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(57) Abstract: The present invention relates to a vehicular glazing, in particular a vehicular glazing that is shaped for the vehicle aperture, that: provides high optical clarity; provides sufficient light transmission; is energy efficient; may be heated to provide effective demisting performance; and meets the required safety standards. The invention also relates to a heating apparatus comprising said vehicular glazing, and a vehicle comprising said vehicular glazing or said heating apparatus.

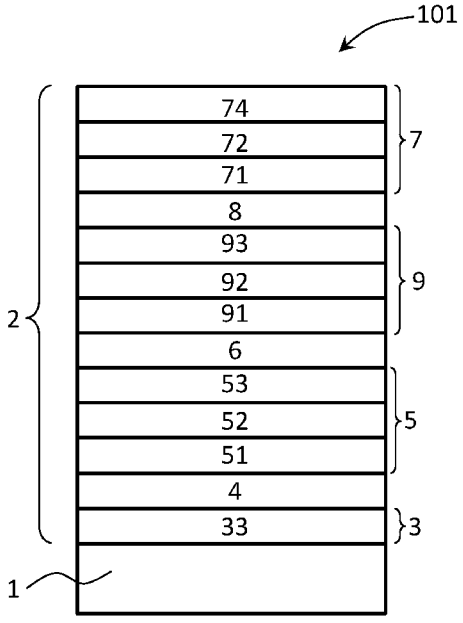


Figure 2

WO 2025/017304 A1

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VEHICULAR GLAZING

The present invention relates to a vehicular glazing and a method manufacturing such a vehicle glazing. The invention also relates to a heating apparatus comprising said vehicular glazing, and a vehicle comprising said vehicular glazing or said heating apparatus.

There is a continual demand on the glass manufacturing industry for automotive glazings which are able to meet the demanding performance requirements of vehicle manufacturers and consumers. Such vehicular glazings must fulfil their primary function of light transmission and also conform to standards relating to safety and energy efficiency. Furthermore, it is desirable that such vehicular glazings are of a pleasant colour in terms of transmission and/or reflection. In addition, in some use cases the vehicular glazings must be shaped to conform to the physical and aesthetic requirements of the structure in which they are placed.

Coatings are often employed to alter the distribution of electromagnetic radiation transmitted by a vehicular glazing, for example by reducing the transmission of infra-red radiation and thereby improve the energy efficiency of the vehicular glazing. In addition, vehicular glazings may comprise heating coatings for reducing condensation on the interior of the vehicular glazing and/or defrosting ice on the exterior of the vehicular glazing. Such heating coatings may comprise transparent conductive layers.

A coating which may be employed to improve the energy efficiency of a pane may include repeat sequences of layers, for example:
'substrate / dielectric layer sequence / [silver-based functional coating/ dielectric layer sequence]$_n$',
with each of the layers not necessarily having the same thicknesses or composition as another. A common silver-based functional coating is a silver-containing layer. It is becoming more common in the glass manufacturing industry for 'n' in the sequence above to equal 2, 3, 4 or even 5 or more, allowing the production of coatings comprising 2, 3, 4, or even 5 or more silver layers. Such coatings may be deposited for example by physical vapour deposition processes, such as sputtering.

With increasing electrification of vehicles there remains a need to provide vehicular glazings with heating coatings which are suitable for hybrid or electric vehicles. Hybrid or electric vehicles may supply heating coatings with electrical supplies in low voltage ranges such as

from 8 to 20 V, in particular 12 or 14 V, medium voltages such as from 40 to 60V, in particular 48V, or even high voltages in excess of 100V. It is desirable to provide a heating coating that is able to perform effectively with a range of voltages, and in particular low voltage ranges.

In order to provide glass panes which conform to the required shape for vehicular glazings, glass panes are often submitted to thermal bending, in which the glass panes are heated to temperatures near or above the softening point of the glass, and then bent with the aid of suitable bending means. Such processes for altering the shape of the glass pane using heat are known as "heat treatments".

Many glass panes comprise soda lime silica glass, which is often produced using a float process. The bending of standard float glass of the soda lime silica type is typically achieved by heating the glass to temperatures in the region of 580 to 690 °C, during which time the glass panes are kept at this temperature range for several minutes before initiating the actual toughening and/or bending process.

As such, the term "heat treatment", in the following description and in the claims refers to thermal processes such as bending during which a coated glass pane reaches temperatures in the range of, for example, 580 to 690 °C for at least 5 minutes, or may be between 1 and 5 minutes during combined bending and heat-treatment processes such a press bending. A glass pane that has undergone such a treatment is referred to as "heat treated".

Coated glass panes may also be submitted to strengthening and bending processes. However, coated glass panes are often incompatible with heat treatments, and may be damaged by the process. Typical damage to coated glass panes caused by heat treatments may be indicated by increased haze (often perceived as cloudiness), pinholes and spots. The function of the glass pane may also be impaired, resulting in a decrease in light transmission and/or a reduction in the effectiveness of a low-emissivity coating, exemplified by an increase in sheet resistance values. As such, a coated glass pane that is damaged by heat treatment may be unacceptable due to its appearance and/or its reduced functional ability. A coated glass pane that exhibits such damage upon heat treatment is known as "non-heat treatable". Conversely, a coated glass pane is deemed to be "heat treatable" if it survives a heat treatment without significant damage. A coated glass pane that exhibits damage upon heating may be "hazy", which reduces the clarity of view transmitted through the glazing to the observer. Therefore, it is particularly desirable to produce "heat treatable" coated glass panes for use as vehicle

windscreens, as a high haze may interfere with driver vision, thereby increasing the risk of accidents. Therefore, it is desirable to produce "heat treatable" coated glass panes for vehicular glazings.

Coatings are often less mechanically stable and durable than the substrate upon which it is deposited, which may lead to scratches and marks which are visually unpleasant. It is thought that mechanical stability and durability is linked to the interfacial adhesion between the layers of the coating. As such, it is desirable to provide a durable coating.

Also, in some cases, vehicular glazings are laminated glazings comprising at least two substrates bonded by an interlayer. Laminated vehicular glazings are required for certain vehicular apertures for reasons of safety, in particular windscreens are laminated vehicular glazings. Coated panes are typically incorporated laminated vehicular glazings such that the coating is adjacent to the interlayer, as the coating may be scratched easily, or may need to be separated from the user where it is electrified for reasons of heating. However, the coating is made up of a sequence of layers, some of which may delaminate in the case of an impact, causing the laminated vehicular glazing to fail. Delamination may be measured, for example, using a pummel test. A durable coating is less likely to delaminate when incorporated in a laminated vehicular glazing.

As can be appreciated by the skilled person, the competing needs of the coating's optical requirements, energy efficiency, heating performance, heat-treatability, and durability must be balanced in order to provide an improved vehicular glazing.

As such, the invention aims to provide a vehicular glazing which: is shaped for the vehicle aperture; provides high optical clarity; provides sufficient light transmission; is energy efficient; may be heated to provide effective demisting performance; and meets the required safety standards, in particular regarding delamination.

Therefore, according to a first aspect of the invention there is provided a vehicular glazing comprising a coated pane, the coated pane comprising a substate and a coating sequence, wherein the coating sequence comprises, in order from the substrate:
a base coating comprising a wetting layer;
a first silver-based functional coating;

a first intermediate coating comprising a barrier layer, at least one dielectric layer, and a wetting layer;

a second silver-based functional coating; and

an outer coating comprising a barrier layer and at least one dielectric layer, wherein:

each wetting layer is from 10 to 150 nm in thickness.

The inventors have found that such a vehicular glazing provides an excellent compromise between the competing requirements, such that it is shaped for the vehicle aperture; provides high optical clarity; provides sufficient light transmission; is energy efficient; may be heated to provide effective demisting performance; and meets the required safety standards, in particular regarding delamination.

As defined herein, a vehicular glazing is a glazing that is adapted or designed to be installed into a vehicle. Such adaptions or design considerations may include, but are not limited to: glazing shape to meet the requirements of a vehicle aperture; marks to indicate that vehicular safety standards are met; encapsulation; application of profiles; application of connectors; and/or application of adhesives or beads.

The vehicular glazing comprises a coated pane. The coated pane comprises a substrate and a coating sequence. The substrate is typically a flat or curved plane with two surfaces, a thickness, and a circumferential edge.

Preferably, the substrate is a glass sheet, such as an aluminosilicate, borosilicate, or soda-lime silica glass sheet, more preferably a soda-lime silica glass sheet. Soda-lime silica glass sheets are particularly well suited to bending operations. Preferably, the substrate is a soda-lime silica glass sheet of thickness less than or equal to 3.5 mm. More preferably, the substrate is a soda-lime silica glass sheet of thickness less than or equal to 2.5 mm. Such thicknesses of soda-lime silica glass sheets are particularly well suited to bending and/or lamination operations. For some vehicular glazings, soda-lime glass sheets of thickness 1.8 mm or less may be employed, for example 1.4 mm, or even 1.0 mm or less. In some embodiments, the substrate may be made up of a glass sheet with an organic layer adhered thereto.

Preferably, the coating sequence is deposited directly on the substrate. Preferably, the coating sequence is deposited by physical vapour deposition, preferably by magnetron sputtering. The coating sequence comprises a series of coatings and layers which are deposited in sequence.

The coating sequence comprises an alternation of coatings with silver-based functional coatings, such that each silver-based functional coating is between two coatings. As defined herein, a coating comprises one or more layers, and the layers therein may be the same or different. As defined herein a layer is deposited in a deposition operation, to form a layer on the substrate. Where two or more adjacent layers of the same composition are formed by substantially the same deposition conditions, these layers are considered to be sub-layers forming a single layer of the same composition – the skilled person will appreciate that this method may be used to "build up" a thicker layer through the deposition of successive sub-layers. A layer may also be a graduated layer, wherein during a single coating operation the composition of the layer is graduated through the thickness of the layer. For the avoidance of doubt, as the skilled person will appreciate, the wetting layer of the intermediate coating is a different layer to the at least one dielectric layer of the intermediate coating, and the barrier layer of the intermediate coating is a different layer to the at least one dielectric layer of the intermediate coating.

Base Coating - The coating sequence comprises a base coating. The base coating is between the substate and the first silver-based functional coating, and is in direct contact with the substrate and the first silver-based functional coating. The base coating comprises at least a wetting layer.

Further layers may be incorporated in the base coating. For example, the base coating may comprise one or more layers between the substrate and the wetting layer. Such a layer between the substrate and the wetting layer may be an ion blocking layer, such as those used to prevent the migration of substrate components, such as glass components, into the coating sequence thereby reducing its performance.

However, preferably the base coating does not comprise a layer between the substrate and the wetting layer. That is, preferably the wetting layer is in direct contact with the substrate.

The base coating may include one or more layers between the wetting layer and the first silver-based functional coating. However, any layers between the wetting layer and the first silver-based functional coating should not significantly impair the function of the wetting layer in improving the performance of the silver-based functional coating. Therefore, layers between the wetting layer and the first silver-based functional coating will be a minor fraction of the overall physical thickness of the base coating.

A beneficial layer which may be employed between the wetting layer and the first silver-based functional coating is a barrier layer. If such a barrier layer is between the base coating wetting layer and the first silver-based functional coating, preferably it is as described herein elsewhere.

However, preferably the base coating does not comprise a layer between the wetting layer and the first silver-based functional coating. That is, preferably the base coating wetting layer is in direct contact with the first silver-based functional coating. The inventors have found that coating sequences without barrier layers between a wetting layer and a silver-based functional coating are more durable, and therefore a vehicular glazing incorporating such a coating sequence is less likely to be marked or scratched during processing, and is more likely to meet the required safety standards when formed as a laminated vehicular glazing.

Outer Coating - The coating sequence comprises an outer coating. The outer coating is above the top-most silver-based functional coating, the top-most silver-based functional coating being the silver-based functional coating that is most distant from the substrate. For example, where there are two silver-based functional coatings, the top-most silver-based functional coating is the second silver-based functional coating, while where there are three silver-based functional coatings the top-most silver-based functional coating is the third silver-based functional coating, and so on. The outer coating comprises a barrier layer and at least one dielectric layer.

The outer coating comprises at least one dielectric layer. The at least one dielectric layer of the outer coating may, for example, comprise an oxide of zinc and tin, a silicon nitride or oxynitride, an aluminium nitride or oxynitride, an oxide of zinc, an oxide of zirconium, an oxide of titanium, an oxide of zirconium and titanium $Zr_xTi_yO_z$, an oxide of silicon and/or aluminium, an oxide of zinc, tin and zirconium.

Layers comprising an oxide of zinc and tin in the outer coating may preferably have a thickness of from 0.5 to 20 nm, more preferably from 5 to 15 nm, even more preferably from 8 to 12. These preferred thicknesses enable further ease of deposition and improvement in optical characteristics such as haze whilst retaining mechanical durability.

Layers in the outer coating based on a silicon nitride or oxynitride, or an aluminium nitride or oxynitride may preferably comprise a thickness of at least 5 nm; preferably from 10 to 60 nm, more preferably from 15 to 45 nm. Such thicknesses provide further improvement in terms of mechanical robustness of the coated pane. Layers based on silicon nitride or oxynitride, or on aluminium nitride or oxynitride, may be mixed aluminium silicon nitride or oxynitride.

Preferably oxide layers in the outer coating are based on essentially stoichiometric metal oxides or nitrides. The use of layers based on essentially stoichiometric metal oxides or nitrides rather than metallic or less than 95% stoichiometric layers leads to an extremely high optical stability of the coating during a heat treatment and effectively assists in keeping optical modifications during heat treatment small. Additionally, the use of layers based on essentially stoichiometric metal oxides or nitrides provides benefits in terms of mechanical robustness.

In some cases, the outer coating may comprise a layer comprising an oxide of zirconium and titanium $Zr_xTi_yO_z$. In some embodiments, the layer comprising an oxide of zirconium and titanium $Zr_xTi_yO_z$ of the outer coating may comprise an atomic proportion of Zr based on Zr and Ti, calculated as x/(x+y), from 0.40 to 0.95.

Preferably, the outer coating comprises an outermost protection layer. The outermost protection layer is the outermost layer of the coating sequence, and provides increased mechanical and/or chemical robustness, for example scratch resistance. Preferably, the outermost protection layer comprises an oxide of zirconium, an oxide of titanium, an oxide of silicon and/or aluminium, an oxide of zinc and tin, or a nitride of silicon and/or aluminium, or mixtures of thereof. Such layers may increase the pummel performance of coated glass panes when incorporated into a laminated glazing.

In some embodiments, the outermost layer comprises a layer based on an oxide of zinc and tin. In addition to zinc and tin, the outermost layer may contain zirconium. Preferably, an outermost layer based on an oxide of zinc, tin and zirconium comprises from 12 to 35 atomic % zirconium. More preferably, the outermost layer based on an oxide of zinc, tin and zirconium comprises from 15 to 33 atomic % zirconium. Most preferably, the outermost layer based on an oxide of zinc, tin and zirconium comprises from 18 to 33 atomic % zirconium.

Alternatively, the outermost protection layer preferably comprises a layer of a silicon oxide. Preferably, the thickness of the protection layer comprising a layer of a silicon oxide is from 1

to 1000 nm, preferably 10 to 500 nm, more preferably from 100 to 400 nm. It has been found that a protection layer comprising a layer of a silicon oxide with such thicknesses is particularly well suited for vehicular glazings bent using a press-bending method, as the protection layer protects the coating from damage during the press-bending process. Such damage may be shown as wrinkling, imprinting or scratching – known as cloth marking – and the like. The outermost protection layer may be provided by physical vapour deposition. However, the outermost protection layer may be provided by other deposition methods, such as sol-gel coating. It has been found that even a very thin layer of silicon oxide, for example from 0.5 to 2 nm, preferably around 1 nm, helps to prevent delamination when adjacent to a polyvinyl butyral (PVB) interlayer.

