panels may be facing each other (situation of Fig. 6 and of the right-hand side of Fig. 7) or may not be facing each other (situation of Fig. 2, 4, 5, the left-hand side of 7 or 8). If they are not facing each other, the two adhesion layers may be oriented so that they occur on surfaces which face away from each other (situation of Fig. 5 and of Fig. 8) or one may be oriented towards the outside of the assemblage of the two glass panels and the other may be oriented towards the inside of the assemblage of the two panels (situation of Fig. 2 and 4). The glass panels may be of the same dimensions or of different dimensions. The edge of any glass panel may be at the same height as the edge of an adjacent panel (situation of Fig. 5, 6 and 7). The edge of any glass panel may also be at a different height than the edge of an adjacent panel, that is to say be offset relative to the position of the edge of an adjacent panel (case of Fig. 2 and 4). The strip system may be composed of a single strip (case of Fig. 2, 4, 5, 6 and 7) or of several strips connected together by soldering during the progression of the process (case of Fig. 8). The strip system (or the single strip) may take the form of a staircase (case of Fig. 2 and 4), of a U (see Fig. 5, 6 and the right-hand side of 7) or may be flat (left-hand side of Fig. 7). In the case of the presence of a thermal insulation layer, the deposition of the adhesion layer may be carried out on the thermal insulation layer or on the side of the glass opposite the thermal insulation layer or on the edge face of the glass panel.

Examples

The following calculation is supplied by way of example:

With an initial pressure of 10^{-4} mbar, the maximum rate of leakage acceptable for ensuring a pressure of less than 10^{-3} mbar inside the glazing unit for 10 years may be evaluated as follows:

Initial pressure inside the glazing unit = 10^{-4} mbar.

The maximum rise in pressure (ΔP) in order to have a pressure of less than 10^{-3} mbar after 10 years is calculated by 10^{-3} mbar – initial pressure = 0.9×10^{-3} mbar.

For a glazing unit with an area of 1 m^2 with a spacing of 0.2 mm between the two glass panels, the volume (V) of the vacuum-insulated glazing unit is 1 m*1 m*0.2×10^{-3} m = 0.2×10^{-3} m^3, which corresponds to 0.2 litre.

Lifetime (L) equivalent to 10 years is equal to 3600 seconds * 24 hours * 365 days * 10 years, which is equivalent to 315 360 000 seconds.

Thus, the maximum rate of leakage = $(\Delta P)*V/L = 5.7 \times 10^{-13}$ mbar.l/sec.

Two sources of rise in pressure may be observed, leaks through the seal (true leaks) or a degassing of the interior surfaces or of the seal of the glazing unit (virtual leaks).

Tightness tests with a standard helium leak detector (such as the detector sold by Pfeiffer under the Smart Test HLT560 reference) were carried out by the inventors in order to quantify the "true" leaks through the seal. The leakage rates measured according to the European standard EN13185, on glazing units with an underlayer deposited by a process according to an embodiment of the present invention, are less than the limit detectable by this type of equipment ($< 5 \times 10^{-10}$ mbar.l/sec).

The leaktight cavity delimited by the tightness seal of a sample manufactured with the tightness seal according to the process according to the invention is connected to the leak detector via an appropriate suction system. The sample is immersed in a chamber with a helium atmosphere (atmosphere comprising more than 99% helium). The leaktight cavity is placed under vacuum ($\sim 5 \times 10^{-3}$ mbar) by the pump of the helium detector. The helium stream detected by the detector is of the order of the background noise of the apparatus ($< 5 \times 10^{-10}$ mbar.l/sec). This proves that there is no helium which penetrates into the cavity through the seal manufactured according to the method described.

Even if this level of rate of leakage is not sufficient to ensure a lifetime of the glazing unit of several years, it is known that, when no leakage of this level is detected, the seal is perfectly leaktight in the very great majority of cases.

