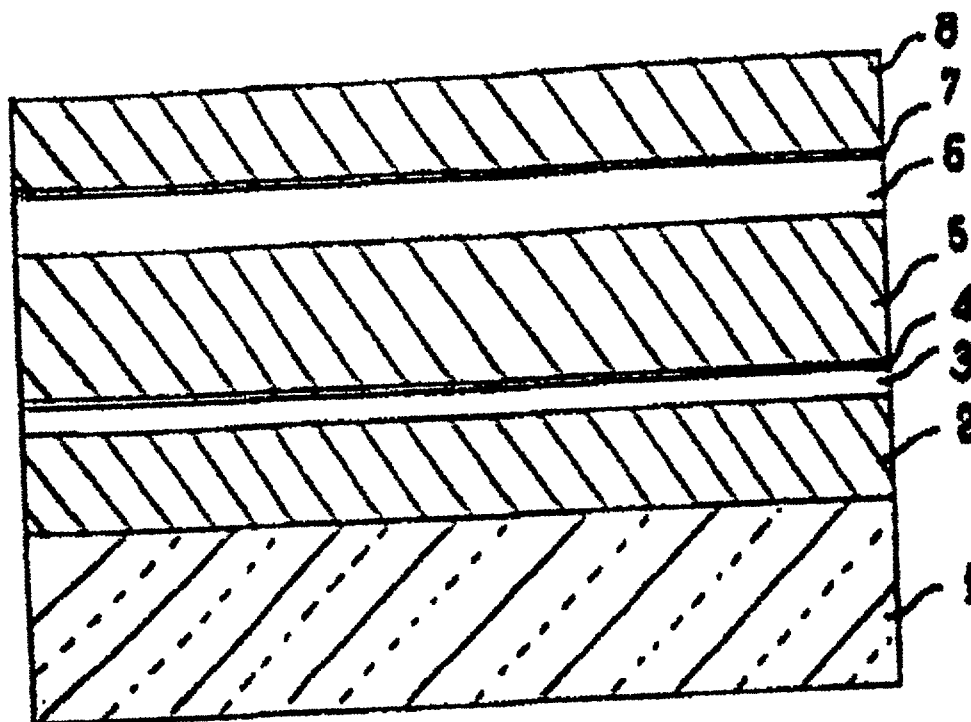


ABSTRACT



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FIG.1

TRANSPARENT SUBSTRATES PROVIDED WITH A STACK OF THIN LAYERS,
APPLICATION TO THERMAL INSULATION AND/OR SOLAR CONTROL GLAZINGS

The invention relates to transparent and in particular glass substrates covered with a stack of thin layers incorporating at least one metal layer able to act on the solar radiation and/or on the infrared radiation of considerable wavelength.

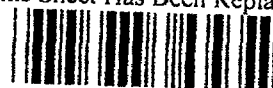
The invention also relates to the use of such substrates for the manufacture of solar protection or control and/or thermal insulation glazings. These glazings are used both for equipping buildings and vehicles, with a particular aim of reducing air conditioning requirements and/or reducing excessive overheating resulting from the ever-increasing size of the glazed surfaces in car bodies.

A known layer stack type for giving such properties to substrates is constituted by at least one metal layer, such as a silver layer, which is placed between two dielectric material layers of the metal oxide type. This stack is generally obtained by a succession of deposits carried out by a method using a vacuum such as magnetic field-assisted cathodic sputtering.

Thus, patent application WO 90/02653 discloses a laminated glazing intended for cars and whose outermost glass substrate with respect to the vehicle body is provided with a stack of five layers on its inner face in contact with the thermoplastic material interlayer. This stack consists of two silver layers intercalated with three zinc oxide layers, the silver layer closest to the outer substrate carrying the stack having a thickness slightly exceeding that of the second silver layer.

The laminated glazings according to said application are used as windscreens, which explains why they have very high light transmission values T_L of approximately 75%, in order to respect the safety standards in force and therefore have a relatively high

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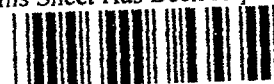
solar factor value SF. (It is pointed out that the solar factor of a glazing is the ratio between the total energy entering the room through said glazing and the incident solar energy).

The object of the invention is to develop a transparent substrate carrying a stack of thin layers having two layers reflecting radiation in the infrared and which are more particularly of a metallic type, so that they have a high selectivity, i.e. the highest possible T_L/SF ratio for a given value of T_L , whilst ensuring that said substrate has an esthetically satisfactory visual appearance in reflection.

The invention relates to a transparent substrate, particularly of glass and having multiple thin layers, on which are successively deposited a first dielectric material layer, a first layer having infrared reflection properties and in particular based on metal, a second dielectric material layer, a second layer having infrared reflection properties, particularly based on metal, and finally a third dielectric material layer. According to the invention, the thickness of the first layer having infrared reflection properties, i.e. that closest to the carrying substrate, corresponds to approximately 50 to 80%, particularly 55 to 75% and preferably 60 to 70% of the thickness of the second layer having infrared reflection properties. An advantageous example corresponds to a thickness of the first layer corresponding to approximately 65% of the second.

This great asymmetry in the thicknesses of the layers having infrared reflection properties makes it possible to advantageously modify the values of T_L and SF so as to obtain glazings having a good selectivity, i.e. a good compromise between the need for transparency and that of providing an optimum protection against solar heat rays.

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Moreover, the choice of such an asymmetry leads to another advantageous consequence. Not only does it make it possible to obtain glazings having an attractive visual appearance, particularly in reflection, i.e. having a neutral "whitewashed" colouring, but said visual appearance remains virtually unchanged no matter what the angle of incidence with which the glazing is observed. This means that a person on the outside viewing the facade of a building entirely equipped with such glazings does not have a visual impression of a change of shade as a function of the location on the facade at which he is looking. This appearance uniformity character is very interesting, because it is presently highly desired by building architects.

Moreover, the visual appearance of the glazing, both in reflection and transmission, can also be refined and controlled by an adequate selection of the materials and the relative thicknesses of the three dielectric material layers.

Thus, according to a non-limitative variant of the invention, the optical thickness of the first layer is chosen approximately equal to that of the third layer. The optical thickness of the second layer is then advantageously chosen above or equal to 110% of the sum of the optical thicknesses of the two other layers and preferably corresponding to approximately 110 to 120% of said sum.

Another variant relating to the relative thicknesses of the dielectric material layers, which is just as advantageous, consists of choosing an optical thickness of the first layer which exceeds the optical thickness of the third layer. Thus, the optical thickness of the first layer can correspond to at least 110% of the optical thickness of the third layer, particularly at least 110 to 140%, especially 115 to 135% and preferably approximately 125% of the optical thickness of the latter. In the case of the drawing, it is recommended that the optical thickness of the second dielectric material layer be chosen approximately equal to the sum of the optical thicknesses of the two other layers.

In both cases, such relative proportions between the optical thicknesses of the layers makes it possible to obtain colours in reflection and even also in transmission, which are esthetically appreciated and in particular blue and green.

However, the second variant has a supplementary advantage compared with the first, to the extent that it optimizes the "non-sensitivity" of the complete stack to thickness variations of the different layers forming it. This means that slight thickness variations of one of the layers in the stack does not lead to flagrant appearance deficiencies between individual glazings or on the surface of the same glazing. This is very important from the industrial standpoint, where manufacture takes place of glazings having a considerable size and/or in large numbers with the aim of retaining appearances and performance characteristics which are as uniform as possible between individual glazing batches, particularly within individual zones of the same glazing.

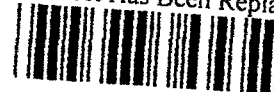
In terms of choice of material for said thin layer stack, it is recommended to place on each of the layers having infrared reflection properties and in particular based on metal, a thin "barrier" layer, particularly when the dielectric layers above the same are deposited by reactive cathodic sputtering in the presence of oxygen. Therefore said barrier layers protect the metal layers in contact with the oxygen and themselves partly oxidize during the deposition of the upper dielectric layer. They are preferably based on a tantalum, titanium or nickel-chromium alloy and have a thickness of 1 to 3 nanometres.

With regards to the layers having properties in the infrared, good results are obtained with silver layers.

The dielectric material layers are in particular based on tantalum (V) oxide, zinc oxide, tin (IV) oxide, niobium (V)

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oxide, titanium (IV) oxide or a mixture of certain of these oxides. It is also possible for one of the layers to be constituted by two superimposed oxide sublayers, one being of tin (IV) oxide and the other of an oxide making it possible to improve the wetting of the layers having infrared reflection properties, such as tantalum (V) oxide or niobium (V) oxide in accordance with French patent application 93/01546 filed on 11.2.1993 and European patent application 94 400 289.8 filed on 10.2.1994, or titanium (IV) oxide.

Each of the oxides given above has advantages. Thus, tin (IV) oxide and zinc oxide have high deposition speeds when deposited by reactive cathodic sputtering, which is of great interest industrially. However, tantalum (V) oxide or niobium (V) oxide make it possible to obtain an increased durability of the stack with respect to mechanical or chemical aggressions and in particular lead to a better wetting of the silver layers when they are positioned below the latter. Mixed oxides can offer a compromise between the deposition rate and the durability and the superimposing of two oxide layers reconciles in an optimum manner the cost of the starting materials and a better wettability of the silver layers.

There is also a supplementary advantage linked with the use of tantalum (V) oxide. A glazing provided with a stack having such a dielectric material can be blue both in reflection and in transmission, which is appreciated from the esthetic standpoint and is also surprising, because usually, in transmission, the colour obtained is complimentary of that obtained in reflection, when the thin layers in question are only slightly or non-absorbent.