The outer coating comprises a barrier layer. Barrier layers of the outer coating may be as described elsewhere in this specification, but preferably the outer coating barrier layer is NiCrOx, and preferably the outer coating barrier is NiCrOx and is in direct contact with the under-lying silver-based functional coating.

Further layers may be incorporated in the outer coating. For example, the outer coating may comprise one or more layers between the barrier layer and the at least one dielectric layer. Such further layers may be, for example, further dielectric layers. However, preferably the outer coating does not comprise a layer between the outer coating barrier layer and the top-most silver-based functional coating, as such layers may harm the silver-based functional coating.

In one embodiment of the invention, the outer coating comprises the progression: a barrier layer of a nichrome oxide / a dielectric layer of a zinc oxide / a dielectric layer of an aluminium nitride, wherein each layer of the outer coating is directly on the preceding layer, and preferably wherein the barrier layer of a nichrome oxide is in direct contact with the underlying silver-based functional coating.

In a particularly preferred embodiment of the invention, the outer coating comprises the progression: a barrier layer of a nichrome oxide of thickness from 0.1 to 3 nm / a dielectric layer of a zinc oxide of thickness from 1 to 10 nm/ a dielectric layer of an aluminium nitride of thickness from 20 to 60, preferably 30 to 50 nm, wherein each layer of the outer coating is directly on the preceding layer, and preferably wherein the barrier layer is directly on the

preceding silver-based functional coating, and preferably the dielectric layer of a zinc oxide is deposited from a ceramic target.

Intermediate Coating - The coating comprises at least a first intermediate coating, the first intermediate coating comprising a barrier layer, at least one dielectric layer, and a wetting layer. The barrier layer, the at least one dielectric layer, and the wetting layer are provided in this order from the substrate. The inventors have found that the at least one dielectric layer between the barrier layer and the wetting layer provides a considerable improvement in the heat-treatability of the coating sequence as shown by reduced haze, leading to a vehicular glazing of greatly improved optical clarity.

In some embodiments, it may be desirable to introduce a third silver-based functional coating into the coating sequence. Such a third silver-based functional coating is introduced to reduce the sheet resistance of the coating sequence, which may allow it to be heated effectively with a lower voltage electrical supply and therefore enable the use of the vehicular glazing in certain heating apparatus and/or may improve the energy efficiency of the vehicular glazing.

Where a third silver-based functional coating is introduced into the coating sequence, it is numbered sequentially from the substrate, i.e. the second silver-based functional coating is between the first and the third, and the third is further from the substrate than the second.

Where a third silver-based functional coating is introduced into the coating sequence, in order to preserve the performance of the coating sequence a second intermediate coating must also be incorporated in the coating sequence. Such a second intermediate coating is numbered sequentially from the substrate.

Therefore, in some embodiments the coating sequence further comprises, between the second silver-based functional coating and the outer coating:
a second intermediate coating comprising a barrier layer, at least one dielectric layer, and a wetting layer; and
a third silver-based functional coating.

Where the coating sequence comprises a second intermediate coating and a third silver-based functional coating, the second intermediate coating is directly upon the second silver-based

functional coating, and the third silver-based functional coating is directly upon the second intermediate coating.

The inventors have found that the addition of a third silver-based functional coating makes the vehicular glazing particularly energy efficient.

In some embodiments, it may be desirable to introduce further silver-based functional coatings into the coating sequence. For example, fourth or fifth or yet more silver-based functional coatings may be introduced.

Therefore, in some embodiments the coating sequence further comprises, between the third silver-based functional coating and the outer coating:
a third intermediate coating comprising a barrier layer, at least one dielectric layer, and a wetting layer; and
a fourth silver-based functional coating.

Where the coating sequence comprises a third intermediate coating and a fourth silver-based functional coating, the third intermediate coating is directly upon the third silver-based functional coating, and the fourth silver-based functional coating is directly upon the third intermediate coating.

Such further silver-based functional coatings are introduced to reduce the sheet resistance of the coating sequence, which may allow it to be heated effectively with a lower voltage electrical supply and therefore enable the use of the vehicular glazing in certain heating apparatus and/or may improve the energy efficiency of the vehicular glazing.

Where further silver-based functional coatings are introduced into the coating sequence, these are numbered sequentially from the substrate.

Where further silver-based functional coatings are introduced into the coating sequence, in order to preserve the performance of the coating sequence further intermediate coatings must also be incorporated in the coating sequence. Such further intermediate coatings are numbered sequentially from the substrate, with each intermediate coating taking the number of the silver-based functional coating directly below it.

Preferably, each further intermediate coating comprises a barrier layer, at least one dielectric layer, and a wetting layer, in this order from the substrate.

Any dielectric layer that is in contact with an overlying wetting layer is distinct from the overlying wetting layer by virtue of their composition and/or deposition method.

Preferably, an at least one dielectric layer of the intermediate coating(s), comprises an oxide of zinc and tin, a silicon nitride or oxynitride, an aluminium nitride or oxynitride, an oxide of zinc, an oxide of zirconium, an oxide of titanium, an oxide of zirconium and titanium $Zr_xTi_yO_z$, an oxide of silicon and/or aluminium, an oxide of zinc and tin with zirconium. Preferably, the at least one dielectric layer of each intermediate coating comprises one of these. The inventors have found that such a progression of layers in an intermediate coating, between the barrier layer and the wetting layer, provides excellent optical clarity.

Where the at least one dielectric layer comprises an oxide of zinc doped with aluminium, preferably the at least one dielectric layer comprises between 1 and 15 % aluminium by weight.

Where the at least one dielectric layer comprises an oxide of zirconium and titanium $Zr_xTi_yO_z$, this preferably comprises an atomic proportion of Zr based on Zr and Ti, calculated as x/(x+y), from 0.40 to 0.95.

Layers in the intermediate coating(s) based on a silicon nitride or oxynitride, or an aluminium nitride or oxynitride may be mixed aluminium silicon nitride or oxynitride. Preferably such layers are deposited as an Al nitride and/or Si nitride layer by reactive sputtering of a Si, Al or mixed SiAl target, in a N_2 containing atmosphere.

Layers comprising an oxide of zinc and tin in the intermediate coating(s) are preferably deposited from metal targets comprising from 40 to 60 weight % tin and from 40 to 60 weight % zinc. Alternatively, a layer comprising an oxide of zinc and tin in the intermediate coating(s) may be deposited from a ceramic target comprising zinc, tin and oxygen with 40 to 60 weight % tin and from 40 to 60 weight % zinc based on metals.

While suitable vehicular glazings may be obtained by the use of a single dielectric layer between the barrier layer and the wetting layer, the inventors have found that improved

vehicular glazings may be obtained with at least two dielectric layers between the barrier layer and the wetting layer. Therefore, preferably the first intermediate coating and/or the second intermediate coating and/or a further intermediate coating comprises at least two dielectric layers between the barrier layer and the wetting layer. Preferably, each intermediate coating comprises at least two dielectric layers between the barrier layer and the wetting layer.

Where there are at least two dielectric layers between the barrier layer and the wetting layer, a first dielectric layer is differentiated from a second adjacent dielectric layer by virtue of their composition and/or deposition method.

The inventors have found that suitable glazings may be provided by the use of two dielectric layers between the barrier layer and the wetting layer. Therefore an intermediate coating, preferably each intermediate coating, comprises, between the barrier layer and the wetting layer, a first dielectric layer below and adjacent to a second dielectric layer. In some embodiments, each intermediate coating consists of a barrier layer, a first dielectric layer, a second dielectric layer, and a wetting layer, in this order.

Preferably, the first dielectric layer is in direct contact with the barrier layer, the second dielectric layer is direct contact with the first dielectric layer, and the wetting layer is in direct contact with the second dielectric layer. The inventors have found that such an arrangement of dielectric layers provides excellent results in terms of heat-treatability as measured by haze, and conductivity.

In some embodiments, the first intermediate coating and/or the second intermediate coating and/or a further intermediate coating comprises between the barrier layer and the wetting layer a first dielectric layer provided by non-reactive sputtering and a second dielectric layer provided over the first dielectric layer by reactive sputtering. Preferably, each intermediate coating comprises between the barrier layer and the wetting layer a first dielectric layer provided by non-reactive sputtering and a second dielectric layer provided over the first dielectric layer by reactive sputtering.

Preferably, the first dielectric layer comprises an oxide of zinc, preferably doped with aluminium, and a second dielectric layer comprising an aluminium nitride or oxynitride. The inventors have found that such a progression of layers, between the barrier layer and the wetting layer, provides excellent optical clarity.

Preferably, the first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, is from 1 to 20 nm, preferably 1 to 10 nm in thickness and the second dielectric layer comprising an aluminium nitride or oxynitride is from 5 to 15 nm in thickness. Even more preferably, the first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, is from 5 to 16, preferably 5 to 8 nm in thickness and the second dielectric layer comprising an aluminium nitride or oxynitride is from 5 to 10 nm in thickness. The inventors have found that such a progression of layers in such thicknesses between the barrier layer and the wetting layer provides excellent optical clarity.

Preferably, the first dielectric layer of the second intermediate coating comprising an oxide of zinc, preferably doped with aluminium, is from 1 to 20, preferably 1 to 10 nm in thickness and the second dielectric layer of the second intermediate coating comprising an aluminium nitride or oxynitride is from 5 to 15 nm in thickness. Even more preferably, the first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, is from 5 to 16, preferably 5 to 8 nm in thickness and the second dielectric layer comprising an aluminium nitride or oxynitride is from 5 to 10 nm in thickness. The inventors have found that such a progression of layers in such thicknesses between the barrier layer and the wetting layer provides excellent optical clarity.

Preferably, a first dielectric layer of each intermediate coating comprises an oxide of zinc doped with aluminium deposited by sputtering from a target comprising zinc oxide doped with aluminium oxide, preferable doped with less than 5 weight percent aluminium oxide. Preferably a second dielectric layer of each intermediate coating comprises a nitride of aluminium deposited by sputtering from a target comprising aluminium metal in a nitrogen atmosphere.

In one embodiment of the invention, each intermediate coating comprises the progression: a barrier layer of a nichrome oxide / a dielectric layer of a zinc oxide / a dielectric layer of an aluminium nitride / a wetting layer of a zinc oxide, wherein each layer of the progression is directly on the preceding layer.

In a particularly preferred embodiment of the invention, each intermediate coating comprises the progression: a barrier layer of a nichrome oxide of thickness from 0.1 to 3 nm / a dielectric layer of a zinc oxide of thickness from 1 to 10 nm/ a dielectric layer of an aluminium nitride

of thickness from 5 to 15 nm / a wetting layer of a zinc oxide, preferably doped with aluminium, of thickness 20 to 150 nm, wherein each layer of the progression is directly on the preceding layer and the barrier layer is directly on the preceding silver-based functional coating, and the wetting layer is directly adjacent to an overlying silver-based functional coating, such a coating progression provides a durable coating that has a reduced chance of damage during processing.

Wetting layer - The coating sequence comprises wetting layers below silver-based functional coatings in the base coating, and in each intermediate coating. The wetting layers are believed to provide a beneficial structure for the subsequent growth of the silver-based functional coatings, thereby improving their conductivity.

Each wetting layer has a thickness of from 10 to 150 nm. The inventors have surprisingly discovered that such wetting layer thicknesses allow for improved durability of the coating, leading to a vehicular glazing that is more scratch resistant and less likely to delaminate.

Preferably, each wetting layer has a thickness of from 19 to 120 nm, such wetting layer thicknesses are associated with yet more improved durability. In some aspects, each wetting layer has a thickness of from 30 to 100 nm, such wetting layer thicknesses are associated with yet more improved durability. In some aspects, each wetting layer has a thickness of from 35 to 95 nm, such wetting layer thicknesses are associated with yet more improved durability, while further maintaining optical requirements.

In some embodiments, the coating comprises three silver-based functional coatings, a first intermediate coating and a second intermediate coating ordered from the substrate, and the wetting layer of the base coating has a thickness greater than 30 nm and preferably from 30 to 60 nm, the wetting layer of the first intermediate coating has a thickness greater than 20 nm and preferably from 25 to 35 nm and the wetting layer of the second intermediate coating has a thickness greater than 15 nm and preferably from 18 to 30 nm.

Preferably, each wetting layer comprises an oxide of zinc. Each wetting layer may comprise the same oxide of zinc. Alternatively, wetting layers may comprise differing oxides of zinc.

In some embodiments an oxide of zinc of a wetting layer comprises at least 70 atomic % zinc based on metals. Where the oxide of zinc comprises at least 70 atomic % zinc based on

metals, preferably the oxide of zinc comprises at least 85 atomic % zinc based on metals, more preferably at least 95 atomic % zinc based on metals. The inventors have found that wetting layers comprising oxides of zinc, especially with a high proportion of zinc metal, provide excellent wetting layers that lead to coating sequences with low sheet resistance and therefore improve heating performance and energy efficiency of the vehicular glazing.

In some embodiments where an oxide of zinc of a wetting layer comprises at least 70 atomic % zinc based on metals, the wetting layer comprises an oxide of zinc doped with aluminium. Such layers allow the deposition of silver-based functional coatings which have improved conductivity. Where a wetting layer comprises an oxide of zinc doped with aluminium such doping is up to about 10 weight %. A typical content of aluminium is about 2 weight %.

In other embodiments the oxide of zinc comprises an oxide of zinc and tin, ZSO, preferably from 20 to 80 atomic % zinc and from 20 to 80 atomic % tin based on metals. Where the oxide of zinc comprises from 20 to 80 atomic % zinc and from 20 to 80 atomic % tin based on metals, preferably the oxide of zinc comprises from 50 to 80 atomic % zinc and from 20 to 50 atomic % tin based on metals, more preferably the oxide of zinc comprises from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin based on metals, yet more preferably from 62 to 68 atomic % zinc and from 32 to 38 atomic % tin based on metals. The inventors have found that the use of an oxide of zinc and tin, ZSO, as a wetting layer as described herein provides coated glass substrates with exceptional durability, heat treatable as defined herein, and provide acceptable sheet resistance.

In other embodiments, an oxide of zinc wetting layer comprises a first oxide of zinc sublayer and a second oxide of zinc sublayer in direct contact with the first oxide of zinc sublayer, wherein the first oxide of zinc sublayer is between the overlying silver-based functional layer and the second oxide of zinc sublayer, such a wetting layer is referred to herein as a "dual wetting layer". Preferably, the first oxide of zinc sublayer is in direct contact with the overlying silver-based functional layer. The first oxide of zinc sublayer and the second oxide of zinc sublayer are distinguished by differing compositions and/or deposition method, and together form a wetting layer with a thickness that is the sum of the individual sublayer thicknesses. However, in order to be considered a dual wetting layer, the first oxide of zinc sublayer must have a thickness of greater than 10 nm, preferably greater than 15 nm, yet more preferably greater than 20 nm. That is, the first oxide of zinc sublayer has a thickness from 10 to 60 nm, preferably 15 to 50 nm, more preferably from 20 to 40 nm.

Preferably the first oxide of zinc sublayer comprises at least 70 atomic % zinc based on metals. Where the oxide of zinc comprises at least 70 atomic % zinc based on metals, preferably the oxide of zinc comprises at least 85 atomic % zinc based on metals, more preferably at least 95 atomic % zinc based on metals. Preferably such layers are aluminium doped and reactively sputtered as discussed elsewhere. As such, preferably the first oxide of zinc sublayer comprises at least 95 atomic % zinc based on metals and has a thickness of from 15 to 50 nm.

Preferably the second oxide of zinc sublayer comprises an oxide of zinc and tin, ZSO, preferably comprising from 20 to 80 atomic % zinc and from 20 to 80 atomic % tin based on metals. Where the oxide of zinc comprises from 20 to 80 atomic % zinc and from 20 to 80 atomic % tin based on metals, preferably the oxide of zinc comprises from 50 to 80 atomic % zinc and from 20 to 50 atomic % tin based on metals, more preferably the oxide of zinc comprises from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin based on metals, yet more preferably from 62 to 68 atomic % zinc and from 32 to 38 atomic % tin based on metals. The second oxide of zinc sublayer of a or each dual wetting layer preferably has a thickness from 20 to 70 nm, more preferably from 30 to 60 nm, yet more preferably from 35 to 55 nm.