The seals with an underlayer deposited by a standard flame spraying process showed numerous leaks due to the porosity of the deposited layer. The values measured with the helium detector are of the order of 10^{-6} - 10^{-7} mbar.l/sec, which is completely insufficient to retain a functional vacuum level inside the glazing unit. With this rate of leakage, for a glazing unit with a surface area of 1 m^2 and with a spacing between panels of 0.2 mm, with an initial pressure of 10^{-4} mbar, the pressure of 10^{-3} mbar is reached after only 180 seconds.

Another aspect of the present invention relates to a glazing unit which may be obtained by any embodiment of the manufacturing process according to the present invention.

Yet another aspect of the present invention relates to a glass panel which may be obtained by the deposition of an adhesion layer on a peripheral zone, in which said deposition is carried out with a process of high-velocity oxy/fuel spraying type, said deposition being as described in any of the embodiments of the manufacturing process according to the present invention.

Patentkrav

1. Fremgangsmåde til fremstilling af mindst en del af en tætning, der sikrer gastætheden mellem mindst en første og en anden glasplade (5) i en rude, hvilken fremgangsmåde omfatter følgende trin:
- afsætning af et første vedhæftningslag (3) på en første perifer zone af den første plade og et andet vedhæftningslag (3) på en anden perifer zone af den anden plade (5);
- sammensvejsning af et første metallisk tætningselement (1) med det første vedhæftningslag;
- sammensvejsning af et andet metallisk tætningselement (1) eller det første metalliske tætningselement med det andet vedhæftningslag;
kendetegnet ved, at afsætningerne af det første og andet vedhæftningslag (3) udføres ved en fremgangsmåde af typen oxygen/brændstof-flammesprøjtning med høj hastighed.

2. Fremgangsmåde ifølge krav 1, kendetegnet ved, at fremgangsmåden yderligere omfatter et trin til afsætning på mindst en del af mindst et af vedhæftningslagene (3) af et metallisk svejselag (2), og ved at mindst en af svejsningerne af et tætningselement er en svejsning ved smeltning af det metalliske svejselag.

3. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at mindst et af svejsetrinnene er en ultralyds- eller induktionssvejsning.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at ruden er en vakuumrude.

5. Fremgangsmåde til fremstilling af en tætning ifølge et hvilket som helst af de foregående krav, hvor sammensvejsningen af et første metallisk tætningselement med det første vedhæftningslag (3) og sammensvejsningen af et andet metallisk tætningselement med det andet vedhæftningslag (3) udføres, idet fremgangsmåden yderligere omfatter svejsningen af det første

tætningselement til det andet tætningselement.

6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at mindst et af vedhæftningslagene (3) udsættes for en reducerende flamme, inden den underkastes svejsningen.

7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at vedhæftningslagene (3) er dannet af et vedhæftningsmateriale, der er valgt fra gruppen bestående af kobber og kobberlegeringer, aluminium og aluminiumlegeringer, jern og jernlegeringer, platin og platinlegeringer, nikkel og nikkellegeringer, guld og guldlegeringer, sølv og sølvlegeringer, tin og tinlegeringer.

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at vedhæftningslagene (3) er dannet af et vedhæftningsmateriale, der har en varmeudvidelseskoefficient på fra 3 til 23.10^{-6} K^{-1}, fortrinsvis fra 4 til 18.10^{-6} K^{-1}, mere fortrinsvis fra 5 til 16.10^{-6} K^{-1}.

9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, som yderligere omfatter et trin til udsættelse af mindst et af vedhæftningslagene (3) for en loddeflus inden svejsningen og/eller inden afsætningen af et metallisk svejselag.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at mindst et af de metalliske tætningselementer (1) har et metallisk svejselag (2) forud for sammensvejsningen med et af vedhæftningslagene.

11. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, som yderligere omfatter følgende trin:
- afsætning i en atmosfære ved atmosfæretryk af et første vedhæftningslag (3) på en første perifer zone af den første plade og et andet vedhæftningslag (3) på en anden perifer zone af den anden plade;
- sammensvejsning i en atmosfære ved atmosfæretryk af et første

metallisk tætningselement (1) med det første vedhæftningslag;
- sammensvejsning i en atmosfære ved atmosfæretryk af et andet metallisk tætningselement (1), der er forskelligt fra det første metalliske tætningselement (1), med det andet vedhæftningslag; og
- sammensvejsning i en atmosfære ved reduceret tryk, og fortrinsvis under vakuum, af det første metalliske tætningselement (1) med det andet metalliske tætningselement (1).

12. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at de metalliske tætningselementer omfatter mindst et materiale, der er valgt blandt kobber og kobberlegeringer, aluminium og aluminiumlegeringer, jern og jernlegeringer.

13. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at de metalliske tætningselementer og/eller vedhæftningsmaterialet er en jernlegering, der omfatter følgende metaller: jern (53-55 vægt-%, for eksempel 53,5 vægt-%), nikkel (28-30 %, for eksempel 29 vægt-%) og cobalt (16-18 %, for eksempel 17 vægt-%), såsom Kovar®.

14. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at fremgangsmåden af typen oxygen/brændstof-flammesprøjtning med høj hastighed omfatter følgende trin:
• i et sprøjteapparat, som omfatter første, anden og tredje indgange, der hver fører til et forbrændingskammer, og en udgang, indsprøjtes et brændstof og oxygen under tryk gennem den første indgang,
• vedhæftningsmaterialet indsprøjtes gennem den anden indgang,
• der udføres en forbrænding mellem brændstoffet og oxygenet for at smelte vedhæftningsmateriale i forbrændingskammeret,
• en gas under tryk indsprøjtes gennem den tredje indgang for at kunne sprøjte det smeltede vedhæftningsmateriale ud af apparatet med overlydshastighed gennem udgangen, og
• udgangen fra apparatet rettes mod en af de perifere zoner for

således at gøre det muligt at danne et af vedhæftningslagene.

15. Fremgangsmåde ifølge krav 14, hvor vinklen mellem udgangens akse og glaspladen er fra 45° til 90 °, fortrinsvis fra 70° til 90°, mere fortrinsvis fra 75° til 90° og endnu mere fortrinsvis fra 80° til 90°.

16. Fremgangsmåde ifølge et hvilket som helst af kravene 14 til 15, kendetegnet ved, at apparatet og glaspladen under dannelsen af vedhæftningslagene bevæges i forhold til hinanden med en hastighed på fra 5 til 30 m/min, fortrinsvis med en hastighed på fra 5 til 20 m/min, mere fortrinsvis med en hastighed på fra 5 til 15 m/min og endnu mere fortrinsvis med en hastighed på fra 7 til 13 m/min.

17. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at den første og anden perifere zone på den første og anden glasplade er beliggende på en kant af henholdsvis den første og anden plade.