The preferred embodiment of the stack according to the invention consists of choosing a thickness of 7 to 9 nanometres for the first metal layer and a thickness of 11 to 13 nanometres for the second. Preferably the optical thickness of the first and third dielectric material layers is between 60 and 90 nanometres,

their geometrical thickness being in particular between 30 and 45 nanometres. The optical thickness of the second layer is between 140 and 170 nanometres, whilst its geometrical thickness is between 70 and 80 nanometres. It is pointed out that the optical thickness is defined in known manner by the product of the real geometrical thickness of the layer and the refractive index of the material forming it. As a function of the envisaged oxide type, the index varies between 1.9 and 2.1 for tin (IV) oxide or tantalum (V) oxide to approximately 2.3 for oxides of the niobium (V) oxide type.

The substrate coated with the stack according to the invention can advantageously be incorporated into a multiple glazing and in particular as one of the glass layers of an insulating double glazing. In the latter case, the double glazing has a light transmission value between 60 and 70% and a solar factor SF of 0.32 to 0.42, which make it completely suitable for use in buildings. Moreover, it preferably has in reflection a virtually unchanged visual appearance no matter what the vision incidence angle, the values of a^* , b^* in the colorimetry system (L, a^* , b^* , c^*) remaining unchanged, below 3 and negative.

It can also form part of a laminated glazing with in particular a light transmission of approximately 70%.

The advantageous details and features of the invention can be gathered from the following non-limitative examples illustrated by fig. 1.

It is pointed out that in all the examples the successive deposits of the layers of the stack take place by magnetic field-assisted cathodic sputtering, but any other deposition procedure can be envisaged provided that it permits a good control and monitoring of the thicknesses of the layers to be deposited.

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The substrates on which the stacks are deposited are 4 mm thick soda-lime-silica glass substrates, except for examples 7 to 10, where the substrates are 6 mm thick. In double glazings, they are assembled with another substrate identical to the first, but in the blank state, by means of a 10 mm space of gas, except for the examples 7 to 8, where there is a 12 mm space of gas.

Fig. 1 shows the stack according to the invention and does not respect proportions with respect to the thicknesses of the layers so as to facilitate understanding. It is possible to see the previously defined substrate 1, surmounted by a first tin (IV) oxide or tantalum (V) oxide layer 2, a first silver layer 3, a titanium or Ni-Cr alloy barrier alloy (partly oxidized) 4, a second tin (IV) or tantalum (V) oxide layer 5, a second silver layer 6, another barrier layer 7 identical to the first and finally a last layer 8 of one of the same oxides.

The deposition installation comprises at least one sputtering chamber equipped with cathodes having targets made from appropriate materials under which the substrate 1 successively passes. These deposition conditions for each of the layers are as follows:

the silver-based layers 3, 6 are deposited with the aid of a silver target, under a pressure of 0.8 Pa in an argon atmosphere, the layers 2, 5 and 8, when based on SnO_2 , are deposited by reactive sputtering with the aid of a tin target under a pressure of 0.8 Pa and in an argon/oxygen atmosphere, including 36 vol. % oxygen,

the layers 2, 5, 8, when based on Ta_2O_5 or Nb_2O_5 are deposited by reactive sputtering respectively with the aid of a tantalum target or a niobium target under a pressure of 0.8 Pa and in an argon/oxygen atmosphere, whereof approximately 10 vol. % is oxygen,

the layers 4, 7 based on Ni-Cr or titanium are deposited with the aid of a nickel-chromium alloy or titanium target under the



same pressure and in an argon atmosphere.

The power densities and travel speeds of the substrate 1 are adjusted in known manner so as to obtain the desired layer thicknesses.

In all the following examples, with the exception of the last, tantalum (V) oxide is chosen as the dielectric material for the layers 2, 5 and 8.

EXAMPLES 1 TO 5

Examples 1, 2 and 5 are comparative examples to the extent that in these three cases, the silver layers 3, 6 have either virtually identical thicknesses (example 1) or different thicknesses, but whereof the asymmetry is reversed compared with that recommended by the invention (examples 2 and 5). Examples 3 and 4 are in accordance with the teachings of the invention.

The following table 1 gives for each of the examples the nature and thicknesses (in nanometres) of the layers of the stack in question. The barrier layers 4, 7 are designated Ni-Cr, knowing that they are in fact partly oxidized once all the layers have been deposited.

TABLE 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	5
Glass	(1)	-	-	-	-	-
Ta ₂ O ₅	(2)	36.5	34.5	32	32	32
Ag	(3)	10	11.5	8	8	12
Ni-Cr	(4)	2	2	2	3	2
Ta ₂ O ₅	(5)	77.5	94.5	77.5	72.5	77.5
Ag	(6)	11	8	12	12.5	8
Ni-Cr	(7)	2	2	2	2	2
Ta ₂ O ₅	(8)	33.5	35	33.5	32	33.5

The following table 2 indicates for each of the above examples the light transmission value T_L as a percentage, the solar factor SF calculated according to DIN standard 67507 (appendix A 233) as a percentage, the dominant wavelength values $\lambda_{\text{dom-t}}$ nanometres and the associated colouring purity pt as a percentage. Also indicated are the light reflection values R_L as a percentage, the dominant wavelength in reflection $\lambda_{\text{dom-r}}$ and the reflection purity p.r. as a percentage, the colorimetry measurements having been performed under normal incidence. All the measurements relate to the substrate fitted as a double glazing, with reference to the illuminant D_{65} .

TABLE 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
T_L	69	66	70	61	62
SF	42	42	42	38	38
$\lambda_{\text{dom-t}}$	493	489	498	490	478
p.t.	2	5	2	4	6
R_L	12	19	10	10	21
$\lambda_{\text{dom-r}}$	561	641	486	487	574
p.r.	3	9	3	6	35

The following table 3 gives the values of the dominant wavelength in reflection $\lambda_{\text{dom-r}}$, the reflection purity p.r. for certain of the preceding examples (the substrate still being installed in a double glazing), but on this occasion measured with an angle of incident relative to the perpendicular to the plane of the substrate of respectively 60 and 70°.

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TABLE 3

	Ex. 1	Ex. 2	Ex. 3	Ex. 5
Lambda-dom-r (60°)	470	569	480	571
p.r. (60°)	5.4	3	4.68	8
R_L (60°)	19	28	20	27
Lambda-dom-r (70°)	462	490	481	-498
p.r. (70°)	4.3	4	3.0	0.8
R_L (70°)	32	39	34	36

Other colorimetry measurements with incidence angles 0 and 60° were performed, on this occasion in the system (L^* , a^* , b^*), for examples 2 and 3, as well as for example 5, which is in all points identical to example 3, except that the silver layers 3 and 6 were reversed and consequently falling outside the conditions recommended by the invention. Table 4 groups the values of a^* and b^* , as well as c^* called saturation and equal to the square root of the sum of the squares of a^* and b^* .

TABLE 4

	Ex. 2	Ex. 3	Ex. 5
a^* (0°)	12.2	- 0.9	- 2.2
b^* (0°)	3.1	- 3.1	22
c^* (0°)	12.6	3.2	22.1
a^* (60°)	- 1	- 0.9	- 1.7
b^* (60°)	2	- 3	6
c^* (60°)	2.2	3.13	6.2

The following conclusions can be drawn from this information.

Under a normal incidence angle, i.e. giving different thicknesses to the silver layers and solely in such a way that the silver layer closest to the substrate is much thinner enabling the obtaining of glazings which are blue in reflection.



It should be noted that the glazings according to the invention, particularly when the chosen dielectric is tantalum (V) oxide, are also blue in transmission.

Thus, only examples 3 and 4 have $\lambda_{\text{dom-r}}$ values of approximately 486 nanometres and $\lambda_{\text{dom-t}}$ values of 490 nanometres, according to table 2. However, the glazings of examples 1 and 5 have in reflection a yellow shade, whereas that of example 2 is a red-purple shade.

In addition, the colouring purity in reflection p.r. of example 2, close to 10%, is much higher than that of examples 3 and 4 according to the invention. (This value of p.r. is even higher for example 5).

Moreover, the glazings of examples 3 and 4 according to the invention have a good selectivity of at least 1.6 or 1.7 with a solar factor remaining equal to or below 42%.

Thus, the obtaining of a favourable colorimetry according to the invention is not to the detriment of the solar protection performance characteristics of the glazings in question.

Tables 3 and 4 make it possible to evaluate the uniformity of the appearance in reflection of the glazings according to certain of the preceding examples. Table 3 shows that the glazing according to example 3 in accordance with the invention retains a blue colour in reflection, with a $\lambda_{\text{dom-r}}$ value remaining virtually constant towards 486 at 0° to 481 at 70°, the purity in reflection also remaining very moderate.

However, the glazing according to example 1, where the silver layers approximately have the same thickness, passes from a yellow colour in reflection under normal incidence to a blue and then violet colour at 60 and then 70°.

Table 4 confirms that only example 3 according to the invention makes it possible to maintain an identical coloured appearance in reflection no matter what the incidence angle, because the values of a^* and b^* remain virtually unchanged, as does the saturation c^* .

This is not the case with the glazings of examples 2 and 5, where the values of a^* and b^* change completely as a function of the incidence angle. Thus, the value of a^* passes, for the glazing of example 2, from a very high positive value of 12.2 at 0° to a very low negative value of -1 at 60° .

Thus, only the examples according to the invention reconcile the selectivity and appearance uniformity.

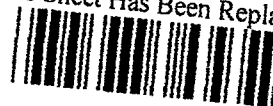
EXAMPLES 6 AND 7

These two examples use as the dielectric material tin (IV) oxide and not tantalum (V) oxide and use for the barrier layers either titanium (example 6) or Ni-Cr (example 7).