Preferably, a dual wetting layer comprises a first oxide of zinc sublayer comprising at least 80 atomic % zinc based on metals and a second oxide of zinc sublayer comprising an oxide of zinc and tin comprising from 20 to 80 atomic % zinc and from 20 to 80 atomic % tin based on metals. More preferably a wetting layer comprises a first oxide of zinc sublayer comprising at least 90 atomic % zinc based on metals and a second oxide of zinc sublayer comprising an oxide of zinc and tin comprising from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin based on metals. The inventors have found that such dual wetting layers may provide coating sequences of exceptionally low haze, low sheet resistance, and surprisingly high durability.

Preferably, the wetting layer of each intermediate coating comprises a dual wetting layer. Preferably, the wetting layer of each intermediate coating comprises a dual wetting layer comprising a first oxide of zinc sublayer comprising at least 90 atomic % zinc based on metals and a second oxide of zinc sublayer comprising an oxide of zinc and tin comprising from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin based on metals. The inventors have found that such dual wetting layers may provide coating sequences of exceptionally low haze, low sheet resistance, and surprisingly high durability.

Preferably, the second oxide of zinc sublayer has a thickness that is greater than the thickness of the first oxide of zinc sublayer.

In a particularly preferred arrangement, each intermediate coating comprises a first dielectric layer of aluminium doped zinc oxide deposited from a ceramic target, a second dielectric layer of a nitride of aluminium in direct contact with the first dielectric layer, and a wetting layer in direct contact with the second dielectric layer and in direct contact with the overlying silver-based functional layer, wherein the wetting layer comprises a first oxide of zinc sublayer of thickness greater than 15 nm and comprising greater than 90 atomic % zinc based on metals and a second oxide of zinc sublayer of thickness greater than the thickness of the first oxide of zinc sublayer and comprising from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin based on metals.

As explained above, additional layers may be between a wetting layer and a silver-based functional coating. However, preferably each wetting layer is in direct contact with the overlying silver-based functional coating. The inventors have found that this produces excellent quality silver-based functional coatings, and increases the durability of the coating. Where there are one or more layers between the wetting layer and the silver-based functional coating, such as barrier for example based on NiCr, these layers should have a total physical thickness of less than 5 nm, preferably less than 3 nm, more preferably less than 1 nm.

Preferably, each wetting layer makes up at least 20% of the physical thickness of the coating, base or intermediate as the case may be, containing said wetting layer, preferably each wetting layer makes up at least 25% of the physical thickness of the coating containing said wetting layer. The inventors have found that the use of wetting layers as described herein may allow for other layers in the base and intermediate coatings to be removed, leading to improved throughput and coating efficiency, while not reducing the performance of the coating sequence and vehicular glazing incorporating the same.

Preferably, the wetting layer of the base coating makes up at least 50% of the physical thickness of the base coating, preferably the wetting layer of the base coating makes up at least 75% of the physical thickness of the base coating, more preferably the wetting layer of the base coating makes up at least 90% of the physical thickness of the base coating, yet more preferably the wetting layer of the base coating makes up at least 95% of the physical

thickness of the base coating, most preferably the base coating consists of the wetting layer. Surprisingly, the inventors have found that a coating sequence with base coating wetting layers of sufficient thickness as described by the present invention may be employed as substantially the entire base coating, yet still provide excellent heat-treatability as indicated by haze, leading to a vehicular glazing of excellent optical clarity.

Preferably, the wetting layer of the base coating has a thickness of from 25 to 75 nm, more preferably from 30 to 50 nm, yet more preferably from 35 to 45 nm. An increased thickness of base coating wetting layer is associated with improved durability and improved pummel performance when the coating sequence is incorporated in a laminated vehicular glazing, however the upper limit of the thickness of the base coating wetting layer is dominated by optical considerations – if the base coating wetting layer is too thick the optical performance of the coating sequence is significantly decreased, in particular the colours of the vehicular glazing may become unacceptable to the consumer.

Preferably, the base coating wetting layer is in direct contact with the substrate. The inventors have found that excellent heat treatability may be achieved even with the absence of an ion blocking layer below the wetting layer.

Preferably, the base coating wetting layer is in direct contact with the substrate and the first silver-based functional coating, that is – preferably the base coating consists of the base coating wetting layer. Most preferably, the base coating consists of a wetting layer comprising ZSO comprising from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin with a thickness from 20 to 60 nm. The inventors have found that excellent heat treatability may be achieved even with the absence of an ion blocking layer below the wetting layer and with the absence of a barrier layer between the wetting layer and the first silver-based functional coating. In addition, the ZSO provides excellent colour tuning potential, allowing the coating sequence to achieve neutral colours and low haze following heat treatment.

Preferably, each wetting layer comprises an oxide of zinc provided by reactive sputtering. As defined herein, reactive sputtering is sputtering from a metallic target, for example zinc metal doped with aluminium, in an atmosphere such that a layer which incorporates atoms from the atmosphere in a significant proportion is deposited on the substrate. Alternatively, a metallic target comprising zinc and tin, preferably 50:50 by weight zinc and tin, may be used to provide an oxide of zinc that is an oxide of zinc and tin, ZSO. The target composition is matched to

the desired composition of the layer. Conversely non-reactive sputtering is defined as sputtering from a ceramic target, for example based on zinc oxide optionally containing tin oxide and optionally doped with aluminium, in an atmosphere containing zero or only a small amount, that is, generally no more than about 10 volume %, of oxygen. The inventors have found that oxide of zinc wetting layers produced by reactive sputtering provide silver-based functional coatings of excellent quality, which lead to a low sheet resistance coating sequence and therefore a vehicular glazing of improved energy efficiency and heating ability.

As described above, intermediate coatings require at least a barrier layer and at least one dielectric layer, as well as the wetting layer, to provide the required balance of sheet resistance, heat-treatability, and durability to the vehicular glazing. Therefore, each intermediate coating wetting layer is preferably at least greater than 10 nm and preferably greater than or equal to 20 nm in thickness to enhance durability of the coating, while ensuring that the barrier layer and at least one dielectric layer are of sufficient thickness to be functional.

Therefore, preferably each wetting layer has a thickness of from 20 to 140 nm, preferably from 30 to 120 nm, more preferably from 40 to 100 nm. The inventors have found that thicker wetting layers improve the durability of the coating, but the thickness is limited by optical considerations, and the need to include the barrier layer and at least one dielectric layer in the intermediate coatings.

Preferably, the average wetting layer thickness is from 20 nm to 100 nm, more preferably from 30 to 80 nm. The inventors have found that such average wetting layer thicknesses provide an excellent balance between durability and haze.

Preferably, the minimum wetting layer thickness is from 10 nm to 100 nm, preferably from 20 nm to 70 nm. Where durability is particularly important, preferably the minimum wetting layer thickness is from 40 nm to 70 nm, more preferably from 50 nm to 70 nm. The inventors have found that such a minimum wetting layer thickness provides an excellent balance between durability and haze.

The maximum difference in thickness of wetting layer, calculated as the difference between the thickness of the thickest wetting layer and the thickness of the thinnest wetting layer, is preferably less than 50 nm, more preferably less than 40 nm, yet more preferably less than

30 nm. The inventors have found that a coating sequence wherein the minimum wetting layer thickness is greater than 20 nm, more preferably greater than 25 nm, yet more preferably greater than 30 nm, and the maximum difference in thickness of wetting layer is less than 50 nm, more preferably less than 40 nm, yet more preferably less than 30 nm, provides particularly durable coatings. It is thought that such a maximum difference in wetting layer thickness helps to balance the stresses through the coating sequence.

Barrier layer – The first intermediate coating and the upper coating each comprise a barrier layer. Preferably, each intermediate coating comprises a barrier layer. Preferably, each barrier layer is in direct contact with the underlying silver-based functional coating. Preferably, a barrier layer is less than 5 nm, more preferably less than 3 nm. Preferably, each barrier layer is less than 5 nm, more preferably less than 3 nm.

Preferably, the barrier layer comprises a layer of nichrome oxide, also known as NiCrOx. The skilled person will appreciate that a barrier layer deposited as a metal, such as NiCr, which is in a coated pane that is subsequently heat treated, will be oxidised to some extent, such that all barrier layers comprise some level of oxygen following heat treatment. Alternative barrier layers include TiOx, ZnOx, SnZnOx, NbOx and/or combinations of the same. In some cases, a double barrier layer, comprising two sub-layers, or even triple barrier layer, comprising three sub-layers, may be used, for example ZnOx/SnZnOx. A particularly preferred double barrier layer comprises: a first sub-layer of ZnOx deposited from a ceramic target in direct contact with the underlying silver layer; and a second sub-layer of ZnSnOx in direct contact with the first sub-layer of ZnSnOx, wherein the first sub-layer preferably comprises a thickness less than or equal to 3 nm and the second sub-layer preferably comprises a thickness less than or equal to 3 nm. It is important that the barrier layer directly adjacent to the silver-based functional coating is deposited non-reactively, i.e. from a ceramic target, or if deposited reactively from a metal target, is deposited with an atmosphere less than 15 volume % oxygen, preferably less than 10% volume % oxygen, even more preferably at most 8 volume % oxygen.

Silver-based functional coating - The coating sequence comprises at least a first silver-based functional coating and a second silver-based functional coating. However, further silver-based functional coatings with associated intermediate coatings, are not excluded. For example, in some embodiments the coating sequence comprises a third silver-based functional layer. In some embodiments, the coating sequence comprises a third silver-based functional

layer and a fourth silver-based functional layer. Such additional silver-based functional coatings may improve the conductivity of the coating and thereby lower the voltage at which the heating coating may be enabled. In addition, additional silver-based functional coatings may improve the energy-efficiency of the vehicular glazing. Additional silver-based functional coatings should be provided with associated dielectric coatings to preserve the functionality of the coating sequence.

The silver-based functional coatings preferably consist essentially of a silver layer without any additive, as is normally the case in the area of low-emissivity and/or solar control coatings. It is, however, within the scope of the invention to modify the properties of the silver-based functional coating(s) by adding doping agents, alloy additives or the like or even adding very thin metal or metal compound layers, as long as the properties of the silver-based functional coating(s) necessary to function as highly light-transmitting and low light-absorbent IR-reflective layer(s), are not substantially impaired thereby.

The thickness of each silver-based functional coating is dominated by its technical purpose. For typical low-emissivity and/or solar control purposes the preferred layer thickness for silver-based functional coatings may preferably be from: 3 to 30 nm; more preferably from 5 to 20 nm; even more preferably from 8 to 18 nm; even more preferably from 10 to 16 nm. With such a layer thickness, light transmittance values of above 70 % and a normal emissivity below 0.05 after a heat treatment may be readily achieved. Preferably, the first silver-based functional coating comprises a thickness of 3 nm to 20 nm, preferably each silver-based functional coating comprises a thickness of 3 nm to 20 nm, more preferably each silver-based functional coating comprises a thickness of 5 to 18 nm.

Preferably, when the coating sequence comprises a third silver-based functional layer m_3, the second silver-based functional layer m_2 is thicker than the first silver-based functional layer m_1, which is thicker than the third silver-based functional layer m_3, that is $Gm_2>Gm_1>Gm_3$, where G is the physical thickness of the layer.

Preferably, when the coating sequence comprises a third silver-based functional layer m_3 and a fourth silver-based functional layer m_4, the second silver-based functional layer m_2 is thicker than the third silver-based functional layer m_3, which is thicker than the first silver-based functional layer m_1, which is thicker than the fourth silver-based functional layer m_4, that is $Gm_2>Gm_3>Gm_1>Gm_4$, where G is the physical thickness of the layer.

Therefore, when there are n silver-based functional layers preferably $Gm_2>Gm_3>...>Gm_{n-1}>Gm_1>Gm_n$, such that the outermost silver-based functional layer is the thinnest silver-based functional layer, the innermost silver-based functional layer is the second thinnest silver-based layer, and the thicknesses of the silver-based functional layers excluding the outermost and the innermost decrease with increasing distance from the substrate.

Lower voltage supplies require lower resistance coatings to achieve the same heating power. Heating powers may be in the range 200 W/m^2 to 1000 W/m^2, with high heating powers within this range being preferred for "defrost" products, while lower heating powers within this range being preferred for "demist" products. Preferably, the heating power is between 300 and 600 W/m^2 for a demist product, which for a 14 V supply corresponds to a sheet resistance of from 0.5 Ω/□ to less than 1.3 Ω/□. This may be achieved by a coating sequence comprising three or more silver-based functional coatings.

The sheet resistance (Rs) is dependent upon the number and thickness of the conductive layers in the coating: a higher number of silver layers, or a greater thickness, will contribute to lower sheet resistance measurements. Preferably, the sheet resistance Rs is less than 1.5, more preferably less than 1.2, more preferably less than 1.0, even more preferably less than 0.8 Ω/□.

In some aspects, the vehicular glazing is a laminated glazing comprising the coated pane, an interlayer, and a further pane bonded to the coated pane by the interlayer, preferably the interlayer is adjacent to the coating sequence. A laminated glazing may be provided as known to the person skilled in the art, preferably as described in WO2021038214A1, WO2021180954A1, US20080318028A1, US20010019759A1, for example.

The vehicular glazing may be, for example, a windscreen, sidelight, rooflight, or backlight.

Vehicular glazings may be adapted for these apertures considering their visible light transparency, coating sequence sheet resistance, energy efficiency, shaping, etc. Typical vehicular glazings are provided with obscuration bands as is known to those in the art.

Preferably, coated pane is bent using a press-bending method. To bend the coated pane it must be first heated to a temperature at which it can be bent. Such a thermally bent coated

pane is considered to be heat treated. Typically the thermally bent coated pane is a thermally bent coated glass pane.

Preferably, glass substrates of the vehicular glazing are heated and then bent by sagging or press-bending, preferably by press-bending.

Coated glass panes that have undergone thermal bending comprise a radius of curvature in at least one direction, preferably coated glass panes that have undergone thermal bending comprise a radius of curvature in at least one direction of from 500 mm to 20000 mm, more preferably coated glass panes that have undergone thermal bending comprise a radius of curvature in at least one direction of from 1000 mm to 8000 mm.

Coated glass panes may be bent as known by the skilled person, and may preferably be bent as described in US10995029B2, EP3538498B1, US11434161B2, WO2018220394A1, WO2020021273A1, for example.

Preferably, the coated pane is a heat-treated coated glass pane with a hazescan value of less than 90, more preferably less than 60, yet more preferably less than 50.

In some embodiments the heat treated coated glass pane exhibits a hazescan value of less than 90. Preferably the hazescan value is less than 80 and even more preferably less than 70 is desirable. In some applications, where clarity is prioritised, a hazescan value of less than 60 is desired, and preferably less than 50.

The vehicular glazing may comprise a thermally toughened coated glass pane. Coated glass panes that have undergone thermal toughening are preferably at least twice as strong as annealed glass of a similar thickness. Coated glass panes that have undergone thermal toughening are preferably at least four times as strong as annealed glass of a similar thickness. Preferably, the thermally strengthened heat treated coated glass pane comprises a compressive stress on the surface of from 400 to 1500 kg/m^2. Where the thermally strengthened heat treated coated glass pane comprises a toughened glass pane, preferably the coated glass pane comprises a compressive stress on the surface of from 750 to 1500 kg/m^2. Alternatively, the thermally strengthened heat treated coated glass pane may comprise a compressive stress on the surface of from 400 to 700 kg/m^2 – such panes are known in the art as "heat strengthened" rather than "toughened".

Preferably, glass panes that have undergone thermal toughening have been submitted to a heat soaking process.