18. Rude, der er opnået ifølge et hvilket som helst af de foregående krav.

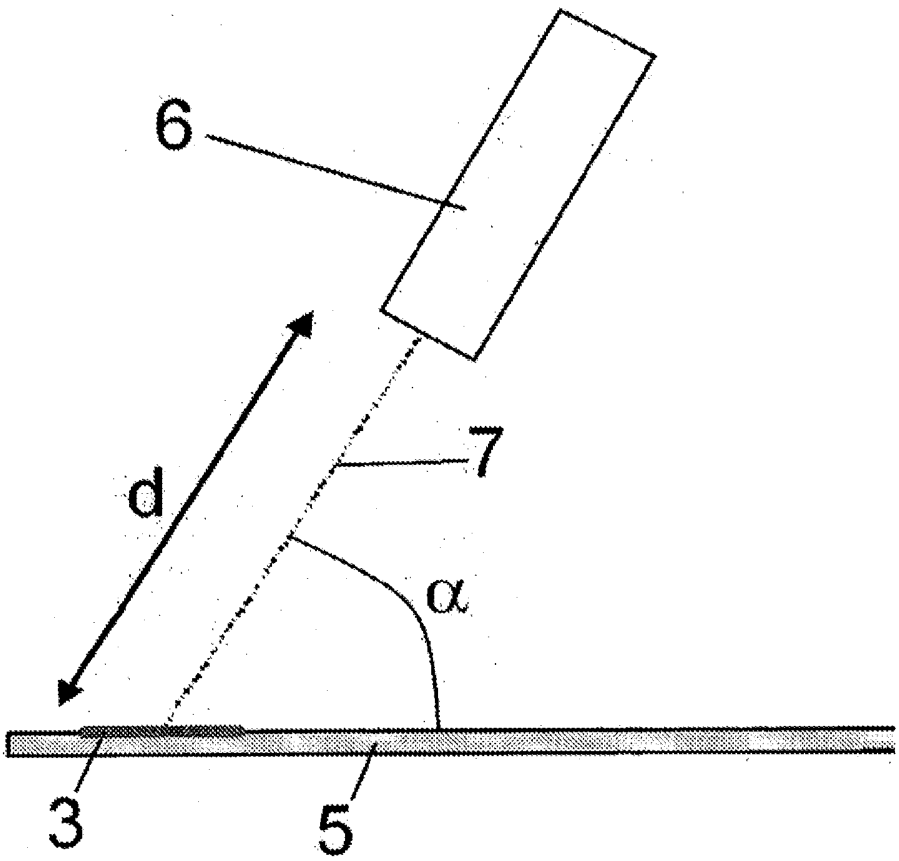

FIG. 1

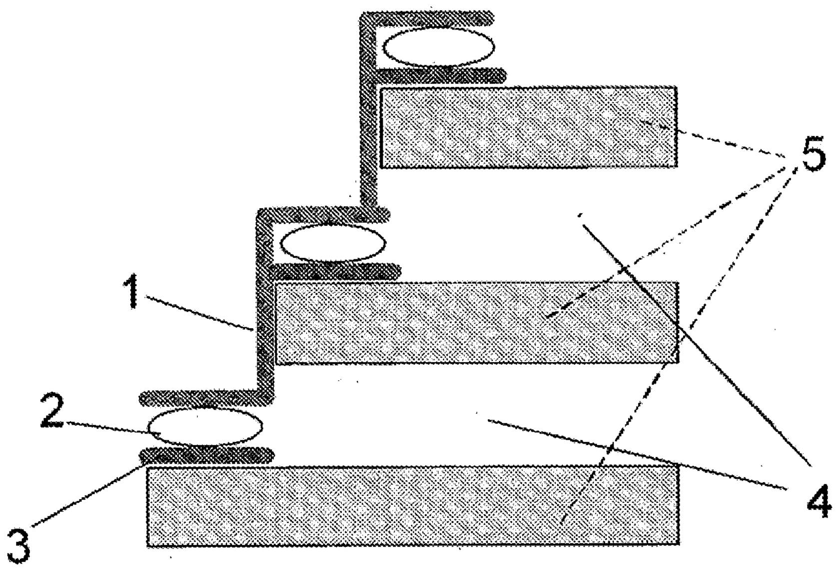