The following table 5 indicates the thickness values in nanometres used for each of the stack layers:

		<u>TABLE 5</u>	
		Ex. 6	Ex. 7
Glass	(1)	-	-
SnO ₂	(2)	34	32
Ag	(3)	8	8
Ti or Ni-Cr	(4)	1	1.5
SnO ₂	(5)	77	74.5
Ag	(6)	12	11.6
Ti or Ni-Cr	(7)	1	1.5
SnO ₂	(8)	35	33





The thus coated substrates were installed in double glazings, as explained hereinbefore. The photometric measurements on the double glazings appear in table 6 (measurements under normal incidence).

TABLE 6

	Ex. 6	Ex. 7
T_L	66	75
SF	38	39
R_L	10.4	9.4
Lambda-dom-r	511	484
p.r.	2	2
a^*	-	- 0.5
b^*	-	- 1.1

These glazings, like those of examples 3 and 4, reveal no significant modification of their visual appearance in reflection, no matter what the measurement angle. In reflection they have a colour towards the greens for example 6 and towards the blues for example 7, but these colours remain very neutral, in view of the very low purity values associated therewith.

Laminated glazings incorporating the covered substrates of the stack according to the invention retain the favourable colorimetry observed in the case of monolithic substrates or substrates installed in double glazings.

Thus, the substrate covered with the stack according to example 3 was assembled with another substrate of the same type, but without a layer, using a standard, 0.3 mm thick, polyvinyl butyral film.

The following table 7 gives for said laminated glazing the already explained values of T_L , p.t. lambda-dom-t, a^* and b^* in connection with the appearance in transmission, as well as the corresponding values R_L , p.r. lambda-dom-r, a^* and b^* concerning



the appearance in reflection on the side of the substrate provided with the stack of layers (same units as hereinbefore).

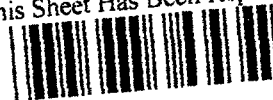
TABLE 7

T_L	70
p.t.	1.2
lambda-dom-t	502
a^*	- 3.27
b^*	0.52
R_L	14
p.r.	8
lambda-dom-r	483
a^*	- 2.2
b^*	- 4.4

Table 7 shows that the incorporation of substrates covered in accordance with the invention in a laminated glazing structure leads to no deterioration of their esthetic colorimetry. The thus obtained laminated glazing remains in the blues or greens, both in transmission and in reflection.

Examples 3, 4 and 6 according to the invention relate to its "first variant" mentioned hereinbefore, i.e. respecting a choice of relative thicknesses between the three oxide layers 2, 5 and 8 which is specific and approximately as follows. The thickness of the layer 2 is approximately equal to that of the layer 8 and the thickness of the layer 5 (in the centre) is slightly greater than the sum of the thicknesses of the two other layers 2 and 8 (in these examples reference can be made to either the geometrical thickness or the optical thickness, because the three layers are made from the same oxide).

The "second variant" according to the invention will now be



illustrated by the following examples and more particularly example 8. In this variant, the thickness ratios between the oxide layers 2, 5 and 8 are slightly modified, the optical thickness of the layer 2 being significantly (25%) higher than that of the layer 8. The optical thickness of the layer 5 (or the sum of the optical thicknesses of the different sublayers forming it) is here approximately equal to the sum of the optical thicknesses of the two other layers 2 and 8.

EXAMPLE 8

The substrate according to example 8 is covered with a stack similar to that described for example 7, the layers 2, 5 and 8 being of tin (IV) oxide, but of different thicknesses.

The following table 8 gives the thickness values in nanometres of all the layers of the stack in question.

TABLE 8

		Ex. 8
Glass	(1)	-
SnO ₂	(2)	41
Ag	(3)	8
Ni-Cr	(4)	1.5
SnO ₂	(5)	74.5
Ag	(6)	12
Ni-Cr	(7)	1.5
SnO ₂	(8)	33

The substrate is fitted in a double glazing. The photometric measurements performed on the double glazing are given in table 9 (measured under normal incidence).

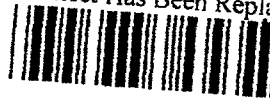


TABLE 9

	Ex. 8
T_L	75
SF	39
R_L	9.1
Lambda-dom-r	486
p.r.	1
a^*	- 0.7
b^*	- 0.5

Comparing these results with those obtained in example 7, it can be seen that identical values of T and SF are obtained. The appearance in reflection is also in the blues, with an even more neutral colour, because the purity is approximately 1% and the values of a^* and b^* are both well below 1. Another advantage of the stack type according to example 7 is that it more easily permits slight thickness variations in the stack layers, from one point to the other of the substrate, without giving rise to noticeable modifications of its visual appearance.

Thus, on performing measurements of a^* and b^* in reflection at different points of the substrate according to example 8 fitted in a double glazing, it is found that the value differences remain below 1, i.e. differences which cannot be noticed by the human eye, even if each of the layers has local thickness variations of $\pm 4\%$. This is very important from the industrial standpoint, because it makes it more easily possible to obtain glazings which are both uniform, i.e. having no local appearance modifications, and reproducible, i.e. having an identical appearance between individual glazings or between individual glazing batches. This means that for a given production line, which has its own performance limits, particularly with regards to the regularity of the layers obtained, such a stack will be less



"sensitive" than others to thickness variations of the layers imposed by the line and will consequently have a better optical quality.

Conversely, on imposing a given optical quality, it is possible with this type of stack, to use a production line under less draconian conditions or to use a production line having slightly inferior performance characteristics.

It is also advantageous from the industrial standpoint for the layer 5 to have a thickness roughly equal to the sum of the thicknesses of the layers 2 and 8. Thus, it is then sufficient to use two targets, here of tin, whereof it is possible to regulate the power values supplied "once and for all" in their respective deposition chambers. The layer 2 is then obtained by the passage of the substrate under one of the targets with settings permitting the deposition of a predefined adequate thickness. In the same way, the layer 8 is obtained by the passage of the substrate under the second target with settings making it possible to obtain the deposition of a previously defined adequate thickness. The layer 5 is obtained by consecutive passages of the substrate under each of the targets, so that on the substrate are superimposed a layer thickness corresponding to that of the layer 2 or 8 and then a layer thickness corresponding to that of the layer 8 or 2, i.e. the sum of the thicknesses of these two layers is formed without calling on a third target.

EXAMPLES 9 TO 12

The aim of these examples is to optimize the wettability and therefore the performance characteristics of at least one of the silver layers. They follow the teaching of European patent application 94 400 289.8.

In the case of examples 9 and 10, the layers 2 and 8 are once

again of tin (IV) oxide, but the layer 5 is subdivided into two superimposed sublayers, the first 5 being of tin (IV) oxide and the second 5 bis of tantalum (V) oxide (for example 9) or niobium (V) oxide (for example 10). A thin metallic sublayer can be optionally provided below the silver layer 6 and which is of NiCr or Sn.

In the case of examples 11 and 12, the layer 2 is also subdivided into two superimposed sublayers, the first 2 being of tin (IV) oxide and the second 2 bis of tantalum (V) oxide (for example 11) or niobium (V) oxide (for example 12). An optional, thin metallic sublayer can be provided beneath the silver layer 3.

Thus, in the case of examples 9 and 10, the wettability of the second silver layer 6 is optimized, whereas in the case of examples 11 and 12, the wettability of the two silver layers 3, 6 is optimized.

Table 10 gives the thicknesses in nanometres of the layers present.

TABLE 10

		Ex. 9 and 10	Ex. 11 and 12
Glass	(1)	-	-
SnO ₂	(2	41	30 - 31
Ta ₂ O ₅ or Nb ₂ O ₅ (2bis)		0	10
Ag	(3)	8	8
Ni-Cr	(4)	1.5	1.5
SnO ₂	(5)	64	64
Ta ₂ O ₅ or Nb ₂ O ₅ (5bis)		10	10
Ag	(6)	12	12
Ni-Cr	(7)	1.5	1.5
SnO ₂	(8)	33	33

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There is a slight improvement to the solar control performance characteristics of the stacks. Moreover, the use of oxides known for their hardness, such as tantalum or niobium (V) oxide, helps to optimize the durability of the overall stack and in particular its mechanical durability. This mechanical strength increase is particularly pronounced for examples 11 and 12.

In conclusion, the glazings according to the invention have both a good selectivity of approximately 1.70, a uniform visual appearance which is attractive to the eye (particularly a blue or green colour in reflection and optionally also in transmission), as well as a range of light transmission values making them suitable for use as solar control glazings in buildings, particularly in the form of double glazings, the stack of thin layers preferably being on face 2 (the faces are conventionally numbered from the outside to the inside of the room in question).

The substrates covered with layers according to the invention can also be used with advantage for producing laminated glazings.

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CLAIMS

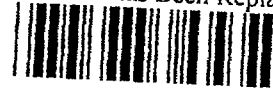
1. Transparent substrate (1), more particularly of glass and having multiple thin layers on which are successively deposited:
a first dielectric material layer (2),
a first layer (3) having infrared reflection properties, particularly based on metal,
a second dielectric material layer (5),
a second layer (6) having infrared reflection properties, particularly based on metal,
a third dielectric material layer (8),
characterized in that the thickness of the first layer (3) having infrared reflection properties corresponds to approximately 50 to 80%, particularly 55 to 75% and preferably 60 to 75% of that of the second layer having infrared reflection properties (6).
2. Transparent substrate (1) according to claim 1, characterized in that the optical thickness of the second dielectric material layer (5) is equal to or greater than 110% of the sum of the optical thicknesses of the two other dielectric material layers (2, 8) and preferably corresponds to approximately 110 to 120% of said sum.
3. Transparent substrate (1) according to claim 2, characterized in that the optical thicknesses of the first dielectric material layer (2) and the third dielectric material layer (8) are approximately equal.
4. Transparent substrate (1) according to claim 1, characterized in that the optical thickness of the first dielectric material layer (2) is greater than the optical thickness of the third dielectric material layer (8) the optical thickness of the first layer (2) corresponding to at least 110%, particularly at

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least 110 to 140% and preferably approximately 125% of the optical thickness of the third layer (8).