It will be appreciated that coating sequences according to the present invention may include further coating layers, and that any further layer may contain additives that modify its properties and/or facilitate its manufacture, for example, doping agents or reaction products of reactive sputtering gases. In the case of oxide based layers, nitrogen may be added to the sputtering atmosphere leading to the formation of oxinitrides rather than oxides, in the case of nitride based layers oxygen may be added to the sputtering atmosphere, also leading to the formation of oxinitrides rather than nitrides.

Care must be taken by performing a proper material, structure and thickness selection when adding any such further partial layer to the basic layer sequence of the inventive pane that the properties primarily aimed at, for example, a high thermal stability, are not significantly impaired thereby.

Also, in the context of the present invention, where a layer is said to be "based on" a particular material or materials this means, unless stated otherwise, that the layer predominantly comprises said material or materials in an amount of at least 50 atomic %, i.e. a layer based on ZnO_x:Al should have a sum of atomic percentages of Zn, O, and Al greater than 50%, preferably greater than 90%.

Where a layer is based on $ZnSnO_x$, "$ZnSnO_x$" or ZSO means an oxide of Zn and Sn as described and defined elsewhere in the description. Preferably the oxide of zinc and tin has a weight ratio of metals Zn:Sn of 1:1. Alternatively, the oxide of zinc and tin may comprise a weight ratio of metals Zn:Sn of from 0.1:1 to 1:0.1.

In some embodiments the coating sequence is deleted around the periphery of the coated glass pane. Such "edge deletion" results in the absence of coating around the periphery of the coated glass pane, to prevent electrification of items adjoined to the coated pane when the coating sequence is electrified. Such edge deletion may be accomplished for example by abrasion, laser, etching and/or masking the pane prior to a coating step.

Preferably, the vehicular glazing further comprises busbars and/or connectors for supplying electrical energy to the coating sequence. The skilled person is aware of such connectors and busbars. The connectors may be soldered to the busbars, preferably with lead-free solder. Busbars and connectors are preferably provided as described in EP3302966A1, US20090321407A1, for example.

According to a second aspect of the present invention, there is provided a method of manufacturing a vehicular glazing according to the first aspect, comprising the steps of:
i) providing a substrate; and
ii) depositing a coating sequence on the substrate to provide a coated pane;
iii) heating the substrate to at least 550 °C to provide a heat-treated substrate; and
iv) bending the heat-treated substrate to provide a vehicular glazing.

Optional or advantageous features of the first aspect of the present invention may be combined with second aspect of the present invention in any combination, and vice versa. In particular, in relation to the second aspect of the present invention it will be appreciated that all features of the first aspect of the present invention, such as the glass substrate, the base coating, intermediate coatings, the outer coating, and the silver-based functional coating, may also be applied to the second aspect of the present invention in any combination.

The skilled person will appreciate that in some embodiments the substrate may be coated, then heat-treated and bent. However, in alternative embodiments the substrate may be heat-treated, bent and then coated.

Therefore, preferably the process comprises the following steps in order:
i) providing a substrate;
ii) depositing a coating sequence on the substrate to provide a coated pane;
iii) heating the substrate to at least 550 °C to provide a heat-treated substrate; and
iv) bending the heat-treated substrate to provide a vehicular glazing.

This provides the advantage that coated panes may be produced in an efficient manner.

Alternatively, the process may comprise the following steps in order:
i) providing a substrate;
ii) heating the substrate to at least 550 °C to provide a heat-treated substrate;

iii) bending the heat-treated substrate to provide a vehicular glazing; and
iv) depositing a coating sequence on the substrate to provide a coated pane.

This provides the advantage that the coating can't be to be damaged during the bending step.

The invention is not limited to a specific production process for the coating. However, it is particularly preferred if at least one of the layers and most preferably all layers are applied by physical vapour deposition, preferably magnetron cathode sputtering, either in the DC mode, in the pulsed mode, in the medium frequency mode or in any other suitable mode, whereby metallic or ceramic targets are sputtered reactively or non-reactively in a suitable sputtering atmosphere. Depending on the materials to be sputtered, planar or rotating tubular targets may be used.

Preferably, the base coating, and/or the silver-based functional coating, and/or the outer coating, and/or an intermediate coating are provided by physical vapour deposition.

In the context of the present invention the term "non-reactive sputtering" includes sputtering an oxidic target in a low oxygen atmosphere (that is with zero, or up to 10 % volume oxygen).

Layers based on an oxide of titanium and zirconium may be produced using reactive sputtering from a TiZr metallic target in Ar/O_2 atmosphere. Alternatively, such layers may be produced by co-sputtering a titanium metallic target and a zirconium metallic target in Ar/O_2 atmosphere. Alternatively, such layers may be produced by sputtering from a $Ti_xZr_yO_x$ ceramic target in an atmosphere with less than 10% oxygen.

Layers based on an oxide of Zn, Ti, ZnSn, InSn, Zr, Al, Sn and/or Si, and/or an (oxi)nitride of Si and/or of Al, may be deposited by non-reactive sputtering. Said layers may be sputtered from ceramic targets.

Layers based on an oxide of Zn, Ti, ZnSn, InSn, Zr, Al, Sn and/or Si, and/or an (oxi)nitride of Si and/or of Al, may also be deposited by reactive sputtering. Said layers may be sputtered from one or more metal targets.

Layers may be provided to their total final thickness in a single coating pass. Alternatively, multiple coating passes using the same coating chemistry may be used to provide a single

layer of final thickness. As used herein, sublayers of substantially the same composition provided by multiple passes are considered together as being a single layer with a thickness equal to the sum of the thicknesses of the sublayers.

To minimize any light absorption in the coating and to reduce the light transmittance decrease during heat treatment where this is not desired, all individual layers of the dielectric coatings are preferably deposited with an essentially stoichiometric composition. In particular, the coating process is preferably carried out by setting up suitable coating conditions such that any oxygen (or nitrogen) deficit of any oxide (or nitride) layer of the coating is kept low, to achieve a high stability of the light transmittance and colour of the coated glass panes during heat treatment. However, barrier coatings, especially those in direct contact with a silver-based functional coating, are deposited as metals or sub-stoichiometric, to allow them to perform their essential barrier task.

Preferably, the coated pane is laminated after bending to provide a laminated vehicular glazing. Laminated glazings are required for some vehicular apertures, especially windscreens.

Preferably, the step of laminating the coated pane comprises the steps of:
i) providing an arrangement comprising the coated glass pane, a further glass pane, and an interlayer between the coated glass pane and the further glass pane; and
ii) submitting the arrangement to a lamination process, preferably in an autoclave.

According to a third aspect of the present invention, there is provided a heating apparatus comprising a vehicular glazing according to the first aspect or manufactured according to the second aspect, wherein the heating apparatus further comprises an electrical supply in electrical connection with the coating sequence. The inventors have found that incorporating the vehicular glazing of the first aspect or manufactured according to the second aspect into a heating apparatus provides a heating apparatus of improved performance.

According to one embodiment said heating apparatus is provided, wherein:
the electrical supply is suitable for supplying electrical energy, and wherein the electrical supply uses a voltage of between 8 and 20 V, preferably 14V; and
the coating sequence comprises three or more silver-based functional coatings, preferably exactly three or exactly four silver-based functional coatings. The inventors have found that three or more silver-based functional coatings, preferably exactly three or exactly four silver-

based functional coatings, in the coating sequence allows for a vehicular glazing that provides the desired heating power density with such electrical supplies for effective demisting performance.

According to an alternative embodiment said heating apparatus is provided, wherein:
the electrical supply is suitable for supplying electrical energy, and wherein the electrical supply uses a voltage of between 40 and 60 V, preferably 48V; and
the coating sequence comprises two or more silver-based functional coatings, preferably exactly two silver-based functional coatings. The inventors have found that two or more silver-based functional coatings, preferably exactly two silver-based functional coatings, in the coating sequence allows for a vehicular glazing that provides the desired heating power density with such electrical supplies for effective demisting performance.
the coating sequence comprises two or more silver-based functional coatings, preferably exactly two silver-based functional coatings.

Optional or advantageous features of the first or second aspects of the present invention may be combined with the third aspect of the present invention in any combination, and vice versa.

According to a fourth aspect of the present invention there is provided a vehicle comprising a vehicular glazing according to the first aspect or manufactured according to the second aspect, or a heating apparatus according to the third aspect. The inventors have found that vehicles comprising such are more energy efficient, and have improved visibility due to excellent heating of the vehicular glazing.

Optional or advantageous features of the first, second or third aspects of the present invention may be combined with the fourth aspect of the present invention in any combination, and vice versa.

Embodiments of the present invention will now be described herein, by way of the non-limiting examples and with reference to Figures 1 to 9, in which:
Figure 1 illustrates a vehicular glazing according to a first embodiment of the present invention;
Figure 2 illustrates a schematic cross-sectional view of the coated glass pane of the vehicular glazing according to a first embodiment of the present invention;

Figure 3 illustrates a schematic cross-sectional view of an alternative vehicular glazing according to a second embodiment of the present invention, wherein the vehicular glazing is a laminated vehicular glazing;

Figures 4 to 9 provide example and comparative example coating sequences;

Figure 10 depicts the effect of increasing average wetting layer thickness on glazing properties; and

Figure 11 depicts the effect of increasing minimum wetting layer thickness on glazing properties.

Figure 1 illustrates a vehicular glazing 100 according to a first embodiment of the present invention. The vehicular glazing 100 comprises a coated pane 101 comprising a substrate and a coating sequence – not shown. While not shown, the vehicular glazing may comprise busbars and connectors suitable for electrification of the coating sequence as is known to those skilled in the art. The vehicular glazing 100 of Figure 1 is shaped to be suitable for an aperture of a vehicle, in particular as a windscreen.

Figure 2 illustrates a schematic cross-sectional view of the coated pane 101 of the vehicular glazing according to a first embodiment of the present invention. The coated glass pane 101 comprises a substrate 1 and a coating sequence 2. The coating sequence 2 comprises, in order from the substrate:

a base coating 3 comprising a wetting layer 33;

a first silver-based functional coating 4;

a first intermediate coating 5 comprising a barrier layer 51, at least one dielectric layer 52, and a wetting layer 53;

a second silver-based functional coating 6; and

an outer coating 7 comprising a barrier layer 71 and at least one dielectric layer 72, wherein: each wetting layer is from 10 to 150 nm in thickness. The embodiment of Figure 2 further comprises an outer protective layer 74 in the outer coating.

The embodiment of Figure 2 further comprises, between the second silver-based functional coating 6 and the outer coating 7:

a second intermediate coating 9 comprising a barrier layer 91, at least one dielectric layer 92, and a wetting layer 93; and

a third silver-based functional coating 8.

Figure 3 illustrates a schematic cross-sectional view of an alternative vehicular glazing according to a second embodiment of the present invention, wherein the vehicular glazing is a laminated vehicular glazing 200. The laminated vehicular glazing 200 comprises a coated pane 201 which is the same as the coated pane 101 of the embodiment of figure 2, an interlayer 202, and a further pane 203. The coated pane 201 comprises a coating sequence – not shown. The coating sequence is adjacent to the interlayer 202.

Example embodiments of the present invention will now be described herein, by way of example only.

Coated panes with coating sequences according to the invention were prepared and compared to comparative examples. The layers of the examples were deposited according to the below deposition parameters as shown in Table 1. Target compositions are provided in weight percentages unless otherwise indicated. Atmosphere compositions are provided in volume percentages based on flow rates unless otherwise indicated. The coating plant was a "Von Ardenne GC 120 V/CSE" equipped with 3400 cm2 WSM and SDM magnetrons connected to DC and MF Power supplies, using AC and/or DC magnetron (or pulsed DC) sputtering devices, medium-frequency sputtering being applied where appropriate. DC supplies were used when sputtering in pure Ar or substoichiometric barriers.

Layer	Target (wt%)	Atmosphere (vol%)	Power
SiNx	Si (90), Al (10)	Ar (62), N_2 (38)	15 kW
ZnSnOx	Zn (50), Sn (50)	Ar (42), O_2 (58)	10 kW
ZnO:Al	Zn (98), Al (2)	Ar (42), O_2 (58)	10 kW
Ag	Ag	Ar (100)	2 kW
NiCrOx	Ni (50), Cr (50)	Ar (93), O_2 (7)	2 kW
AZO	ZnO_2 (98), Al_2O_3 (2)	Ar (95), O_2 (5)	4 kW
AlNx	Al (100)	Ar (64), N_2 (36)	25 kW

Table 1

Silver-based functional coatings consisting of single silver layers were produced from silver targets in an Ar sputter atmosphere without any added oxygen and at a partial pressure of residual oxygen below 10^{-5} mbar. However, alternative silver-based functional coatings, such as doped silver layers, or silver multi-layers, may be employed.

Example and comparative example coating sequences are shown in Figures 4 to 9. For each comparative example and example coating sequence coated panes with 4 mm float glass substrate (light transmittance in the region of 90%) and 2.1 mm float glass substrate (light transmittance in the region of 90%) were produced.

Following preparation of the coated panes, the 4 mm coated panes were heat treated at 650 °C for 5 minutes, and then assessed for durability by oil rub (50), oil rub (500) and mini-brush tests, and assessed for heat-treatability by hazescan.

Tvis %: Light Transmittance – The values stated for the percentage (%) light transmittance of the coated glass panes as deposited on 4 mm float glass without lamination were derived from measurements using illuminant A, for a 2 degree observer across wavelengths ranging from 380 to 780 nm. For laminated vehicular glazings intended to be automotive windscreens, it is necessary that the visible light transmittance is in excess of 70%. Preferably, a laminated vehicular glazing according to the present invention has a visible light transmission of 70% or more. When considering the transmission of monolithic panes, it is sufficient that visible light transmission is of 65% or more, as when constructed as a laminate light transmission may increase to the required level, due to refractive index matching with the polymer interlayer.

Rs Ω/□ HT: Sheet Resistance – Sheet resistance measurements were made, following heat treatment, using a NAGY SRM 12. This device utilises an inductor to generate eddy currents in a 100mm x 100mm coated sample. This produces a measurable energy loss in a parallel pick up coil, the magnitude of which is related to the resistivity of the sample. With this method the sheet resistance can be calculated, and is provided in Ω/□. In general, the sheet resistance should be low to provide improved energy efficiency. In the present invention, the sheet resistance of the coating following heat treatment is preferably less than 1.5, more preferably less than 1.2 Ω/□.

Hazescan – A haze scoring system was applied to each of the examples and comparative examples, wherein the haze was measured following heat treatment. The quality assessment evaluation system described hereinafter was also used to more clearly distinguish the visual quality of coatings under bright light conditions; properties that are not fully reflected by standard haze values measured in accordance with ASTM D 1003. The evaluation system considers the effects of scattered reflected light in a tighter cone angle than conventional haze measurements corresponding to the human perception of where the coating is damaged or

imperfect. This assessment analyses the light levels in images of heat treated samples taken using fixed lighting conditions and geometries.

To generate the images used to calculate hazescan values, samples are placed inside a black box, 30 cm away from the camera lens. Samples are illuminated using a standard 1200 lumen light with a brightness between 2400 and 2800 Lux, as measured at the samples position. The sample is then photographed using a standard aperture size and exposure length of f5.6 and 1 second with focal length of 105 mm and ISO 400. The greyscale of each pixel in the resulting image is then recorded, with a value of 0 representing black and 255 representing white. Statistical analysis of these values is undertaken to give an overall assessment of the haze of the sample, referred to herein as the hazescan value. The lower the hazescan value recorded, the more superior the results. In general, a hazescan value of less than 90, preferably less than 80 and even more preferably less than 70 is achieved. In some specialist applications, where clarity is prioritised, a hazescan value of less than 60 is achieved.