FIG. 2

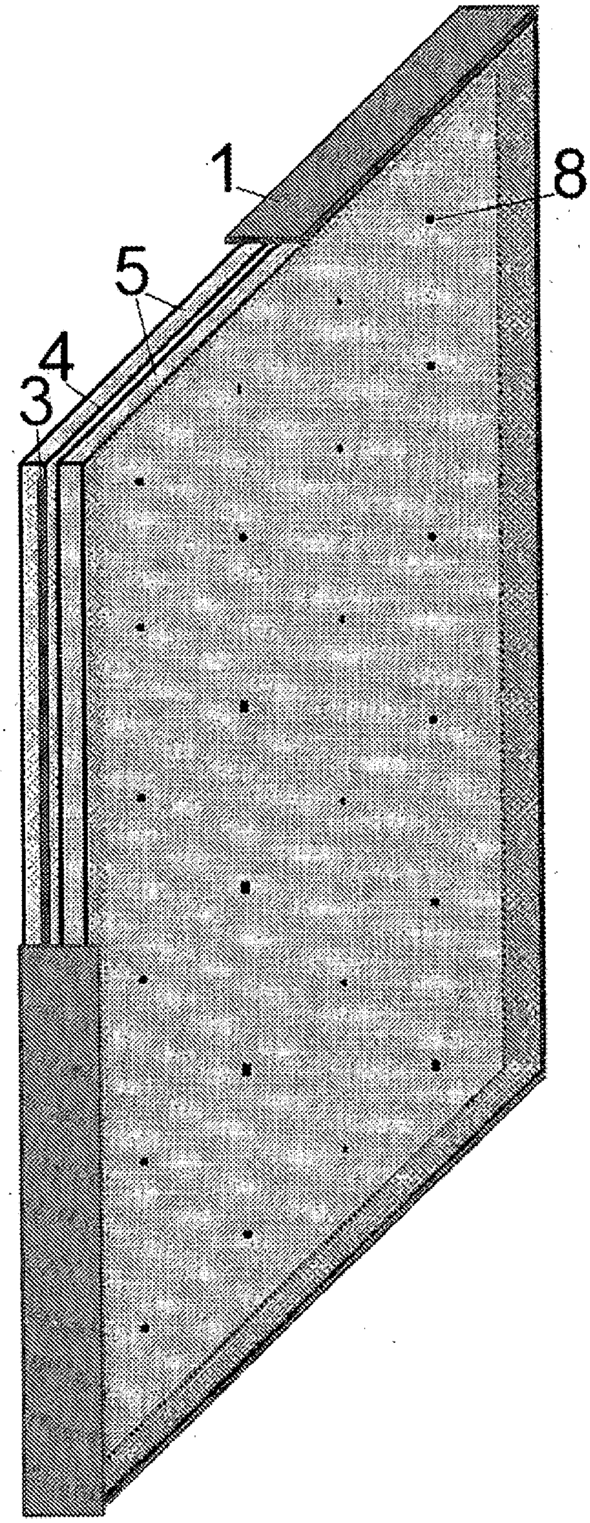

FIG. 3

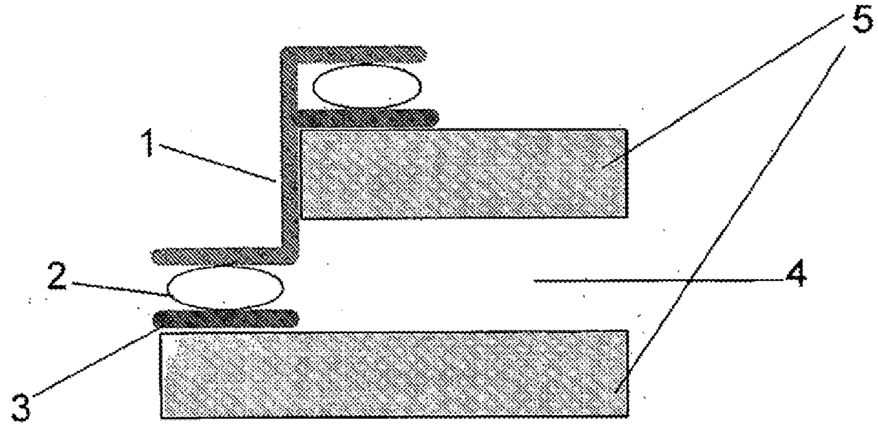

FIG. 4

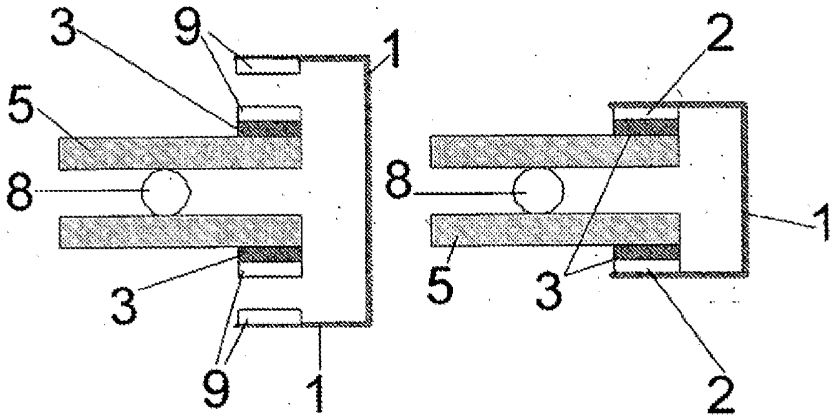