5. Transparent substrate (1) according to claim 4, characterized in that the optical thickness of the second dielectric material layer (5) is approximately equal to the sum of the optical thicknesses of the first and third dielectric layers (2, 8).

6. Transparent substrate (1) according to any one of the preceding claims, characterized in that each of the layers having infrared reflection properties (3, 6) is surmounted by a thin, partly oxidized, "barrier" metal layer (4, 7), particularly based on titanium or a nickel-chromium alloy and preferably having a thickness of 1 to 3 nanometres.

7. Transparent substrate (1) according to any one of the preceding claims, characterized in that the layers (3, 6) having infrared reflection properties are based on silver.

8. Transparent substrate (1) according to any one of the preceding claims, characterized in that at least one of the three dielectric material layers (2, 5, 8) is based on tantalum (V) oxide, tin (IV) oxide, zinc oxide, niobium (V) oxide, titanium (IV) oxide or mixtures of said oxides, or is constituted by a first tin (IV) oxide layer surmounted by a second layer of tantalum (V) oxide, niobium (V) oxide or titanium (IV) oxide.

9. Transparent substrate according to any one of the preceding claims, characterized in that the thickness of the first layer having infrared reflection properties (3) is between 7 and 9 nanometres.

10. Transparent substrate (1) according to any one of the preceding claims, characterized in that the thickness of the second layer having infrared reflection properties (6) is between 1 and 13 nanometres.



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11. Transparent substrate (1) according to any one of the preceding claims, characterized in that the optical thickness of the first (2) and third (8) dielectric material layer is between 60 and 90 nanometres and in that the optical thickness of the second dielectric material layer (5) is between 140 and 170 nanometres.
12. Laminated glazing, characterized in that it incorporates the substrate according to any one of the preceding claims and in that it has a light transmission T_L of approximately 70% and a colour in external reflection in the blues or greens.
13. Multiple glazing, particularly double glazing, characterized in that it incorporates the substrate according to any one of the claims 1 to 11 and in that it has a light transmission (T_L) between 60 and 70% and a solar factor (SF) of 0.32 to 0.42.
14. Multiple glazing, particularly double glazing, characterized in that it incorporates the substrate according to any one of the claims 1 to 11 and it has a colour in external reflection in the blues and optionally also in transmission, particularly when the layers (2, 5, 8) are of tantalum (V) oxide.
15. Multiple glazing according to claim 14, characterized in that its optical appearance in external reflection remains virtually identical no matter what the incidence angle, the values of a^* and b^* in the colorimetry system (L , a^* , b^* , c^*) remaining unchanged and below 3 and having a negative sign.
16. Application of the substrate according to any one of the claims 1 to 11 to the production of multiple insulating glazings, such as double glazings or laminated glazings.

TRANSPARENT SUBSTRATES PROVIDED WITH A STACK OF THIN LAYERS,
APPLICATION TO THERMAL INSULATION AND/OR SOLAR CONTROL GLAZINGS

The invention relates to transparent and in particular glass substrates covered with a stack of thin layers incorporating at least one metal layer able to act on the solar radiation and/or on the infrared radiation of considerable wavelength.

The invention also relates to the use of such substrates for the manufacture of solar protection or control and/or thermal insulation glazings. These glazings are used both for equipping buildings and vehicles, with a particular aim of reducing air conditioning requirements and/or reducing excessive overheating resulting from the ever-increasing size of the glazed surfaces in car bodies.

A known layer stack type for giving such properties to substrates is constituted by at least one metal layer, such as a silver layer, which is placed between two dielectric material layers of the metal oxide type. This stack is generally obtained by a succession of deposits carried out by a method using a vacuum such as magnetic field-assisted cathodic sputtering.

Thus, patent application WO 90/02653 discloses a laminated glazing intended for cars and whose outermost glass substrate with respect to the vehicle body is provided with a stack of five layers on its inner face in contact with the thermoplastic material interlayer. This stack consists of two silver layers intercalated with three zinc oxide layers, the silver layer closest to the outer substrate carrying the stack having a thickness slightly exceeding that of the second silver layer.

The laminated glazings according to said application are used as windscreens, which explains why they have very high light transmission values T_L of approximately 75%, in order to respect the safety standards in force and therefore have a relatively high

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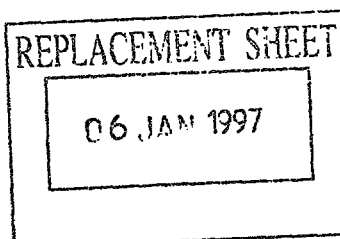
solar factor value SF. (It is pointed out that the solar factor of a glazing is the ratio between the total energy entering the room through said glazing and the incident solar energy).

The object of the invention is to develop a transparent substrate carrying a stack of thin layers having two layers reflecting radiation in the infrared and which are more particularly of a metallic type, so that they have a high selectivity, i.e. the highest possible T_L/SF ratio for a given value of T_L , whilst ensuring that said substrate has an esthetically satisfactory visual appearance in reflection.

The invention relates to a transparent substrate, particularly of glass and having multiple thin layers, on which are successively deposited a first dielectric material layer, a first layer having infrared reflection properties and in particular based on metal, a second dielectric material layer, a second layer having infrared reflection properties, particularly based on metal, and finally a third dielectric material layer. According to the invention, the thickness of the first layer having infrared reflection properties, i.e. that closest to the carrying substrate, corresponds to approximately 50 to 80%, particularly 55 to 75% and preferably 60 to 70% of the thickness of the second layer having infrared reflection properties. An advantageous example corresponds to a thickness of the first layer corresponding to approximately 65% of the second.

This great asymmetry in the thicknesses of the layers having infrared reflection properties makes it possible to advantageously modify the values of T_L and SF so as to obtain glazings having a good selectivity, i.e. a good compromise between the need for transparency and that of providing an optimum protection against solar heat rays.

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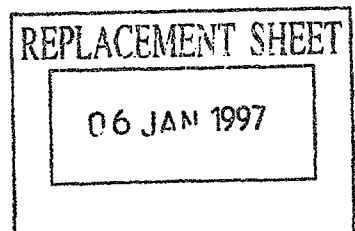


Moreover, the choice of such an asymmetry leads to another advantageous consequence. Not only does it make it possible to obtain glazings having an attractive visual appearance, particularly in reflection, i.e. having a neutral "whitewashed" colouring, but said visual appearance remains virtually unchanged no matter what the angle of incidence with which the glazing is observed. This means that a person on the outside viewing the facade of a building entirely equipped with such glazings does not have a visual impression of a change of shade as a function of the location on the facade at which he is looking. This appearance uniformity character is very interesting, because it is presently highly desired by building architects.

Moreover, the visual appearance of the glazing, both in reflection and transmission, can also be refined and controlled by an adequate selection of the materials and the relative thicknesses of the three dielectric material layers.

Thus, according to a non-limitative variant of the invention, the optical thickness of the first layer is chosen approximately equal to that of the third layer. The optical thickness of the second layer is then advantageously chosen above or equal to 110% of the sum of the optical thicknesses of the two other layers and preferably corresponding to approximately 110 to 120% of said sum.

Another variant relating to the relative thicknesses of the dielectric material layers, which is just as advantageous, consists of choosing an optical thickness of the first layer which exceeds the optical thickness of the third layer. Thus, the optical thickness of the first layer can correspond to at least 110% of the optical thickness of the third layer, particularly at least 110 to 140%, especially 115 to 135% and preferably approximately 125% of the optical thickness of the latter. In the case of the drawing, it is recommended that the optical thickness of the second dielectric material layer be chosen approximately equal to the sum of the optical thicknesses of the two other layers.



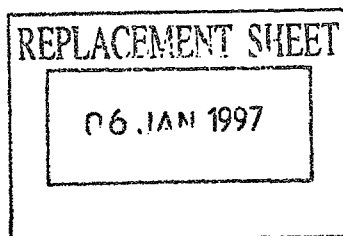
In both cases, such relative proportions between the optical thicknesses of the layers makes it possible to obtain colours in reflection and even also in transmission, which are esthetically appreciated and in particular blue and green.

However, the second variant has a supplementary advantage compared with the first, to the extent that it optimizes the "non-sensitivity" of the complete stack to thickness variations of the different layers forming it. This means that slight thickness variations of one of the layers in the stack does not lead to flagrant appearance deficiencies between individual glazings or on the surface of the same glazing. This is very important from the industrial standpoint, where manufacture takes place of glazings having a considerable size and/or in large numbers with the aim of retaining appearances and performance characteristics which are as uniform as possible between individual glazing batches, particularly within individual zones of the same glazing.

In terms of choice of material for said thin layer stack, it is recommended to place on each of the layers having infrared reflection properties and in particular based on metal, a thin "barrier" layer, particularly when the dielectric layers above the same are deposited by reactive cathodic sputtering in the presence of oxygen. Therefore said barrier layers protect the metal layers in contact with the oxygen and themselves partly oxidize during the deposition of the upper dielectric layer. They are preferably based on a tantalum, titanium or nickel-chromium alloy and have a thickness of 1 to 3 nanometres.

With regards to the layers having properties in the infrared, good results are obtained with silver layers.

The dielectric material layers are in particular based on tantalum (V) oxide, zinc oxide, tin (IV) oxide, niobium (V)



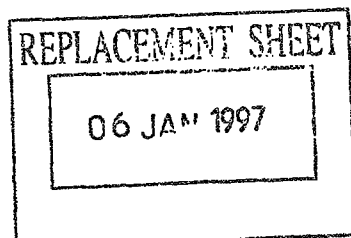
oxide, titanium (IV) oxide or a mixture of certain of these oxides. It is also possible for one of the layers to be constituted by two superimposed oxide sublayers, one being of tin (IV) oxide and the other of an oxide making it possible to improve the wetting of the layers having infrared reflection properties, such as tantalum (V) oxide or niobium (V) oxide in accordance with French patent application 93/01546 filed on 11.2.1993 and European patent application 94 400 289.8 filed on 10.2.1994, or titanium (IV) oxide.