Rs Ω/□ HT-L: Sheet Resistance - Sheet resistance measurements were made, following heat treatment and lamination, using a Suragus EddyCus® TF Portable 1010. This device utilises an inductor to generate eddy currents in a 300mm x 300mm coated sample. This produces a measurable magnetic field, the magnitude of which is related to the resistivity of the sample. With this method the sheet resistance can be calculated, and is provided in Ω/□. In general, the sheet resistance should be low to provide improved energy efficiency. In the present invention, the sheet resistance of the coating following lamination is preferably less than 1.5, more preferably less than 1.2 Ω/□.

Pummel - Laminated glass panes are stored in a freezer (-20±2 °C) for a minimum of 4 hours, then are hammered with a 500 g ball-pein hammer on the outer surface of the glass pane not carrying the coating to produce glass crumble over the surface, then the pane thawed for at least an hour at which point the quantity of broken glass fragments from the glass pane carrying the coating still adhering to the polyvinyl butyral film is assessed. If no broken glass adheres to the polyvinyl butyral film, the pummel value is zero; if the polyvinyl butyral film is completely covered with glass crumble, the pummel value is ten. In order to comply with the safety properties, the pummel value must be between 3 and 7, pummel value below 3 is unlikely to adequately protect vehicle occupants from collisions, while a pummel value above 7 more likely to cause pedestrian or occupant injury in the event that the pedestrian or

occupant impacts the glazing. Preferably, pummel is in the range 4 to 6, as this range represents an excellent compromise between occupant protection and impact safety.

While pummel is a suitable test for measuring delamination, other tests may be required by regulatory bodies. For example, 200g Dart, 227g Ball, 2260g ball, Headform, Mean Break Height may be used. However, a pummel pass is a good indication that other tests will be passed.

227 g Ball - Laminated glass pane samples 305±5 mm square are stored in a temperature controlled environment for at least 4 hours, then a 227 g ball dropped from a specified height.

Test temp. °C	Drop Height
40±2	9.00
-20±2	8.50
25±4	9.14

A sample is deemed to have passed provided the ball does not pass through the sample, the sample does not break into large pieces, and weight of fragments detached from non-impacted side is <12g, there is no interlayer tear. 80% of samples (n=10) must pass each test. Preferably, laminated vehicular glazings according to the invention do not allow a 227g ball to pass through when dropped from 9.00 m, 8.50 m, or 9.14 m, when the glazing is at a temperature of 40±2, -20±2, and 25±4 °C, respectively.

Mean Break Height - Laminated glass pane samples (n=12) 305±5 mm square are stored in a temperature controlled environment (23±2 °C) for at least 4 hours, then a 2260 g ball dropped from increasing heights. A sample passes, unless the ball passes through the sample within 5 seconds. The mean break height, i.e. the height at which 50% of theoretical samples will break, is calculated. The test is passed if the mean break height is greater than 5.0 m. Preferably, a laminated vehicular glazing according to the invention has a mean break height with a 2260 g ball of greater than 5.0 m, more preferably greater than 5.5m.

200g Dart - Laminated glass pane samples (n=10) 305±5 mm square are stored in a temperature controlled environment (25±4 °C) for at least 4 hours, then a 200 g dart dropped from 9.14 m. A sample passes, unless the dart passes through the sample and no delamination occurs greater than 38 mm from a crack. The test is passed if all samples pass, and no more

than one sample breaks into large pieces. Preferably, a laminated vehicular glazing according to the invention does not allow a 200 g dart dropped from 9.14 m to pass through.

Headform - Laminated glass vehicular glazings (n=4) are stored in a temperature controlled environment (23±2 °C) for at least 4 hours, then a 10±0.2 kg headform dropped from 1.50 m. A glazing passes, unless there is: exposed interlayer on the impact side >20 mm^2; interlayer tear >35 mm; or delamination greater than 4 mm within 60 mm of impact point. The test is passed if all glazings pass. Preferably, a laminated vehicular glazing according to the invention, when impacted with a 10 kg headform, has <20mm^2 exposed interlayer on the impacted side.

Heat treated coated monolithic glass panes are suitable for use as monolithic vehicle glazings, such as sidelights, when adapted therefore, for example by shaping.

2.1 mm coated panes were heat treated to at least 500 °C for 5 minutes to simulate a bending process, then the coated panes were laminated by forming a sandwich of the coated glass pane, PVB sheet (0.8 mm), and a further glass pane (2.1 mm float soda-lime silica). This arrangement is processed by exposure to a vacuum to remove moisture and then formed into a laminated pane in an autoclave at a pressure of 11 bar and a temperature of 125 °C for 40 minutes. Thereafter, the light transmission, sheet resistance and pummel of the laminated coated panes was measured.

The Tvis %: Light Transmittance – The values stated for the percentage (%) light transmittance of the coated glass panes are suitable for use as laminated applications where toughened panes are required. In particular, hazescan of the examples according to present invention measured following heat treatment was remarkably low, in some cases less than 50.

Minibrush HT – Durability - A wetted Mink-Bürsten TEB-309969 31 mm diameter polypropylene, 10 mm fibre height, 4 rows of fibres brush is passed over the coating, using a Sheen Instruments Ltd Wet abrasion scrub tester 903. The samples are placed on the equipment with coating uppermost and fixed using clamps. An approximately 2.5 cm diameter sized drop of water is placed onto the sample, directly below the brush head. The brush is placed on the glass and rubbed back and forth across the sample surface for 500 strokes. When mounted on the arm, the combined weight of the brush and sliding part of the arm

(total load on sample) is 209 g. The samples are examined for scratches and are compared to images from reference samples to be graded with a score from 0 to 4, a lower score is better. A score of 0 can be given for no discernible wear. A score of 1 or 2 is a pass and a score of 3 or 4 is a fail.

Oil rub HT – Durability - An oil soaked felt pad is passed over the coating, under a load of 0.9 kg, using a Sheen Instruments Ltd Wet abrasion scrub tester 903. The samples are placed on the equipment with coating uppermost and fixed using clamps. A felt square (1.2cm square) cut from Erichsen felt strips (DIN 68 861) is soaked in Immersion Oil for Microscopy from Merck Chemicals Ltd. This is placed on the glass and rubbed back and forth across the sample surface for 50, or 500, strokes. The samples are examined for scratches and are compared to images from reference samples to be graded on the Oil Rub Test Delamination Scale from 0 to 9, a lower score is better. If all of the coating is removed the sample score is 10.

However, a pummel pass is a good indication that other tests will be passed.

Monolithic glass panes are suitable for use as monolithic vehicle glazings, such as sidelights, when adapted therefore, for example by shaping.

The results of assessments of a first series of monolithic coated panes with examples and comparative example coating sequences following heat treatment are shown in table 2.

Example	Tvis %	Rs Ω/□ HT	Hazescan	Mini-brush	Oil 50	Oil 500	Pummel
E1-1 (C)	79.0	0.84	40	2.5	0	3	1.5
E1-2 (C)	73.0	0.95	98	3.5	5	9	0
E1-3 (C)	57.8	1.70	227	0.5	0	0	7
E1-4	69.3	1.09	118	3.5	5	8	3
E1-5	60.0	1.15	88	0.75	0	1	4.5
E1-6	58.5	1.50	201	0.5	1	3	4.5

Table 2

E1-1 (Comparative): E1-1 is typical triple silver coating sequence, with wetting layers less than 10 nm in thickness comprising zinc oxide doped with aluminium, and is heat treatable as shown by the excellent low hazescan value of 40. In addition, E1-1 has desirable transparency and sheet resistance measurements. However, this coating sequence has poor mechanical

durability, as indicated by minibrush of 2.5 and pummel of 1.5. Such durability means that the coating sequence of E1-1, when incorporated in a laminated vehicular glazing, would be expected to cause failure of the laminated glazing during regulated testing.

E1-2 (Comparative) : Considering the improvements in durability obtained by the coating sequence of E1-1, and wishing to provide a coating sequence suitable for a vehicular glazing that is durable, heat-treatable, heatable with electrical supply less than 100V, and energy efficient, the inventors adapted E1-1 to provide E1-2 by incorporating an oxide of zinc wetting layer from 10 to 150 nm in thickness as the base coating. As such, in this comparative example the oxide of zinc wetting layer made up the base coating. In this example, all the wetting layers are ZnOx doped with aluminium. E1-2 has worse light transmission and sheet resistance, and significantly worse haze. However, the durability of E1-2 is improved compared to E1-1.

E1-3 (Comparative): E1-3 is an alternative coating sequence adapted from E1-1, in that Al:ZnO wetting layers of the base and intermediate coatings are of increased thickness and the ZnSnOx and AlNx of the intermediate coatings are removed. E1-3 exhibits excellent durability, with oil rub (50) and oil rub (500) of 0, mini-brush 0.5, such that it forms a benchmark for these parameters. When laminated, a pummel score of 7 is achieved. Such properties mean that a pane carrying the coating sequence of E1-3 would be expected to be processed in a similar manner to an uncoated pane. However, E1-3 is a non-heat treatable coating sequence, as shown by a poor hazescan value in excess of 150. In addition, the sheet resistance of the coating sequence is in excess of 1.5 Ω/□, making it unsuitable for heating with energy sources of less than 100 V. The sheet resistance also indicates that the energy efficiency of such a glazing could be improved.

E1-4: E1-2 was adapted to provide E1-4 by incorporating oxide of zinc wetting layers from 20 to 150 nm in thickness in each dielectric coating of the coating sequence. To maintain the overall thickness of the intermediate dielectric coatings AlNx layers were reduced in thickness and ZnSnOx layers were removed. As such, this example has a first dielectric layer of zinc oxide and a second dielectric layer of aluminium nitride in the intermediate coating. Surprisingly, transparency was maintained, sheet resistance was only slightly worsened and still within requirements, and durability and pummel improved. Such durability means that the coating sequence of E1-4, when incorporated in a laminated vehicular glazing, might be

expected to pass regulated testing. However, a further increase in durability was sought, and haze indicated that E1-4 was less heat treatable than desired.

E1-5: E1-1 was adapted to provide E1-5 by incorporating oxide of zinc wetting layers in the intermediate dielectric coatings of increased thickness. To maintain the overall thickness of the intermediate dielectric coating AlNx layers were reduced in thickness. Transparency reduced, and sheet resistance increased, haze worsened, and durability significantly improved. E1-5 surprisingly is almost as durable as benchmark coating sequence E1-3, and has pummel score within requirements. Such durability means that the coating sequence of E1-5, when incorporated in a laminated vehicular glazing, might be expected to pass regulated testing. Thereafter, the inventors considered further modifications to improve the coating sequence yet further.

E1-6: E1-5 was adapted to provide E1-6 by incorporating oxide of zinc wetting layers in the intermediate dielectric coatings of increased thickness. To maintain the overall thickness of the intermediate dielectric coating AlNx layers were removed. Transparency reduced, and sheet resistance was increased, haze significantly increased, but durability maintained.

The inventors considered alternative zinc oxide compositions for wetting layers. The results of assessments of a second series of monolithic coated panes with examples and comparative example coating sequences following heat treatment are shown in table 3.

Example	Tvis %	Rs Ω/□	Hazescan	Mini-brush	Oil 50	Oil 500	Pummel
E2-1	76.5	1.15	45	2.5	4	9	0
E2-2	71.1	1.42	194	1	0	0	5
E2-3	76.6	1.10	37	1.5	0	9	0
E2-4	73.4	1.08	67	2	0	2	0
E2-5	67.2	1.12	48	0.5	0	0	5
E2-6	67.4	1.41	118	0	0	0	5.5
E2-7	64.9	1.15	107	3	0	1	
E2-8	57.4	1.43	137	3.5	9	10	
E2-9	66.1	1.18	158	3.5	9	9	
E2-10	72.6	1.10	43	0.5	0	0	
E2-11	60.2	1.22	38	1	2	8	
E2-12	68.6	1.14	62	2	0	0.5	
E2-13	68.6	1.08	42	1	0	1	
E2-14	75.7	1.10	61	2	0	0	

E2-15	67.6	1.12	141	1	0	0	
E2-16	66.3	1.00	115	2	0	0	
E2-17	72.3	1.20	65	0	0	2	

Table 3

E2-1: E2-1 is a triple silver coating sequence, wherein the zinc oxide doped with aluminium wetting layers have been replaced with ZnSnOx wetting layers, and is heat treatable as shown by the excellent low hazescan value of 45. In addition, E2-1 has desirable transparency and sheet resistance measurements. However, this coating sequence has poor mechanical durability, as indicated by oil rub 500 of 9, oil rub 50 of 4, minibrush of 2.5 and pummel of 0. Such durability means that the coating sequence of E2-1, when incorporated in a laminated vehicular glazing, would be expected to cause failure of the laminated glazing during regulated testing.

E2-2: E2-2 is an alternative coating sequence adapted from E2-1, in that no barrier layers are present, and the AlNx of the intermediate coatings are removed. E2-2 exhibits excellent durability, with oil rub (50) and oil rub (500) of 0, mini-brush 1 and pummel 5. Such durability means that the coating sequence of E2-2, when incorporated in a laminated vehicular glazing, would be expected to meet the regulatory requirements. However, E2-2 is a non-heat treatable coating sequence, as shown by a poor hazescan value in excess of 150. In addition, the sheet resistance of the coating sequence following lamination is in excess of 1.4 Ω/□, making it unsuitable for heating with an electrical supply of less than 40 V. The sheet resistance also indicates that the energy efficiency could be improved.

E2-3: The inventors adapted E2-1 to provide E2-3 by incorporating an oxide of zinc wetting layer of increased thickness as the base coating. Other wetting layers are less than 20 nm. In this example, all the wetting layers are ZnSnOx. As such, in this example the oxide of zinc wetting layer made up the base coating. Surprisingly, E2-3 maintains the desirable transparency of E2-1, but has both improved haze and sheet resistance, and is therefore a particularly good heat-treatable coating sequence. Furthermore, E2-3 exhibits improved durability according to oil rub (50) and mini-brush when compared to E2-1. However, it would be desirable to further improve oil rub (500), and pummel, as a laminated vehicular glazing incorporating the coating sequence of E2-3 would still likely cause the failure of a laminated glazing during regulated testing.

E2-4: E2-3 was adapted to provide E2-4 by incorporating oxide of zinc comprising tin, ZSO, wetting layers in each intermediate layer of increased thickness in each dielectric coating of the coating sequence. To maintain the overall thickness of the intermediate dielectric coatings AlNx layers were reduced in thickness. Surprisingly, transparency was maintained, sheet resistance improved yet further, and durability significantly improved considering oil rub (50), oil rub (500). However, a further increase in durability was sought.

E2-5: E2-4 was adapted to provide E2-5 by incorporating oxide of zinc comprising tin, ZSO, wetting layers in the intermediate dielectric coatings of increased thickness. To maintain the overall thickness of the intermediate dielectric coating AlNx layers were reduced in thickness. Transparency and sheet resistance were maintained, haze was reduced to almost match E1-1, and durability significantly improved, as indicated by oil rub (50) 0, oil rub (500) 0, and crucially mini-brush 0.5 and pummel of 5. Such durability means that the coating sequence of E2-5, when incorporated in a laminated vehicular glazing, might be expected to pass regulated testing. Thereafter, the inventors considered further modifications to improve the coating sequence yet further.

E2-6: E2-5 was adapted to provide E2-6 by removing the aluminium nitride layers of the intermediate coatings and further increasing the thickness of the oxide of zinc wetting layers of the intermediate dielectric coatings. Durability was yet further improved. However, sheet resistance increased beyond the required level, and haze was significantly increased. The coating sequence may be beneficial for some vehicular glazings, such as vehicle side-lights, but is unlikely to be suitable for a laminated windscreen. This indicates that it is desirable that the intermediate coatings each comprise a first dielectric layer and a second dielectric layer between the barrier layer and the wetting layer. Preferably, the first dielectric layer is a zinc oxide and the second dielectric layer is aluminium nitride.