FIG. 5

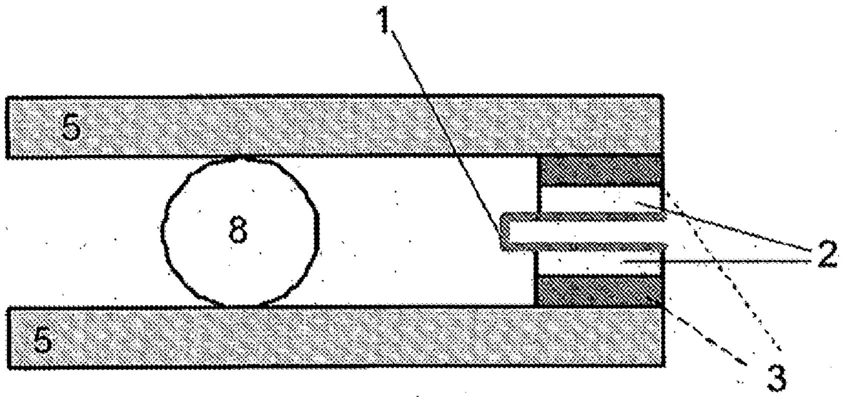

FIG. 6

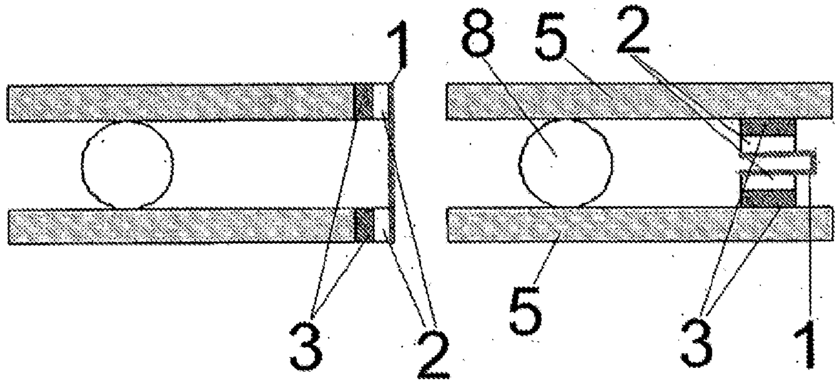

FIG. 7

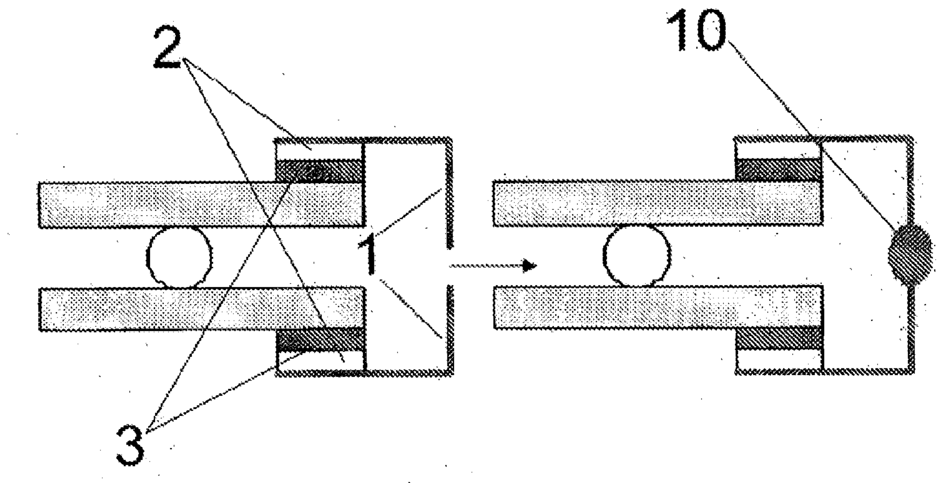

FIG. 8