Each of the oxides given above has advantages. Thus, tin (IV) oxide and zinc oxide have high deposition speeds when deposited by reactive cathodic sputtering, which is of great interest industrially. However, tantalum (V) oxide or niobium (V) oxide make it possible to obtain an increased durability of the stack with respect to mechanical or chemical aggressions and in particular lead to a better wetting of the silver layers when they are positioned below the latter. Mixed oxides can offer a compromise between the deposition rate and the durability and the superimposing of two oxide layers reconciles in an optimum manner the cost of the starting materials and a better wettability of the silver layers.

There is also a supplementary advantage linked with the use of tantalum (V) oxide. A glazing provided with a stack having such a dielectric material can be blue both in reflection and in transmission, which is appreciated from the esthetic standpoint and is also surprising, because usually, in transmission, the colour obtained is complimentary of that obtained in reflection, when the thin layers in question are only slightly or non-absorbent.

The preferred embodiment of the stack according to the invention consists of choosing a thickness of 7 to 9 nanometres for the first metal layer and a thickness of 11 to 13 nanometres for the second. Preferably the optical thickness of the first and third dielectric material layers is between 60 and 90 nanometres,

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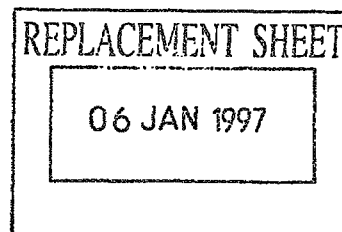
their geometrical thickness being in particular between 30 and 45 nanometres. The optical thickness of the second layer is between 140 and 170 nanometres, whilst its geometrical thickness is between 70 and 80 nanometres. It is pointed out that the optical thickness is defined in known manner by the product of the real geometrical thickness of the layer and the refractive index of the material forming it. As a function of the envisaged oxide type, the index varies between 1.9 and 2.1 for tin (IV) oxide or tantalum (V) oxide to approximately 2.3 for oxides of the niobium (V) oxide type.

The substrate coated with the stack according to the invention can advantageously be incorporated into a multiple glazing and in particular as one of the glass layers of an insulating double glazing. In the latter case, the double glazing has a light transmission value between 60 and 70% and a solar factor SF of 0.32 to 0.42, which make it completely suitable for use in buildings. Moreover, it preferably has in reflection a virtually unchanged visual appearance no matter what the vision incidence angle, the values of a^* , b^* in the colorimetry system (L, a^* , b^* , c^*) remaining unchanged, below 3 and negative.

It can also form part of a laminated glazing with in particular a light transmission of approximately 70%.

The advantageous details and features of the invention can be gathered from the following non-limitative examples illustrated by fig. 1.

It is pointed out that in all the examples the successive deposits of the layers of the stack take place by magnetic field-assisted cathodic sputtering, but any other deposition procedure can be envisaged provided that it permits a good control and monitoring of the thicknesses of the layers to be deposited.



The substrates on which the stacks are deposited are 4 mm thick soda-lime-silica glass substrates, except for examples 7 to 10, where the substrates are 6 mm thick. In double glazings, they are assembled with another substrate identical to the first, but in the blank state, by means of a 10 mm space of gas, except for the examples 7 to 8, where there is a 12 mm space of gas.

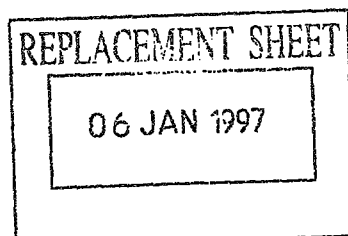
Fig. 1 shows the stack according to the invention and does not respect proportions with respect to the thicknesses of the layers so as to facilitate understanding. It is possible to see the previously defined substrate 1, surmounted by a first tin (IV) oxide or tantalum (V) oxide layer 2, a first silver layer 3, a titanium or Ni-Cr alloy barrier alloy (partly oxidized) 4, a second tin (IV) or tantalum (V) oxide layer 5, a second silver layer 6, another barrier layer 7 identical to the first and finally a last layer 8 of one of the same oxides.

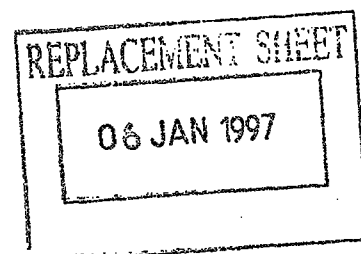
The deposition installation comprises at least one sputtering chamber equipped with cathodes having targets made from appropriate materials under which the substrate 1 successively passes. These deposition conditions for each of the layers are as follows:

the silver-based layers 3, 6 are deposited with the aid of a silver target, under a pressure of 0.8 Pa in an argon atmosphere, the layers 2, 5 and 8, when based on SnO_2 , are deposited by reactive sputtering with the aid of a tin target under a pressure of 0.8 Pa and in an argon/oxygen atmosphere, including 36 vol. % oxygen,

the layers 2, 5, 8, when based on Ta_2O_5 or Nb_2O_5 are deposited by reactive sputtering respectively with the aid of a tantalum target or a niobium target under a pressure of 0.8 Pa and in an argon/oxygen atmosphere, whereof approximately 10 vol. % is oxygen,

the layers 4, 7 based on Ni-Cr or titanium are deposited with the aid of a nickel-chromium alloy or titanium target under the





same pressure and in an argon atmosphere.

The power densities and travel speeds of the substrate 1 are adjusted in known manner so as to obtain the desired layer thicknesses.

In all the following examples, with the exception of the last, tantalum (V) oxide is chosen as the dielectric material for the layers 2, 5 and 8.

EXAMPLES 1 TO 5

Examples 1, 2 and 5 are comparative examples to the extent that in these three cases, the silver layers 3, 6 have either virtually identical thicknesses (example 1) or different thicknesses, but whereof the asymmetry is reversed compared with that recommended by the invention (examples 2 and 5). Examples 3 and 4 are in accordance with the teachings of the invention.

The following table 1 gives for each of the examples the nature and thicknesses (in nanometres) of the layers of the stack in question. The barrier layers 4, 7 are designated Ni-Cr, knowing that they are in fact partly oxidized once all the layers have been deposited.

TABLE 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	5
Glass	(1)	-	-	-	-	-
Ta ₂ O ₅	(2)	36.5	34.5	32	32	32
Ag	(3)	10	11.5	8	8	12
Ni-Cr	(4)	2	2	2	3	2
Ta ₂ O ₅	(5)	77.5	94.5	77.5	72.5	77.5
Ag	(6)	11	8	12	12.5	8
Ni-Cr	(7)	2	2	2	2	2
Ta ₂ O ₅	(8)	33.5	35	33.5	32	33.5

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The following table 2 indicates for each of the above examples the light transmission value T_L as a percentage, the solar factor SF calculated according to DIN standard 67507 (appendix A 233) as a percentage, the dominant wavelength values $\lambda_{\text{dom-t}}$ nanometres and the associated colouring purity pt as a percentage. Also indicated are the light reflection values R_L as a percentage, the dominant wavelength in reflection $\lambda_{\text{dom-r}}$ and the reflection purity p.r. as a percentage, the colorimetry measurements having been performed under normal incidence. All the measurements relate to the substrate fitted as a double glazing, with reference to the illuminant D₆₅.

TABLE 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
T_L	69	66	70	61	62
SF	42	42	42	38	38
$\lambda_{\text{dom-t}}$	493	489	498	490	478
p.t.	2	5	2	4	6
R_L	12	19	10	10	21
$\lambda_{\text{dom-r}}$	561	641	486	487	574
p.r.	3	9	3	6	35

The following table 3 gives the values of the dominant wavelength in reflection $\lambda_{\text{dom-r}}$, the reflection purity p.r. for certain of the preceding examples (the substrate still being installed in a double glazing), but on this occasion measured with an angle of incident relative to the perpendicular to the plane of the substrate of respectively 60 and 70°.

TABLE 3

	Ex. 1	Ex. 2	Ex. 3	Ex. 5
Lambda-dom-r (60°)	470	569	480	571
p.r. (60°)	5.4	3	4.68	8
R _L (60°)	19	28	20	27
Lambda-dom-r (70°)	462	490	481	-498
p.r. (70°)	4.3	4	3.0	0.8
R _L (70°)	32	39	34	36

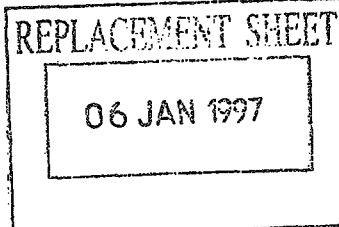
Other colorimetry measurements with incidence angles 0 and 60° were performed, on this occasion in the system (L*, a*, b*), for examples 2 and 3, as well as for example 5, which is in all points identical to example 3, except that the silver layers 3 and 6 were reversed and consequently falling outside the conditions recommended by the invention. Table 4 groups the values of a* and b*, as well as c* called saturation and equal to the square root of the sum of the squares of a* and b*.

TABLE 4

	Ex. 2	Ex. 3	Ex. 5
a* (0°)	12.2	- 0.9	- 2.2
b* (0°)	3.1	- 3.1	22
c* (0°)	12.6	3.2	22.1
a* (60°)	- 1	- 0.9	- 1.7
b* (60°)	2	- 3	6
c* (60°)	2.2	3.13	6.2

The following conclusions can be drawn from this information.