E2-7: E2-5 was adapted to provide E2-7, wherein the base coating wetting layer of zinc oxide was deposited using non-reactive sputtering of a ceramic target at a power of 10 kW, rather than by reactive sputtering of ZSO in E2-5. Hazescan was considerably increased, and durability reduced, indicating that it is preferable to deposit wetting layers using a reactive sputtering method.

E2-8: E2-5 was adapted to provide E2-8, wherein zinc oxide dielectric layers were removed from the intermediate coatings. Hazescan was considerably increased to 137 and durability

worsened as indicated by oil rub (50) 9, oil rub (500) 10, and mini-brush 3.5, and sheet resistance increased, indicating that it is preferable to maintain zinc oxide dielectric layers in the intermediate coatings.

E2-9: E2-5 was adapted to provide E2-9, wherein aluminium nitride dielectric layers of intermediate coatings were replaced with silicon nitride layers of equivalent thickness. Hazescan was considerably increased to 158 and durability worsened as indicated by oil rub (50) 9, oil rub (500) 9, and mini-brush 3.5, indicating that it is preferable to use aluminium nitride dielectric layers in the intermediate coatings.

E2-10: E2-5 was adapted to provide E2-10, wherein the thickness of the base coating wetting layer was further increased from 37.6 to 59.2 nm. This provides a coating sequence of more neutral reflection when used as a monolithic pane which is not laminated. E2-10 appears to be extremely durable, with mini-brush 0.5 and oil rub 50 and 500 of 0, heat-treatable with haze of 43, and excellent energy efficiency indicated by sheet resistance of 1.10 Ω/□. Therefore, such a coating sequence is of particular benefit for insulated vehicular glazings.

E2-11: E2-5 was adapted to provide E2-11, wherein a ZnSnOx layer of 8.5 nm in thickness was inserted between the first dielectric layer of zinc oxide and the second dielectric layer of aluminium nitride of the intermediate coatings. Durability and light transmission decreased, and sheet resistance increased. Therefore, preferably no ZnSnOx layer is provided between a first dielectric layer of zinc oxide and a second dielectric layer of aluminium nitride of the intermediate coatings. Preferably, each intermediate coating comprises a first dielectric layer of AZO in direct contact with a second dielectric layer of aluminium nitride.

E2-12: E2-5 was adapted to provide E2-12, wherein an ion blocking base layer of SiNx of thickness 11 nm was inserted into the base coating below the wetting layer, without modifying the base coating wetting layer thickness. Durability, Haze, and sheet resistance were not improved by the inclusion of this layer. Therefore, it appears that it is beneficial that the wetting layer makes up a large proportion of the base coating and/or is in direct contact with the substrate.

E2-13: E2-5 was adapted to provide E2-13, wherein the wetting layer of the base coating was increased in thickness. Sheet resistance and haze were slightly improved, and durability

maintained at a high level. As such, it is shown that the wetting layer of the base coating may be modified to tune optical properties without compromising durability and sheet resistance.

E2-14: E2-5 was adapted to provide E2-14, wherein the base coating wetting layer of zinc oxide ZSO was reactively sputtered at a power of 4 kW, instead of 10 kW as in E2-5. Sheet resistance was maintained, but haze and durability worsened, as indicated by hazescan and minibrush. Therefore, the use of higher powers when reactively depositing a wetting layer of a zinc oxide from a metal target is preferred. Preferably, the wetting layers are deposited from a metallic target using a power of at least 20 W per linear cm of sputtering target, preferably at least 25 W per linear cm of sputtering target.

E2-15: E2-5 was adapted to produce E2-15, by removing the outermost layer of an oxide of zinc and tin. Sheet resistance was only slightly increased, and durability very slightly worsened. However, haze was increased. Therefore, preferably an oxygen blocking layer, such as an oxide of zinc and tin, is above the outermost silver.

E2-16: E2-5 was adapted to produce E2-16 by replacing NiCrOx barrier layers with an alternative barrier layer, comprising a first sub-layer of AZO and a second sub-layer of ZnSnOx. Sheet resistance was improved, but haze increased, and durability slightly worsened. However, haze of 115 is still suitable for many applications where optical clarity is not of primary importance. E2-16 indicates that alternative barrier layers may be used, and an alternative barrier layer comprising a first sub-layer of AZO and a second sub-layer of ZnSnOx is particularly preferred when low sheet resistance is desired in preference to optical clarity.

E2-17: E2-5 was adapted to produce E2-17 by altering the layer thicknesses to provide an alternative stack of alternative optical properties, suitable for use in a laminated glazing. This stack provides a good balance between sheet resistance, light transmission, and durability.

The inventors considered alternative coating sequences. The results of assessments of a third series of monolithic coated panes with examples and comparative example coating sequences following heat treatment are shown in Table 4.

Example	Tvis %	Rs Ω/□	Hazescan	Mini-brush	Oil 50	Oil 500	Pummel

E3-1	69.61	0.986	116	1			
E3-2	73.21	0.896	58	0.5	0	0	4.5

Table 4

E3-1: E2-17 was adapted to have a wetting layer in the base coating of a zinc oxide comprising tin, a dual wetting layer in the first intermediate coating of a first sublayer of zinc oxide comprising greater than 70 atomic % zinc based on metals, and a dual wetting layer in the second intermediate coating of a sublayer of a zinc oxide comprising greater than 70 atomic % zinc based on metals, with a the first and second intermediate coatings each comprising a second dual wetting layer sublayer of an oxide of zinc and tin, and wherein all wetting layers were greater than 25 nm. This combination provides adequate sheet resistance, but it is desirable that haze is improved.

E3-2: E3-1 was adapted such that each intermediate coating comprised a first dielectric layer of AZO, a second dielectric layer of aluminium nitride. This provided a coating that is heat-treatable, as shown by a low hazescan score of 58, has excellent sheet resistance, and is also extremely durable, as indicated by oil rub, minibrush and pummel.

Therefore, the inventors have found that particularly beneficial coating sequences may be formed with dual wetting layers comprising a first sublayer of an oxide of zinc comprising greater than 70% zinc based on metals and a second sublayer of an oxide of zinc and tin.

The inventors considered alternative coating sequences comprising four or more silver-based functional layers. The results of assessments of a fourth series of monolithic coated panes with examples and comparative example coating sequences following heat treatment are shown in Table 5.

Example	Tvis %	Rs Ω/□	Hazescan	Mini-brush	Oil 50	Oil 500	Pummel
E4-1	55.3	1.141	154	0			5.5
E4-2	58.9	1.315	156	0.5	0	1	5
E4-3	56.2	1.103	169	0.5	0	0	
E4-4	72	0.914	102	0	0	0	0
E4-5	68.6	0.843	106	1			0.5

E4-6	70.5	0.807	44	0	0	0	3
E4-1	55.3	1.141	154	0			5.5

Table 5

E4-1, E4-2: Coating sequences comprising four silver layers were prepared, comprising wetting layers of an oxide of zinc and tin and intermediate coatings comprising a first dielectric layer of AZO, without intermediate coating dielectric layers of aluminium nitride. Sheet resistance and haze were higher than desired, but the coatings showed excellent durability.

E4-3: A further coating sequence based on E4-1 was prepared, wherein intermediate coatings each comprise a dual wetting layer comprising a first oxide of zinc sublayer and a second oxide of zinc sublayer. Durability was maintained and sheet resistance slightly improved, but haze was not improved.

E4-4, E4-5: Further coating sequences based E4-1 was prepared, where nitride of aluminium layers of intermediate coatings were inserted between the first dielectric layers of AZO in the intermediate coatings and the wetting layer. Sheet resistance and haze were improved, but durability significantly affected.

E4-6: A further coating sequence based on E4-1 was prepared where nitride of aluminium layers of intermediate coatings were inserted between the first dielectric layers of AZO in the intermediate coatings and the wetting layer, and wherein intermediate coatings each comprise a dual wetting layer comprising a first oxide of zinc sublayer and a second oxide of zinc sublayer. Remarkably, sheet resistance and haze are improved considerably, and durability is also maintained.

The influence of wetting layer thickness was investigated using the sequence:
Glass / w_1 / Ag (12.5) / NiCrOx (0.3) / AZO (6) / AlNx (8.5) / w_2 / Ag (13.2) / NiCrOx (0.3) / AZO (6) / AlNx (8.5) / w_3 / Ag (13.2) / NiCrOx (0.3) / AZO (6) / AlNx (40.9) / ZnSnOx (11), where physical layer thicknesses of the layers are provided in parentheses, each wetting layer w was ZnSnOx sputtered from a metallic target as in, for example, E2-1.

Table 6 shows the varying thicknesses of wetting layers, and tested properties.

	S1	S2	S3	S4

w_1 thickness / nm	43.1	37.6	59.2	59.2
w_2 thickness / nm	17.0	65.0	65.0	65.0
w_3 thickness / nm	19.0	54.5	54.5	62.9
Average wetting layer thickness / nm	26.4	52.4	59.6	62.4
Smallest wetting layer thickness / nm	17.0	37.6	54.5	59.2
Maximum Difference	26.1	27.4	10.5	5.8
Rs HT	1.11	1.12	1.10	1.10
Haze	42	48	43	43
mini-brush	2	0.5	0.5	0.5
oil 50	1	0	0	0
oil 500	8	0	0	0

Table 6

The influence of wetting layer thickness was investigated using the sequence: Glass / w_1 / Ag (13.5) / NiCrOx (0.3) / AZO (6) / AlNx (8.5) / w_2 / Ag (13.9) / NiCrOx (0.3) / AZO (6) / AlNx (8.5) / w_3 / Ag (10.6) / NiCrOx (0.3) / AZO (6) / AlNx (28.9) / ZnSnOx (9), where physical layer thicknesses of the layers are provided in parentheses, each wetting layer w was ZnSnOx sputtered from a metallic target as in, for example, E2-1.

Table 7 shows the varying thicknesses of wetting layers, and tested properties.

	S5	S6	S7	S8	S9
w_1 thickness / nm	41.2	10.3	20.3	10.3	20.3
w_2 thickness / nm	69.9	69.9	69.9	10.3	20.3
w_3 thickness / nm	60.3	60.3	60.3	10.3	20.3
Average wetting layer thickness / nm	57.1	46.8	50.2	10.3	20.3
Smallest wetting layer thickness / nm	41.2	10.3	20.3	10.3	20.3
Maximum Difference	28.7	59.6	49.6	0	0
Rs HT	1.14	1.34	1.37	1.16	1.2
Haze	66	221	220	169	112
mini-brush	0.5	3.5	3.5	3	2.5
oil 50	0	6	5	5	0
oil 500	2	9	8	8	3

Table 7

As shown by the worsened haze and durability of S6 and S7 compared to S5, the base coating wetting layer is preferably greater than 25 nm and the maximum difference is less than 45 nm. This is confirmed by S8 and S9, wherein even with a lower maximum difference the smallest wetting layer is not sufficiently thick so provide the desired durability. In addition, S9

has improved durability compared to S7, indicating that simply increasing the thickness of the wetting layers is not always sufficient to arrive at excellent durability, but that a consideration of the maximum difference in thickness between the wetting layers is also important in some cases. This applies to wetting layers based on oxides of zincs, oxides of zinc and tin, and dual wetting layers comprising a sublayer of an oxide of zinc and a sublayer of an oxide of zinc and tin and discussed elsewhere.

Figure 10 depicts the effect of increasing wetting layer average thickness upon sheet resistance, hazescan, and durability measured by mini-brush and oil 500, linear trend lines are added.

From Figure 10 it can be seen that with an increase in average wetting layer thickness, durability increases considerably, as shown by a decreasing trend in both oil rub 500 and min-brush. Sheet resistance remains constant. Therefore, the increase in durability from increased average wetting layer thickness must be balanced against the optical requirements.. Therefore, preferably the average wetting layer thickness is from 30 nm to 100 nm, more preferably from 50 to 80 nm when considering optical and durability requirements.

Figure 11 depicts the effect of increasing minimum wetting layer thickness on the sheet resistance, hazescan, and durability measured by mini-brush and oil 500, linear trend lines are added. From Figure 11 it can be seen that with an increase in minimum wetting layer thickness, durability increases considerably, as shown by a decreasing trend in both oil rub 500 and min-brush. Therefore, the increase in durability from increased minimum wetting layer thickness must be balanced against the other requirements of energy efficiency, while also considering the optical requirements. Therefore, preferably the minimum wetting layer thickness is from 20 nm to 100 nm, preferably from 25 nm to 80 nm. Where durability is particularly important, preferably the minimum wetting layer thickness is from 30 nm to 75 nm.

Furthermore, the influence of maximum difference in thickness of wetting layer, calculated as the difference between the thickness of the thickest wetting layer and the thickness of the thinnest wetting layer, is indicated by the results of table 7. The maximum difference in thickness of wetting layer, calculated as the difference between the thickness of the thickest wetting layer and the thickness of the thinnest wetting layer, is preferably less than 50 nm, more preferably less than 40 nm, yet more preferably less than 30 nm. The inventors have

found that a coating sequence wherein the minimum wetting layer thickness is greater than 20 nm, more preferably greater than 25 nm, yet more preferably greater than 30 nm, and the maximum difference in thickness of wetting layer is less than 50 nm, more preferably less than 40 nm, yet more preferably less than 30 nm, provides particularly durable coatings.

In summary, it is particularly beneficial to provide a vehicular glazing comprising a coating sequence:

[ZnOx / Ag / barrier / at least one dielectric layer /]n;

Wherein each ZnOx layer is from 20 to 150 nm in thickness, preferably the at least one dielectric layer comprises a first dielectric layer and a second dielectric layer as discussed elsewhere herein, preferably the ZnOx layer is an oxide of zinc and tin or a dual wetting layer as discussed elsewhere herein.

Therefore, according to a fifth aspect of the present invention there is provided a vehicular glazing comprising a coated pane, the coated pane comprising a substate and a coating sequence, wherein the coating sequence comprises n progressions of layers, wherein each progression comprises in order from the substrate:

a wetting layer;

a silver-based functional coating;

a barrier layer; and

at least one dielectric layer, and wherein:

n is greater than or equal to 2, preferably greater than or equal to 3; and

each wetting layer is from 10 to 150 nm in thickness, preferably from 20 to 100 nm in thickness, and preferably the at least one dielectric layer comprises a first dielectric layer and a second dielectric layer as discussed elsewhere herein, and preferably each wetting layer comprises an oxide of zinc, preferably an oxide of zinc and tin, preferably an oxide of zinc and tin comprising from 60 to 70 atomic % zinc and from 30 to 40 atomic % tin based on metals. Alternatively, the wetting layers of this fifth aspect can include one or more dual wetting layers.

The progressions of layers do not overlap – that is, layers are not shared between two adjacent progressions of layers. For example, the dielectric layer of a first progression does not contain the wetting layer of a second progression. Preferably, each silver-based functional coating is in direct contact with the underlying wetting layer and the overlying barrier layer.

Optional features of the first to fourth aspects of the invention may be applied to the fifth aspect and vice versa.

The inventors have found that the combination of particular silver-based functional layer thickness pattern with a particular wetting layer thickness pattern provides beneficial optical properties while maintaining desirable mechanical properties, as shown by the examples.

Therefore, according to a sixth aspect of the present invention there is provided a vehicular glazing comprising a coated pane, the coated pane comprising a substate and a coating sequence, wherein the coating sequence comprises:

x silver-based functional coatings m_i, where i is numbered sequentially from the substrate and x is the total number of silver-based functional coatings in the coating sequence and is greater than or equal to 3; and

x+1 dielectric coatings d_j, where j is numbered sequentially from the substrate, wherein the dielectric coatings are positioned before and after each silver-based functional coating, and wherein:

each dielectric coating comprises a wetting layer w_j from 10 to 150 nm in thickness, each wetting layer taking the number of the containing dielectric layer;

the layer thickness of the silver-based functional coating closest to the substrate Gm_1 is greater than the layer thickness of the silver-based functional coating furthest from the substrate Gm_x, that is $Gm_1 > Gm_x$;

at least one, preferably each, silver-based functional coating between the silver-based functional coating closest to the substrate m_1 and the silver-based functional coating furthest from the substrate m_x has a layer thickness Gm_i greater than the layer thickness of the silver-based functional coating closest to the substrate Gm_1, that is $Gm_i > Gm_1 > Gm_x$ where $2 \leq i \leq m-1$;

the layer thickness of the wetting layer of the dielectric coating closest to the substrate Gw_1 is less than the layer thickness of the wetting layer furthest from the substrate Gw_{x+1}, that is $Gw_1 < Gw_{x+1}$;

at least one, preferably each, wetting layer of the dielectric coatings between the dielectric coating closest to the substrate d_1 and the dielectric coating furthest from the substrate d_{x+1} has a layer thickness Gw_j greater than the thickness of the wetting layer of the dielectric coating furthest from the substrate Gw_{x+1}, such that $Gw_j > Gw_{x+1} > Gw_1$ where $2 \leq j \leq x$.