Under a normal incidence angle, i.e. giving different thicknesses to the silver layers and solely in such a way that the silver layer closest to the substrate is much thinner enabling the obtaining of glazings which are blue in reflection.



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It should be noted that the glazings according to the invention, particularly when the chosen dielectric is tantalum (V) oxide, are also blue in transmission.

Thus, only examples 3 and 4 have $\lambda_{\text{dom-r}}$ values of approximately 486 nanometres and $\lambda_{\text{dom-t}}$ values of 490 nanometres, according to table 2. However, the glazings of examples 1 and 5 have in reflection a yellow shade, whereas that of example 2 is a red-purple shade.

In addition, the colouring purity in reflection p.r. of example 2, close to 10%, is much higher than that of examples 3 and 4 according to the invention. (This value of p.r. is even higher for example 5).

Moreover, the glazings of examples 3 and 4 according to the invention have a good selectivity of at least 1.6 or 1.7 with a solar factor remaining equal to or below 42%.

Thus, the obtaining of a favourable colorimetry according to the invention is not to the detriment of the solar protection performance characteristics of the glazings in question.

Tables 3 and 4 make it possible to evaluate the uniformity of the appearance in reflection of the glazings according to certain of the preceding examples. Table 3 shows that the glazing according to example 3 in accordance with the invention retains a blue colour in reflection, with a $\lambda_{\text{dom-r}}$ value remaining virtually constant towards 486 at 0° to 481 at 70°, the purity in reflection also remaining very moderate.

However, the glazing according to example 1, where the silver layers approximately have the same thickness, passes from a yellow colour in reflection under normal incidence to a blue and then violet colour at 60 and then 70°.

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Table 4 confirms that only example 3 according to the invention makes it possible to maintain an identical coloured appearance in reflection no matter what the incidence angle, because the values of a^* and b^* remain virtually unchanged, as does the saturation c^* .

This is not the case with the glazings of examples 2 and 5, where the values of a^* and b^* change completely as a function of the incidence angle. Thus, the value of a^* passes, for the glazing of example 2, from a very high positive value of 12.2 at 0° to a very low negative value of -1 at 60° .

Thus, only the examples according to the invention reconcile the selectivity and appearance uniformity.

EXAMPLES 6 AND 7

These two examples use as the dielectric material tin (IV) oxide and not tantalum (V) oxide and use for the barrier layers either titanium (example 6) or Ni-Cr (example 7).

The following table 5 indicates the thickness values in nanometres used for each of the stack layers:

TABLE 5

		Ex. 6	Ex. 7
Glass	(1)	-	-
SnO ₂	(2)	34	32
Ag	(3)	8	8
Ti or Ni-Cr	(4)	1	1.5
SnO ₂	(5)	77	74.5
Ag	(6)	12	11.6
Ti or Ni-Cr	(7)	1	1.5
SnO ₂	(8)	35	33

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The thus coated substrates were installed in double glazings, as explained hereinbefore. The photometric measurements on the double glazings appear in table 6 (measurements under normal incidence).

TABLE 6

	Ex. 6	Ex. 7
T_L	66	75
SF	38	39
R_L	10.4	9.4
Lambda-dom-r	511	484
p.r.	2	2
a*	-	- 0.5
b*	-	- 1.1

These glazings, like those of examples 3 and 4, reveal no significant modification of their visual appearance in reflection, no matter what the measurement angle. In reflection they have a colour towards the greens for example 6 and towards the blues for example 7, but these colours remain very neutral, in view of the very low purity values associated therewith.

Laminated glazings incorporating the covered substrates of the stack according to the invention retain the favourable colorimetry observed in the case of monolithic substrates or substrates installed in double glazings.

Thus, the substrate covered with the stack according to example 3 was assembled with another substrate of the same type, but without a layer, using a standard, 0.3 mm thick, polyvinyl butyral film.

The following table 7 gives for said laminated glazing the already explained values of T_L , p.t. lambda-dom-t, a* and b* in connection with the appearance in transmission, as well as the corresponding values R_L , p.r. lambda-dom-r, a* and b* concerning

the appearance in reflection on the side of the substrate provided with the stack of layers (same units as hereinbefore).

TABLE 7

T_L	70
p.t.	1.2
lambda-dom-t	502
a^*	- 3.27
b^*	0.52
R_L	14
p.r.	8
lambda-dom-r	483
a^*	- 2.2
b^*	- 4.4

Table 7 shows that the incorporation of substrates covered in accordance with the invention in a laminated glazing structure leads to no deterioration of their esthetic colorimetry. The thus obtained laminated glazing remains in the blues or greens, both in transmission and in reflection.

Examples 3, 4 and 6 according to the invention relate to its "first variant" mentioned hereinbefore, i.e. respecting a choice of relative thicknesses between the three oxide layers 2, 5 and 8 which is specific and approximately as follows. The thickness of the layer 2 is approximately equal to that of the layer 8 and the thickness of the layer 5 (in the centre) is slightly greater than the sum of the thicknesses of the two other layers 2 and 8 (in these examples reference can be made to either the geometrical thickness or the optical thickness, because the three layers are made from the same oxide).

The "second variant" according to the invention will now be

illustrated by the following examples and more particularly example 8. In this variant, the thickness ratios between the oxide layers 2, 5 and 8 are slightly modified, the optical thickness of the layer 2 being significantly (25%) higher than that of the layer 8. The optical thickness of the layer 5 (or the sum of the optical thicknesses of the different sublayers forming it) is here approximately equal to the sum of the optical thicknesses of the two other layers 2 and 8.

EXAMPLE 8

The substrate according to example 8 is covered with a stack similar to that described for example 7, the layers 2, 5 and 8 being of tin (IV) oxide, but of different thicknesses.

The following table 8 gives the thickness values in nanometres of all the layers of the stack in question.

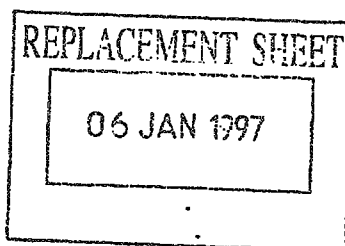
TABLE 8

		Ex. 8
Glass	(1)	-
SnO ₂	(2)	41
Ag	(3)	8
Ni-Cr	(4)	1.5
SnO ₂	(5)	74.5
Ag	(6)	12
Ni-Cr	(7)	1.5
SnO ₂	(8)	33

The substrate is fitted in a double glazing. The photometric measurements performed on the double glazing are given in table 9 (measured under normal incidence).

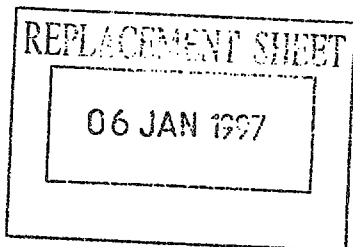
TABLE 9

	Ex. 8
T_L	75
SF	39
R_L	9.1
Lambda-dom-r	486
p.r.	1
a^*	- 0.7
b^*	- 0.5



Comparing these results with those obtained in example 7, it can be seen that identical values of T and SF are obtained. The appearance in reflection is also in the blues, with an even more neutral colour, because the purity is approximately 1% and the values of a^* and b^* are both well below 1. Another advantage of the stack type according to example 7 is that it more easily permits slight thickness variations in the stack layers, from one point to the other of the substrate, without giving rise to noticeable modifications of its visual appearance.

Thus, on performing measurements of a^* and b^* in reflection at different points of the substrate according to example 8 fitted in a double glazing, it is found that the value differences remain below 1, i.e. differences which cannot be noticed by the human eye, even if each of the layers has local thickness variations of $\pm 4\%$. This is very important from the industrial standpoint, because it makes it more easily possible to obtain glazings which are both uniform, i.e. having no local appearance modifications, and reproducible, i.e. having an identical appearance between individual glazings or between individual glazing batches. This means that for a given production line, which has its own performance limits, particularly with regards to the regularity of the layers obtained, such a stack will be less



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"sensitive" than others to thickness variations of the layers imposed by the line and will consequently have a better optical quality.

Conversely, on imposing a given optical quality, it is possible with this type of stack, to use a production line under less draconian conditions or to use a production line having slightly inferior performance characteristics.

It is also advantageous from the industrial standpoint for the layer 5 to have a thickness roughly equal to the sum of the thicknesses of the layers 2 and 8. Thus, it is then sufficient to use two targets, here of tin, whereof it is possible to regulate the power values supplied "once and for all" in their respective deposition chambers. The layer 2 is then obtained by the passage of the substrate under one of the targets with settings permitting the deposition of a predefined adequate thickness. In the same way, the layer 8 is obtained by the passage of the substrate under the second target with settings making it possible to obtain the deposition of a previously defined adequate thickness. The layer 5 is obtained by consecutive passages of the substrate under each of the targets, so that on the substrate are superimposed a layer thickness corresponding to that of the layer 2 or 8 and then a layer thickness corresponding to that of the layer 8 or 2, i.e. the sum of the thicknesses of these two layers is formed without calling on a third target.

EXAMPLES 9 TO 12

The aim of these examples is to optimize the wettability and therefore the performance characteristics of at least one of the silver layers. They follow the teaching of European patent application 94 400 289.8.

In the case of examples 9 and 10, the layers 2 and 8 are once

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again of tin (IV) oxide, but the layer 5 is subdivided into two superimposed sublayers, the first 5 being of tin (IV) oxide and the second 5 bis of tantalum (V) oxide (for example 9) or niobium (V) oxide (for example 10). A thin metallic sublayer can be optionally provided below the silver layer 6 and which is of NiCr or Sn.

In the case of examples 11 and 12, the layer 2 is also subdivided into two superimposed sublayers, the first 2 being of tin (IV) oxide and the second 2 bis of tantalum (V) oxide (for example 11) or niobium (V) oxide (for example 12). An optional, thin metallic sublayer can be provided beneath the silver layer 3.

Thus, in the case of examples 9 and 10, the wettability of the second silver layer 6 is optimized, whereas in the case of examples 11 and 12, the wettability of the two silver layers 3, 6 is optimized.

Table 10 gives the thicknesses in nanometres of the layers present.

TABLE 10

		Ex. 9 and 10	Ex. 11 and 12
Glass	(1)	-	-
SnO ₂	(2)	41	30 - 31
Ta ₂ O ₅ or Nb ₂ O ₅ (2bis)		0	10
Ag	(3)	8	8
Ni-Cr	(4)	1.5	1.5
SnO ₂	(5)	64	64
Ta ₂ O ₅ or Nb ₂ O ₅ (5bis)		10	10
Ag	(6)	12	12
Ni-Cr	(7)	1.5	1.5
SnO ₂	(8)	33	33

There is a slight improvement to the solar control performance characteristics of the stacks. Moreover, the use of oxides known for their hardness, such as tantalum or niobium (V) oxide, helps to optimize the durability of the overall stack and in particular its mechanical durability. This mechanical strength increase is particularly pronounced for examples 11 and 12.

In conclusion, the glazings according to the invention have both a good selectivity of approximately 1.70, a uniform visual appearance which is attractive to the eye (particularly a blue or green colour in reflection and optionally also in transmission), as well as a range of light transmission values making them suitable for use as solar control glazings in buildings, particularly in the form of double glazings, the stack of thin layers preferably being on face 2 (the faces are conventionally numbered from the outside to the inside of the room in question).

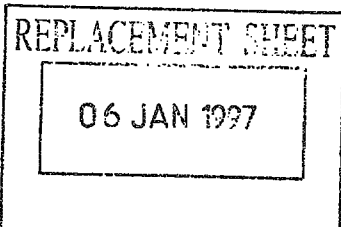
The substrates covered with layers according to the invention can also be used with advantage for producing laminated glazings.



CLAIMS

1. Transparent substrate (1), more particularly of glass and having multiple thin layers on which are successively deposited:
a first dielectric material layer (2),
a first layer (3) having infrared reflection properties, particularly based on metal,
a second dielectric material layer (5),
a second layer (6) having infrared reflection properties, particularly based on metal,
a third dielectric material layer (8),
characterized in that the thickness of the first layer (3) having infrared reflection properties corresponds to approximately 50 to 80%, particularly 55 to 75% and preferably 60 to 75% of that of the second layer having infrared reflection properties (6).
2. Transparent substrate (1) according to claim 1, characterized in that the optical thickness of the second dielectric material layer (5) is equal to or greater than 110% of the sum of the optical thicknesses of the two other dielectric material layers (2, 8) and preferably corresponds to approximately 110 to 120% of said sum.
3. Transparent substrate (1) according to claim 2, characterized in that the optical thicknesses of the first dielectric material layer (2) and the third dielectric material layer (8) are approximately equal.
4. Transparent substrate (1) according to claim 1, characterized in that the optical thickness of the first dielectric material layer (2) is greater than the optical thickness of the third dielectric material layer (8) the optical thickness of the first layer (2) corresponding to at least 110%, particularly at

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least 110 to 140% and preferably approximately 125% of the optical thickness of the third layer (8).

5. Transparent substrate (1) according to claim 4, characterized in that the optical thickness of the second dielectric material layer (5) is approximately equal to the sum of the optical thicknesses of the first and third dielectric layers (2, 8).

6. Transparent substrate (1) according to any one of the preceding claims, characterized in that each of the layers having infrared reflection properties (3, 6) is surmounted by a thin, partly oxidized, "barrier" metal layer (4, 7), particularly based on titanium or a nickel-chromium alloy and preferably having a thickness of 1 to 3 nanometres.

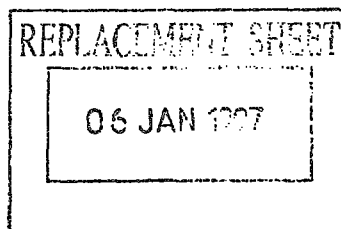
7. Transparent substrate (1) according to any one of the preceding claims, characterized in that the layers (3, 6) having infrared reflection properties are based on silver.

8. Transparent substrate (1) according to any one of the preceding claims, characterized in that at least one of the three dielectric material layers (2, 5, 8) is based on tantalum (V) oxide, tin (IV) oxide, zinc oxide, niobium (V) oxide, titanium (IV) oxide or mixtures of said oxides, or is constituted by a first tin (IV) oxide layer surmounted by a second layer of tantalum (V) oxide, niobium (V) oxide or titanium (IV) oxide.

9. Transparent substrate according to any one of the preceding claims, characterized in that the thickness of the first layer having infrared reflection properties (3) is between 7 and 9 nanometres.

10. Transparent substrate (1) according to any one of the preceding claims, characterized in that the thickness of the second layer having infrared reflection properties (6) is between 1 and 13 nanometres.

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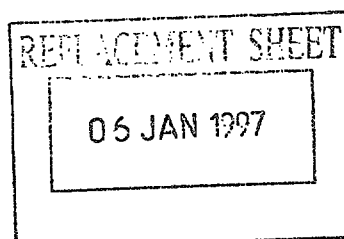




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11. Transparent substrate (1) according to any one of the preceding claims, characterized in that the optical thickness of the first (2) and third (8) dielectric material layer is between 60 and 90 nanometres and in that the optical thickness of the second dielectric material layer (5) is between 140 and 170 nanometres.
12. Laminated glazing, characterized in that it incorporates the substrate according to any one of the preceding claims and in that it has a light transmission T_L of approximately 70% and a colour in external reflection in the blues or greens.
13. Multiple glazing, particularly double glazing, characterized in that it incorporates the substrate according to any one of the claims 1 to 11 and in that it has a light transmission (T_L) between 60 and 70% and a solar factor (SF) of 0.32 to 0.42.
14. Multiple glazing, particularly double glazing, characterized in that it incorporates the substrate according to any one of the claims 1 to 11 and it has a colour in external reflection in the blues and optionally also in transmission, particularly when the layers (2, 5, 8) are of tantalum (V) oxide.
15. Multiple glazing according to claim 14, characterized in that its optical appearance in external reflection remains virtually identical no matter what the incidence angle, the values of a^* and b^* in the colorimetry system (L, a^* , b^* , c^*) remaining unchanged and below 3 and having a negative sign.
16. Application of the substrate according to any one of the claims 1 to 11 to the production of multiple insulating glazings, such as double glazings or laminated glazings.

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ABSTRACT

TRANSPARENT SUBSTRATES PROVIDED WITH A STACK OF THIN LAYERS,
APPLICATION TO THERMAL INSULATION AND/OR SOLAR CONTROL GLAZINGS

The invention relates to a transparent substrate (1), more particularly of glass and having multiple thin layers on which are successively deposited:

a first dielectric material layer (2),

a first layer (3) having infrared reflection properties, particularly based on metal,

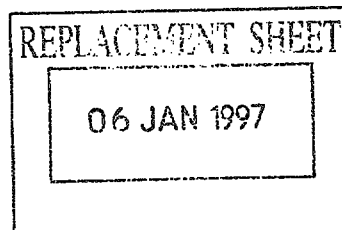
a second dielectric material layer (5),

a second layer (6) having infrared reflection properties, particularly based on metal,

a third dielectric material layer (8),

characterized in that the thickness of the first layer (3) having infrared reflection properties corresponds to approximately 50 to 80%, particularly 55 to 75% and preferably 60 to 75% of that of the second layer having infrared reflection properties (6).

FIGURE 1



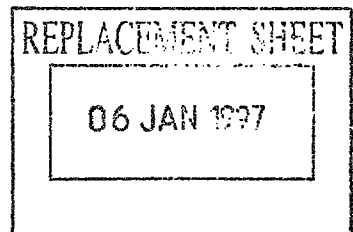
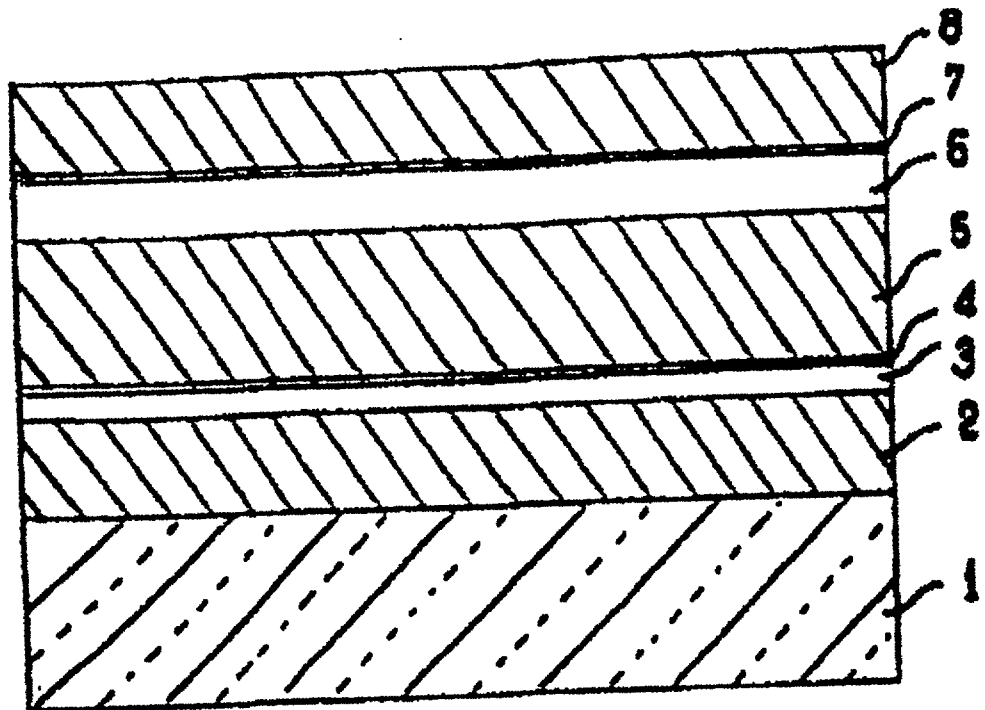


FIG. 1

solar factor value SF. (It is pointed out that the solar factor of a glazing is the ratio between the total energy entering the room through said glazing and the incident solar energy).