The layer thicknesses G of this sixth aspect are physical layer thicknesses. The inventors have found that such an arrangement of silver-based functional layers and wetting layers provides a durable, low sheet resistance coating with high light transmission.

When the coating sequence comprises three silver based functional layers it is particularly beneficial that the silver-based functional coatings have the pattern $Gm_2 > Gm_1 > Gm_3$ where Gm_i is the physical layer thickness of the silver-based functional coating m_i, where i is the number of the silver-based functional layer m counted from the substrate and the wetting layers have the pattern $Gw_2 > Gw_3 > Gw_1$, where Gw_j is the physical layer thickness of the wetting layer w_j, where j is the number of the dielectric coating containing the wetting layer counted from the substrate.

When the coating sequence comprises four silver based functional layers it is particularly beneficial that the silver-based functional coatings have the pattern $Gm_2 > Gm_3 > Gm_1 > Gm_4$ where Gm_i is the physical layer thickness of the silver-based functional coating m_i, where i is the number of the silver-based functional layer m counted from the substrate.

As such, preferably the coating sequence comprises i silver-based functional layers, and $Gm_2 > Gm_3 > \ldots Gm_{i-1} > Gm_1 > Gm_i$, such that the outermost silver-based functional layer is the thinnest silver-based functional layer, the innermost silver-based functional layer is the second thinnest silver-based layer, and the thicknesses of the silver-based functional layers excluding the outermost and the innermost decrease with increasing distance from the substrate.

Optional features of the first to fifth aspects of the invention may be applied to the sixth aspect and vice versa.

The inventors have discovered that useful coating sequences comprising exactly one silver-based functional coating may be prepared.

As such, according to a further disclosure, there is provided a vehicular glazing comprising a coated pane, the coated pane comprising a substate and a coating sequence, wherein the coating sequence comprises, in order from the substrate:
a base coating comprising a wetting layer;
a silver-based functional coating; and
an outer coating comprising a barrier layer and at least one dielectric layer, wherein:

the wetting layer is from 10 to 150 nm in thickness; and
the coating sequence comprises exactly one silver-based functional coating.

According to this further disclosure, preferably the wetting layer is from 20 to 100 nm in thickness, more preferably from 30 to 80 nm in thickness.

According to this further disclosure, preferably the coating sequences comprises, more preferably consists of:
Glass / ZnOx / Ag / NiCrOx / AZO / AlNx / outermost layer,
wherein ZnOx may include Sn as discussed elsewhere herein.

Applicable optional features of the first to sixth aspects of the invention may be applied to this further disclosure.

Claims

1. A vehicular glazing comprising a coated pane, the coated pane comprising a substate and a coating sequence, wherein the coating sequence comprises, in order from the substrate:
a base coating comprising a wetting layer;
a first silver-based functional coating;
a first intermediate coating comprising a barrier layer, at least one dielectric layer, and a wetting layer;
a second silver-based functional coating; and
an outer coating comprising a barrier layer and at least one dielectric layer, wherein:
each wetting layer is from 10 to 150 nm in thickness.

2. A vehicular glazing according to claim 1, wherein the at least one dielectric layer of the first intermediate coating comprises an oxide of zinc and tin, a silicon nitride or oxynitride, an aluminium nitride or oxynitride, an oxide of zinc, an oxide of zirconium, an oxide of titanium, an oxide of zirconium and titanium $Zr_xTi_yO_z$, an oxide of silicon and/or aluminium, an oxide of zinc and tin with zirconium, preferably the at least one dielectric layer of each intermediate coating comprises one of these.

3. A vehicular glazing according to claim 1 or claim 2, wherein the first intermediate coating comprises a first dielectric layer and a second dielectric layer, preferably the first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, and the second dielectric layer comprising an aluminium nitride or oxynitride, preferably the first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, is from 1 to 10 nm in thickness and the second dielectric layer comprising an aluminium nitride or oxynitride is from 5 to 15 nm in thickness.

4. A vehicular glazing according to any preceding claim, wherein the coating sequence further comprises, between the second silver-based functional coating and the outer coating:
a second intermediate coating comprising a barrier layer, at least one dielectric layer, and a wetting layer; and
a third silver-based functional coating.

5. A vehicular glazing according to claim 4, wherein the at least one dielectric layer of the second intermediate coating comprises a silicon nitride or oxynitride, an aluminium nitride or oxynitride, an oxide of zinc doped with aluminium, or an oxide of tin and zinc.

6. A vehicular glazing according to claim 5, wherein the second intermediate coating comprises a first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, and a second dielectric layer comprising an aluminium nitride or oxynitride, preferably the first dielectric layer comprising an oxide of zinc, preferably doped with aluminium, is from 1 to 10 nm in thickness and the second dielectric layer comprising an aluminium nitride or oxynitride is from 5 to 15 nm in thickness.

7. A vehicular glazing according to any preceding claim, wherein each wetting layer comprises an oxide of zinc, preferably the oxide of zinc comprises at least 70 atomic % zinc based on metals or the oxide of zinc comprises from 20 to 80 atomic % zinc and from 20 to 80 atomic % tin based on metals.

8. A vehicular glazing according to any preceding claim, wherein each wetting layer is in direct contact with the overlying silver-based functional coating.

9. A vehicular glazing according to any preceding claim, wherein at least one and preferably each wetting layer makes up at least 20% of the physical thickness of the coating containing said wetting layer, preferably each wetting layer makes up at least 25% of the physical thickness of the coating containing said wetting layer.

10. A vehicular glazing according to any preceding claim, wherein the wetting layer of the base coating makes up at least 50% of the physical thickness of the base coating, preferably the wetting layer of the base coating makes up at least 75% of the physical thickness of the base coating, more preferably the wetting layer of the base coating makes up at least 90% of the physical thickness of the base coating, yet more preferably the wetting layer of the base coating makes up at least 95% of the physical thickness of the base coating, most preferably the base coating consists of the wetting layer.

11. A vehicular glazing according to any preceding claim, wherein each wetting layer is provided by reactive sputtering.

12. A vehicular glazing according to any preceding claim, wherein the base coating wetting layer and/or an intermediate coating wetting layer, preferably each wetting layer, has a thickness of from 19 to 140 nm, preferably from 30 to 120 nm, more preferably from 40 to 100 nm.

13. A vehicular glazing according to any preceding claim, wherein each barrier layer is in direct contact with the underlying silver-based functional coating and/or wherein each barrier layer comprises NiCrOx or TiOx, preferably each barrier layer comprises NiCrOx.

14. A vehicular glazing according to any preceding claim, wherein the coating sequence comprises a dual wetting layer comprising a first oxide of zinc sublayer and a second oxide of zinc sublayer in direct contact with the first oxide of zinc sublayer, wherein the first oxide of zinc sublayer is between the overlying silver-based functional layer and the second oxide of zinc sublayer.

15. A vehicular glazing according to any preceding claim, wherein each silver-based functional coating comprises a layer based on silver, preferably consists of a layer consisting of at least 95 atomic % silver.

16. A vehicular glazing according to any preceding claim, wherein the vehicular glazing is a laminated glazing comprising the coated pane, an interlayer, and a further pane bonded to the coated pane by the interlayer, preferably the interlayer is adjacent to the coating sequence.

17. A vehicular glazing according to any preceding claim, wherein the vehicular glazing is a windscreen, sidelight, rooflight, or backlight.

18. A vehicular glazing according to any preceding claim, wherein the vehicular glazing comprises a bent pane, preferably the bent pane is bent using a press-bending method.

19. A method of manufacturing a vehicular glazing according to any preceding claim, comprising the steps of:

i) providing a substrate;

ii) depositing a coating sequence on the substrate to provide a coated pane;

iii) heating the substrate to at least 550 °C to provide a heat-treated substrate; and

iv) bending the heat-treated substrate to provide a vehicular glazing.

20. A method according to claim 19, wherein the coated pane is laminated after bending to provide a laminated vehicular glazing.

21. A heating apparatus comprising a vehicular glazing according to any of claims 1 to 18, or manufactured according to claims 19 or 20, wherein the heating apparatus further comprises an electrical supply in electrical connection with the coating sequence.

22. A heating apparatus according to claim 21 wherein:
the electrical supply is suitable for supplying electrical energy, wherein the electrical supply uses a voltage of between 8 and 20 V, preferably 14V; and
the coating sequence comprises three or more silver-based functional coatings, preferably exactly three silver-based functional coatings layers.

23. A heating apparatus according to claim 21 wherein:
the electrical supply is suitable for supplying electrical energy, wherein the electrical supply uses a voltage of between 40 and 60 V, preferably 48V; and
the coating sequence comprises two or more silver-based functional coatings, preferably exactly two silver-based functional coatings.

24. A heating apparatus according to any of claims 21 to 23, wherein the vehicular glazing is a laminated automotive windscreen.

25. A vehicle comprising a vehicular glazing according to any of claims 1 to 18, manufactured according to claims 19 or 20, or a heating apparatus according to any of claims 21 to 24.

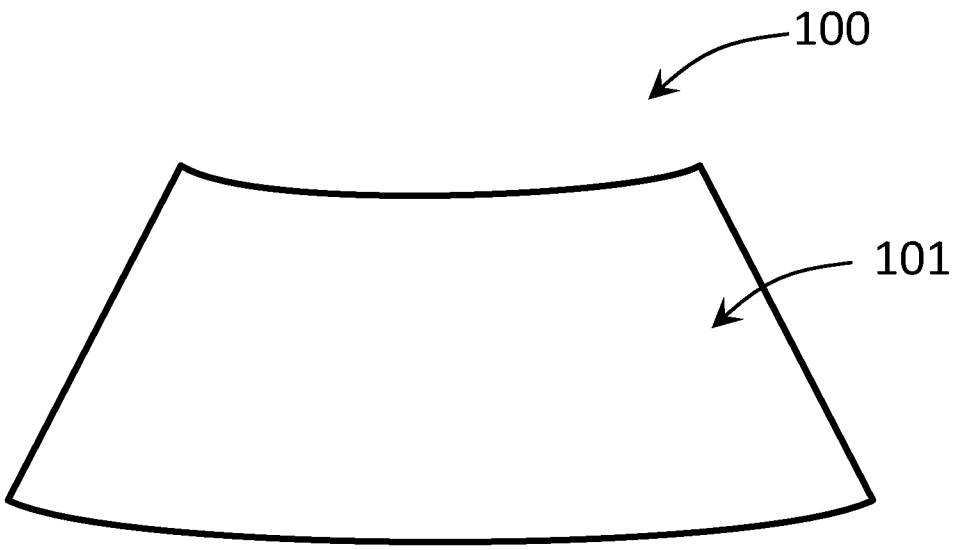


Figure 1

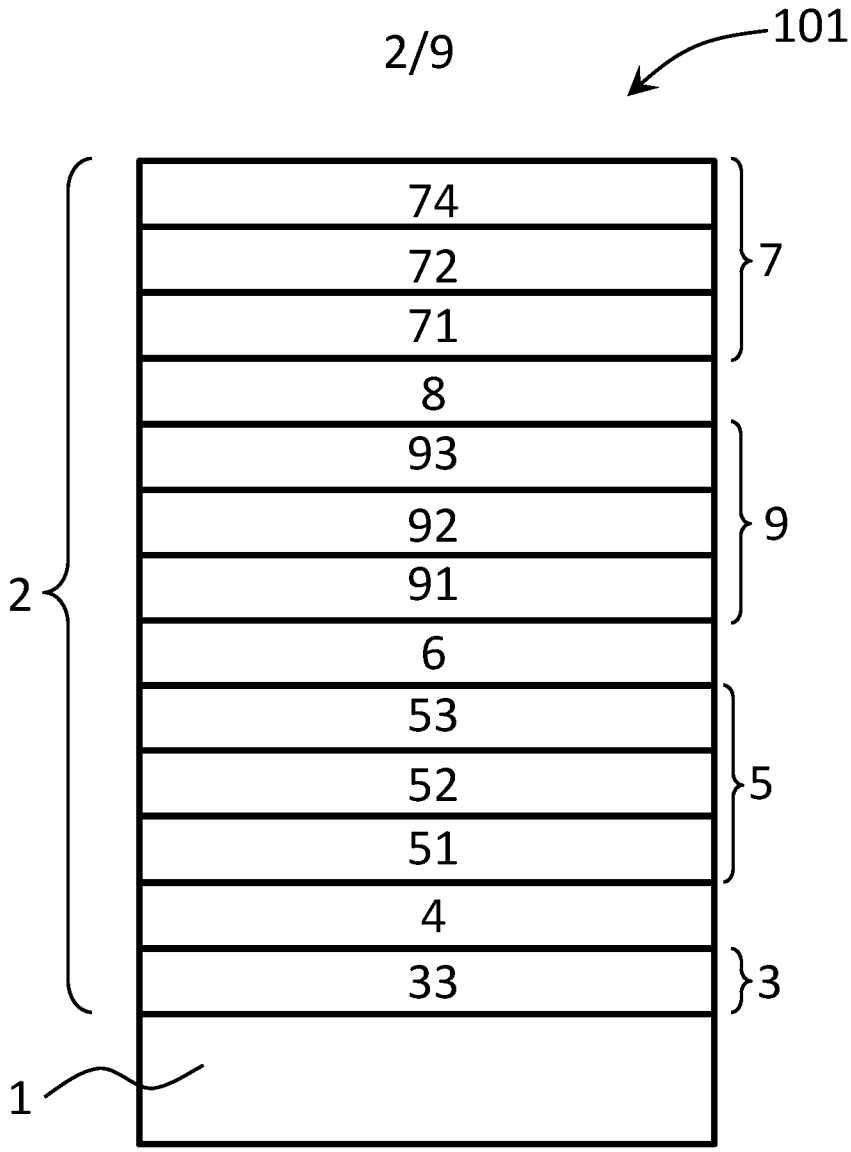


Figure 2

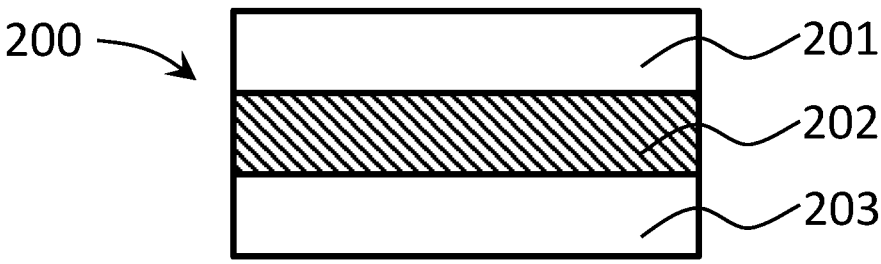


Figure 3

R241123R2	R271123R2	R271123R1	R281123R1	R281123R2	R291123R1
E1-1 (C)	E1-2 (C)	E1-3 (C)	E1-4	E1-5	E1-6
Glass	Glass	Glass	Glass	Glass	Glass
SiNx (22.1)					
ZnSnOx (15)					
ZnO:Al (6)	ZnO:Al (43.1)	ZnO:Al (43.1)	ZnO:Al (43.1)	ZnO:Al (37.6)	ZnO:Al (43.1)
Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)
NiCrOx (0.3)	NiCrOx (0.3)		NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (57)	AlNx (57)		AlNx (30.9)	AlNx (8.5)	
ZnSnOx (11)	ZnSnOx (11)				
ZnO:Al (6)	ZnO:Al (6)	ZnO:Al (72.5)	ZnO:Al (43.1)	ZnO:Al (65)	ZnO:Al (72.5)
Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)
NiCrOx (0.3)	NiCrOx (0.3)		NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (46.4)	AlNx (46.4)		AlNx (23.3)	AlNx (8.5)	
ZnSnOx (13)	ZnSnOx (13)				
ZnO:Al (6)	ZnO:Al (6)	ZnO:Al (60.9)	ZnO:Al (43.1)	ZnO:Al (54.5)	ZnO:Al (60.9)
Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)
NiCrOx (0.3)	NiCrOx (0.3)		NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (20.4)	AlNx (20.4)	AlNx (20.4)	AlNx (20.4)	AlNx (40.9)	AlNx (20.4)
ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)