5 The object of the invention is to develop a transparent substrate carrying a stack of thin layers having two layers reflecting radiation in the infrared and which are more particularly of a metallic type, so that they have a high selectivity, i.e. the highest possible T_L/SF ratio for a given value of T_L , whilst ensuring that said substrate has an aesthetically satisfactory visual appearance in reflection.

10

The invention relates to a multiple glazing pane or laminated glazing pane, incorporating a transparent substrate, particularly of glass and having multiple thin layers, on which are successively deposited a first dielectric material layer, a first layer having infrared reflection properties and in particular based on metal, a second
15 dielectric material layer, a second layer having infrared reflection properties, particularly based on metal, and finally a third dielectric material layer. According to the invention, the thickness of the first layer having infrared reflection properties, i.e. that closest to the carrying substrate, corresponds to approximately 50 to 70% of the thickness of the second layer having infrared reflection properties. An advantageous
20 example corresponds to a thickness of the first layer corresponding to approximately 65% of the second.

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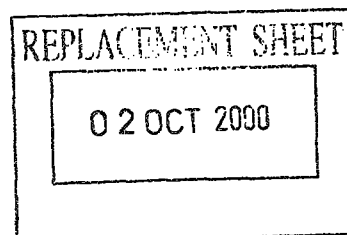
This great asymmetry in the thicknesses of the layers having infrared reflection properties makes it possible to advantageously modify the values of T_L and SF so as to
25 obtain glazings having a good selectivity, i.e. a good compromise between the need for transparency and that of providing an optimum protection against solar heat rays.

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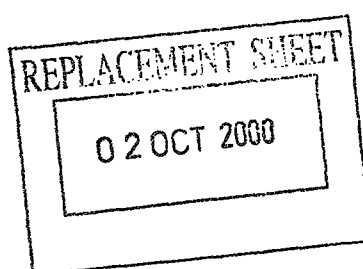
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oxide, titanium (IV) oxide or a mixture of certain of these oxides. It is also possible for one of the layers to be constituted by two superimposed oxide sublayers, one being of tin (IV) oxide and the other of an oxide making it possible to improve the wetting of the layers having infrared reflection properties, such as tantalum (V) oxide or niobium (V) oxide in accordance with the teaching of French patent FR-A-2701475 and European patent application EP-A-611213, or titanium (IV) oxide.

Each of the oxides given above has advantages. Thus, tin (IV) oxide and zinc oxide have high deposition speeds when deposited by reactive cathodic sputtering, which is of great interest industrially. However, tantalum (V) oxide or niobium (V) oxide make it possible to obtain an increased durability of the stack with respect to mechanical or chemical aggressions and in particular lead to a better wetting of the silver layers when they are positioned below the latter. Mixed oxides can offer a compromise between the deposition rate and the durability and the superimposing of two oxide layers reconciles in an optimum manner the cost of the starting materials and a better wettability of the silver layers.

There is also a supplementary advantage linked with the use of tantalum (V) oxide. A glazing provided with a stack having such a dielectric material can be blue both in reflection and in transmission, which is appreciated from the aesthetic standpoint and is also surprising, because usually, in transmission, the colour obtained is complimentary of that obtained in reflection, when the thin layers in question are only slightly or non-absorbent.

The preferred embodiment of the stack according to the invention consists of choosing a thickness of 7 to 9 nanometres for the first metal layer and a thickness of 11 to 13 nanometres for the second. Preferably the optical thickness of the first and third dielectric material layers is between 60 and 90 nanometres,



“sensitive” than others to thickness variations of the layers imposed by the line and will consequently have a better optical quality.

5 Conversely, on imposing a given optical quality, it is possible with this type of stack, to use a production line under less draconian conditions or to use a production line having slightly inferior performance characteristics.

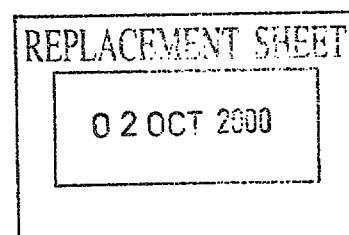
10 It is also advantageous from the industrial standpoint for the layer 5 to have a thickness roughly equal to the sum of the thicknesses of the layers 2 and 8. Thus, it is then sufficient to use two targets, here of tin, whereof it is possible to regulate the power values supplied “once and for all” in their respective deposition chambers. The layer 2 is then obtained by the passage of the substrate under one of the targets with settings permitting the deposition of a predefined adequate thickness. In the same way, the layer 8 is obtained by the passage of the substrate under the second target with settings making it possible to obtain the deposition of a previously defined adequate thickness. 15 The layer 5 is obtained by consecutive passages of the substrate under each of the targets, so that on the substrate are superimposed a layer thickness corresponding to that of the layer 2 or 8 and then a layer thickness corresponding to that of the layer 8 or 2, i.e. the sum of the thicknesses of these two layers is formed without calling on a third target. 20

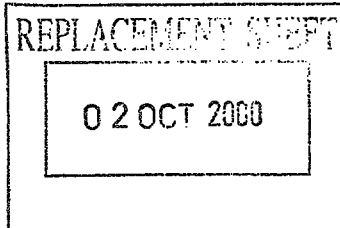
EXAMPLES 9 TO 12

25 The aim of these examples is to optimize the wettability and therefore the performance characteristics of at least one of the silver layers. They follow the teaching of European patent application EP-A-611213.

In the case of examples 9 and 10, the layers 2 and 8 are once

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CLAIMS:

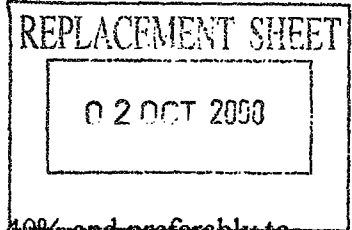
1. Multiple glazing pane or laminated glazing pane, incorporating a transparent substrate (1), notably of glass, having thin multiple films on which are deposited, in succession:

- a first coating of dielectric material (2),
- a first film (3) having reflective properties in the infrared, notably based upon metal,
- a second coating of dielectric material (5),
- a second film (6) having reflective properties in the infrared, notably based upon metal,
- a third coating of dielectric material (8), characterized in that the thickness of the first film having reflective properties in the infrared (3), that is to say that which is nearest the supporting substrate, corresponds to from 50 to 70%, and notably 65%, of that of the second film having reflective properties in the infrared (6), in such a way that the visual appearance of said glazing pane in external reflection remains virtually identical, whatever the angle of incidence, the values of a^* and b^* in the colorimetric system (L, a^* , b^* , c^*) remaining unchanged and of negative sign.

2. Glazing pane according to claim 1, characterized in that the optical thickness of the second coating of dielectric material (5) is greater than or equal to 110% of the sum of the optical thicknesses of the other two coatings (2, 8) of dielectric material, and preferably corresponds to 110-120% of said sum.

3. Glazing pane according to claim 2, characterized in that the optical thicknesses of the first coating of dielectric material (2) and of the third coating of dielectric material (8) are equal.

4. Glazing pane according to claim 1, characterized in that the optical thickness of the first coating of dielectric material (2) is greater than the optical thickness of the third coating of dielectric material (8), the optical thickness of the first coating (2)



corresponding, notably, to at least 110%, notably at least 110 to 140% and preferably to 125%, of the optical thickness of the third coating (8).

5. Glazing pane according to claim 4, characterized in that the optical thickness of the second coating of dielectric material (5) is equal to the sum of the optical thicknesses of the first and third dielectric coatings (2, 8).

6. Glazing pane according to one of the preceding claims, characterized in that each of the films having reflective properties in the infrared (3, 6) is overlain by a partly oxidized "barrier" fine metallic film (4, 7), notably based upon a nickel-chrome alloy or titanium, and preferably having a thickness of 1 to 3 nanometres.

7. Glazing pane according to one of the preceding claims, characterized in that the films (3, 6) having reflective properties in the infrared are based upon silver.

8. Glazing pane according to one of the preceding claims, characterized in that at least one of the three coatings of dielectric material (2, 5, 8) is based upon tantalum oxide, tin oxide, zinc oxide, niobium oxide, titanium oxide or a mixture of said oxides, or again is constituted of a first film of tin oxide overlain by a second film of tantalum oxide, niobium oxide or titanium oxide.

9. Glazing pane according to one of the preceding claims, characterized in that the thickness of the first film having reflective properties in the infrared (3) lies between 7 and 9 nanometres.

10. Glazing pane according to one of the preceding claims, characterized in that the thickness of the second film having reflective properties in the infrared (6) lies between 11 and 13 nanometres.

11. Glazing pane according to one of the preceding claims, characterized in that the optical thickness of the first (2) and third (8) coatings of dielectric material lies between



60 and 90 nanometres and in that the optical thickness of the second coating of dielectric material (5) lies between 140 and 170 nanometres.

12. Glazing pane, notably double glazing pane, according to one of claim 1 to 11, characterized in that it has a light transmission (T_L) of from 60 to 70% and a solar factor (FS) of 0.32 to 0.42.

13. Glazing pane, notably double glazing pane, according to one of claims 1 to 11, characterized in that it has a colour in external reflection in the blues and possibly also in transmission, notably when the coatings (2, 5, 8) are of tantalum oxide.

14. Glazing pane according to any preceding claim, in which the values of a^* and b^* remain less than 3.