Figure 4

R200123R1	R230123R2	R120123R5	R180123R2	R160223R1	R200123R2
E2-1	E2-2	E2-3	E2-4	E2-5	E2-6
Glass	Glass	Glass	Glass	Glass	Glass
SiNx (22.1)					
ZnSnOx (21)	ZnSnOx (43.1)	ZnSnOx (43.1)	ZnSnOx (43.1)	ZnSnOx (37.6)	ZnSnOx (43.1)
Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)
NiCrOx (0.3)		NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (57)		AlNx (57)	AlNx (30.9)	AlNx (8.5)	
ZnSnOx (17)	ZnSnOx (72.5)	ZnSnOx (17)	ZnSnOx (43.1)	ZnSnOx (65)	ZnSnOx (72.5)
Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)
NiCrOx (0.3)		NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (46.4)		AlNx (46.4)	AlNx (23.3)	AlNx (8.5)	
ZnSnOx (19)	ZnSnOx (60.9)	ZnSnOx (19)	ZnSnOx (43.1)	ZnSnOx (54.5)	ZnSnOx (60.9)
Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)
NiCrOx (0.3)		NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (20.4)	AlNx (20.4)	AlNx (20.4)	AlNx (20.4)	AlNx (40.9)	AlNx (20.4)
ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)

Figure 5

R240223R3	R200323R1	R200323R2	R220323R1	R220323R2	R220223R1
E2-7	E2-8	E2-9	E2-10	E2-11	E2-12
Glass	Glass	Glass	Glass	Glass	Glass
					SiNx (11)
AZO (37.6) [10kW]	ZnSnOx (37.6)	ZnSnOx (37.6)	ZnSnOx (59.2)	ZnSnOx (37.6)	ZnSnOx (37.6)
Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)		AZO (6)	AZO (6)	AZO (6)	AZO (6)
				ZnSnOx (8.5)	
AlNx (8.5)	AlNx (8.5)	SiNx (8.5)	AlNx (8.5)	AlNx (8.5)	AlNx (8.5)
ZnSnOx (65)	ZnSnOx (71)	ZnSnOx (65)	ZnSnOx (65)	ZnSnOx (56.5)	ZnSnOx (65)
Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)		AZO (6)	AZO (6)	AZO (6)	AZO (6)
				ZnSnOx (8.5)	
AlNx (8.5)	AlNx (8.5)	SiNx (8.5)	AlNx (8.5)	AlNx (8.5)	AlNx (8.5)
ZnSnOx (54.5)	ZnSnOx (60.5)	ZnSnOx (54.5)	ZnSnOx (54.5)	ZnSnOx (46)	ZnSnOx (54.5)
Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (6)
AlNx (40.9)	AlNx (40.9)	AlNx (40.9)	AlNx (40.9)	AlNx (40.9)	AlNx (40.9)
ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)	ZnSnOx (11)

Figure 6

R230223R1	R280223R1	R040423R1	R050423R1	R020623R1
E2-13	E2-14	E2-15	E2-16	E2-17
Glass	Glass	Glass	Glass	Glass
ZnSnOx (48.6)	ZnSnOx (37.6) [4kW]	ZnSnOx (37.6)	ZnSnOx (37.6)	ZnSnOx (40.7)
Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (12.5)	Ag (13.2)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	AZO (2) / SnZnOx (2)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (4.5)
AlNx (8.5)	AlNx (8.5)	AlNx (8.5)	AlNx (8.5)	
ZnSnOx (65)	ZnSnOx (65)	ZnSnOx (65)	ZnSnOx (65)	ZnSnOx (79.2)
Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (13.2)	Ag (14)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	AZO (2) / SnZnOx (2)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (4.5)
AlNx (8.5)	AlNx (8.5)	AlNx (8.5)	AlNx (8.5)	
ZnSnOx (54.5)	ZnSnOx (54.5)	ZnSnOx (54.5)	ZnSnOx (54.5)	ZnSnOx (68.3)
Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.9)	Ag (10.8)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	AZO (2) / SnZnOx (2)	NiCrOx (0.3)
AZO (6)	AZO (6)	AZO (6)	AZO (6)	AZO (4.5)
AlNx (40.9)	AlNx (40.9)	AlNx (51.9)	AlNx (40.9)	AlNx (30.7)
ZnSnOx (11)	ZnSnOx (11)		ZnSnOx (11)	ZnSnOx (8.5)

Figure 7

R201123R1 - J	R240124R1 (A)
E3-1	E3-2
Glass	Glass
ZnSnOx (40.7)	ZnSnOx (43)
Ag (13.2)	Ag (13.5)
NiCrOx (0.3)	NiCrOx (0.3)
AZO (4.5)	AZO (6)
	AlNx (8.5)
ZnSnOx (40.7)	ZnSnOx (39.8)
Al:ZnO (38.5)	Al:ZnO (28.9)
Ag (14)	Ag (13.8)
NiCrOx (0.3)	NiCrOx (0.3)
AZO (4.5)	AZO (12)
	AlNx (8.5)
ZnSnOx (40.7)	ZnSnOx (35.8)
Al:ZnO (27.6)	Al:ZnO (20)
Ag (10.8)	Ag (11.7)
NiCrOx (0.3)	NiCrOx (0.3)
AZO (4.5)	AZO (5)
AlNx (30.7)	AlNx (30.7)
ZnSnOx (8.5)	ZnSnOx (8.5)

Figure 8

R120923R3	R291123R2 - F(A)	F291123R2 - J	R301123R1 - F(A)	R110923R1	R301123R1 - J(E)
E4-1	E4-2	E4-3	E4-4	E4-5	E4-6
Glass	Glass	Glass	Glass	Glass	Glass
ZnSnOx (43.2)	ZnSnOx (41)	ZnSnOx (41)	ZnSnOx (41)	ZnSnOx (43.1)	ZnSnOx (41)
Ag (10.5)	Ag (10.4)	Ag (10.4)	Ag (10.4)	Ag (10.6)	Ag (10.4)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (5)	AZO (5)	AZO (5)	AZO (6)	AZO (5)
			AlNx (8.5)	AlNx (8.5)	AlNx (8.5)
ZnSnOx (76.9)	ZnSnOx (71.9)	ZnSnOx (38.2)	ZnSnOx (71.9)	ZnSnOx (68.6)	ZnSnOx (38.2)
		Al:ZnO (33.7)			Al:ZnO (33.7)
Ag (13.7)	Ag (12.6)	Ag (12.6)	Ag (12.6)	Ag (13.7)	Ag (12.6)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (9.8)	AZO (9.8)	AZO (9.8)	AZO (6)	AZO (9.8)
			AlNx (8.5)	AlNx (8.5)	AlNx (8.5)
ZnSnOx (71.1)	ZnSnOx (59.5)	ZnSnOx (35.2)	ZnSnOx (59.5)	ZnSnOx (62.6)	ZnSnOx (35.2)
		Al:ZnO (24.3)			Al:ZnO (24.3)
Ag (13.6)	Ag (11.9)	Ag (11.9)	Ag (11.9)	Ag (13.6)	Ag (11.9)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (14.8)	AZO (14.8)	AZO (14.8)	AZO (6)	AZO (14.8)
			AlNx (8.5)	AlNx (8.5)	AlNx (8.5)
ZnSnOx (77)	ZnSnOx (61.4)	ZnSnOx (32.3)	ZnSnOx (61.4)	ZnSnOx (68.6)	ZnSnOx (32.3)
		Al:ZnO (29.1)			Al:ZnO (29.1)
Ag (10.3)	Ag (9)	Ag (9)	Ag (9)	Ag (10.2)	Ag (9)
NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)	NiCrOx (0.3)
AZO (6)	AZO (6.9)	AZO (6.9)	AZO (6.9)	AZO (6)	AZO (6.9)
AlNx (31.9)	AlNx (30)	AlNx (30)	AlNx (30)	AlNx (32.3)	AlNx (30)
ZnSnOx (7.5)	ZnSnOx (9.5)	ZnSnOx (9.5)	ZnSnOx (9.5)	ZnSnOx (8.5)	ZnSnOx (9.5)

Figure 9

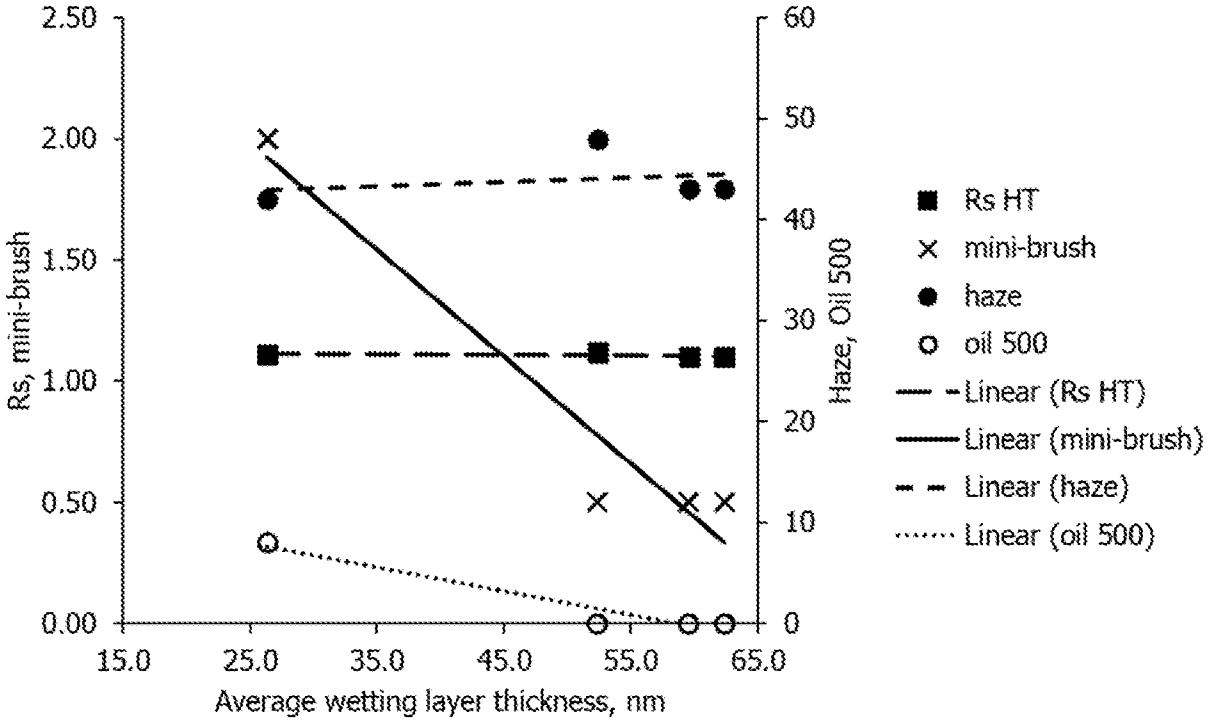


Figure 10

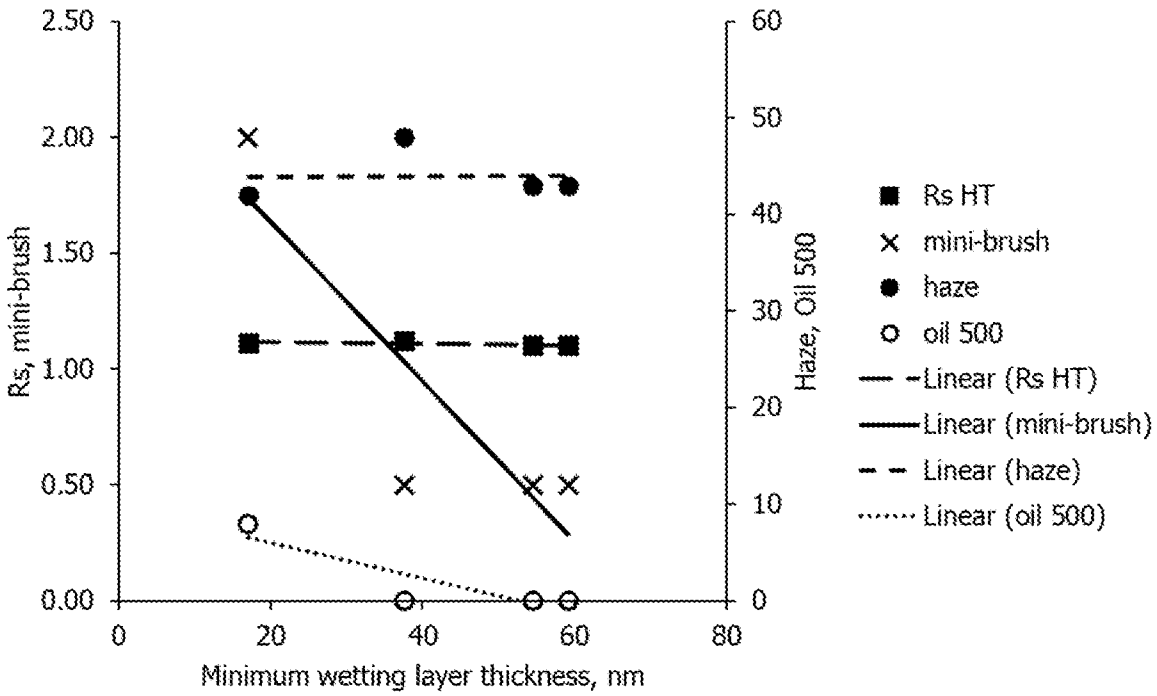


Figure 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051871

A. CLASSIFICATION OF SUBJECT MATTER
INV. C03C17/00 C03C17/36 B32B17/10
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)
C03C B32B

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 Y	DE 20 2019 102388 U1 (SAINT GOBAIN [FR]) 6 May 2019 (2019-05-06) abstract paragraphs [0001] - [0002], [0007], [0011], [0016] - [0018], [0031] - [0036], [0040] - [0046] table 1 -----	1,2,4,5, 7-25 3,6
X Y	DE 10 2016 114281 A1 (ARDENNE GMBH VON [DE]) 8 February 2018 (2018-02-08) abstract paragraphs [0001] - [0006], [0029] - [0030], [0044] - [0046], [0049] in particular examples shown in figures 4D, 4E, 4F, 4G, 4H and 5 -----	1,2,4,5, 7-25 3,6

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

[x] See patent family annex.

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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 December 2024	09/01/2025

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	Philippart, Anahí

2

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051871

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 2020/255331 A1 (XU YONGLI [US] ET AL) 13 August 2020 (2020-08-13) abstract in particular example shown in figure 17	1,2,7-25
Y	US 2016/257611 A1 (NOETHE AXEL [DE] ET AL) 8 September 2016 (2016-09-08) the whole document in particular examples 1-2 (table 1)	3,6
A	US 2014/362434 A1 (SCHMITZ CHRISTOPH [DE] ET AL) 11 December 2014 (2014-12-11) the whole document	1-25

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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