Title: COATED SUBSTRATE WITH A VERY LOW SOLAR FACTOR

Abstract: The present invention relates to coated substrates with a very low solar factor, in particular transparent substrates coated with a stack of layers comprising one or more layers of metal, and comprising, in succession starting from the substrate, at least: first layer of dielectric material, first absorbent layer, an infrared reflective layer, second absorbent layer, last layer of dielectric material, the thickness and the nature of the layers being selected such that the total light absorption of the coated substrate is higher than or equal to 35% when the substrate is a 6 mm clear soda-lime glass. Such coated substrates are used, for example, as glazing units for buildings or vehicles, in laminated structures or as optical filters.
Coated Substrate with a Very Low Solar Factor

The present invention relates to coated substrates, in particular transparent substrates coated with a stack of layers comprising one or more metal layers.

Such coated substrates are used, for example, as glazing units for buildings or vehicles, in single, double or laminated structures and as optical filters.

It is desirable that glazing units for buildings or vehicles do not allow too substantial a proportion of total incident solar radiation to pass through so as not to overheat the interior of the building or the passenger compartment, while providing a light transmission (\(LT = \text{percentage of incident light flux - of illuminant D65 - transmitted by a substrate}\)) that is suitable in order to supply a sufficient level of illumination to the interior of the building. The transmission of the total incident solar radiation can be expressed in terms of the solar factor (\(SF = \text{percentage of incident energy radiation, which, on the one hand, is directly transmitted by the substrate and, on the other hand, is absorbed by this then radiated by its opposite face to the energy source}\)). These somewhat conflicting requirements express the requirement to obtain a glazing unit with an elevated selectivity (\(S\)), defined by the ratio of light transmission to the solar factor. It is also desirable that glazing units meet certain aesthetic criteria in terms of light reflection (\(LR = \text{percentage of incident light flux - of illuminant D65 - reflected by a substrate}\)) and reflected colour.

The light absorption (\(LA\)) is the percentage of incident light flux (of illuminant D65) absorbed by a substrate, the sum of \(LT + LR + LA\) being equal to 100%.

The present description uses the definitions of the Internationale Commission on Illumination – “Commission Internationale de l’Eclairage” (CIE).
Substrates bearing a coating with a high light transmission, low emissivity and reduced solar factor are known. The patent documents FR 2,641,271 and FR 2,641,272 of the Applicant describe a substrate of vitreous material bearing a multilayer coating, which comprises a reflective layer of silver sandwiched between two transparent and non-absorbent layers, one on the bottom and one on the top.

The patent document FR 2,733,495 of the Applicant describes sun protection stacks based on two layers of silver separated by non-absorbent layers, in particular of metal oxides. A fine sacrificial metal layer is deposited on each of the silver layers. This fine metal layer acts as a barrier to protect the silver layer from oxidation when the upper metal oxide layer is deposited. Its thickness is adjusted so that when the upper layer is deposited, it oxidises sufficiently to permit a maximum light transmission. In FR 2,733,495 the stack retains a high light transmission in the order of 76% on a 6 mm single clear glass substrate and a low absorption. The solar factor is in the order of 43% when the substrate is a 6 mm single clear glass sheet and in the order of 37% for a double glazing unit.

To further decrease the solar factor of the glazing a possibility could be to increase the thickness of the metal layer(s) of the stack or to increase the number of metal layers. However, this has the disadvantage of increasing the light reflection (LR) and of producing reflected colours in the glazing that are generally considered unpleasing.

US 6,190,776 describes a heat treatable stack formed from a first dielectric layer / a first layer of Cr / a layer of Ag or Cu / a second layer of Cr / a second dielectric layer. This stack provides non-neutral reflected colours both before and after thermal treatment. For architectural applications with a low solar factor, the colorimetric index a* varies between 1.35 and 10.30 and index b* varies between -7.80 and 31.70, which gives purple to orange colourations. The light absorption of the glazing are around 23% after heat treatment.
Metallic barriers are also known that have a protective function during a subsequent thermal treatment. These barrier layers do not remain metallic, but oxidise during the thermal treatment and are no longer absorbent.

There are also sun protection stacks comprising absorbent layers. However, it is not obvious to add an absorbent layer without causing the light transmission to fall. Therefore, it is particularly difficult to maintain a significant selectivity while retaining a stack that is neutral (or aesthetically acceptable) in reflection.

EP 185 314 describes a stack comprising an absorbent layer, a layer of silver and a fine layer of stainless steel. The light reflection in this case is very high (up to 67%) and the LT is not more than 12%. These characteristics do not meet the desired criteria.

Stacks of the type Si₃N₄ / NiCr / Ag / NiCr / Si₃N₄ are described in US 5,800,933. Non-absorbent layers of Si₃N₄ can be doped with stainless steel. The nickel-chromium layers have thicknesses in the order of 0.7 to 0.8 nm. These stacks are adapted to obtain a light transmission of more than 70% and a low emissivity. The total absorption of such a stack on a clear glass is very low (in the order of 14% in a double glazing, LT = 70%, LR = 16%).

WO 02/48065 describes stacks with double layers of silver comprising an absorbent layer inserted directly between two dielectric layers. This absorbent layer must be placed either between the two layers of silver, "in" the intermediate dielectric, or "in" the upper dielectric. The solar factor attained is 26 to 31% in double glazing. The aim of these stacks is to preserve good optical properties after toughening. The insertion of an absorbent layer between two dielectric layers has the drawback to complicate the manufacturing process. Indeed, the deposition conditions of the dielectric layer (in non metallic condition) must be interrupted to deposit an absorbing layer in metallic conditions.
EP 1 032 543 describes a sun protection stack comprising a non-absorbent layer, a first infrared reflective layer, a sacrificial barrier, a second non-absorbent layer, a second infrared reflective layer, a second sacrificial barrier and a last non-absorbent layer. An absorbent layer is added under either one of the infrared reflective layers. Such stacks have a solar factor in the order of 31% (in double glazing).

However, there is a need to provide coated substrates, wherein the solar factor is still lower and the other optical characteristics remain favourable: low reflection from the coated side and from the non-coated side, high selectivity, aesthetically pleasing reflected colour etc.

It has been discovered that the required combination of optical properties can be achieved and other advantages obtained by a substrate coated with different layers in accordance with claim 1 of the present invention.

The present invention in particular relates to a substrate coated with a stack of layers, comprising, in succession starting from the substrate, at least:

i) a layer of dielectric material,
ii) an absorbent layer,
iii) an infrared reflective layer,
iv) an absorbent layer,
v) a layer of dielectric material,

the thickness and the nature of the layers being selected such that the stack of layers would provide a 6 mm clear soda-lime glass with a light absorption (with respect to the glass side : Lₐ₆₅) higher than or equal to 35%, preferably higher than 37%, and further preferred higher than 39%, and lower than 67%, preferably lower than 60%, and further preferred lower than 55%. It is to be noted that the light absorption to be considered is the light absorption of the finished product, the coated substrate being either heat treated or not heat treated.
The term substrate should be understood to mean any transparent substrate generally made of vitreous material, whether clear or coloured: glass, glass ceramic, organic glass, polycarbonate, PET, various transparent polymers; in particular of soda-lime glass.

It is particularly advantageous if the stack comprises at least two infrared reflective layers deposited in the following sequence, starting from the substrate:

- a first layer of dielectric material,
- a first absorbent layer,
- a first infrared reflective layer,
- an intermediate layer,
- a last infrared reflective layer,
- a last absorbent layer,
- a last layer of dielectric material.

A further possibility could be to deposit more than two infrared reflective layers. In this case, at least a first absorbent layer must be deposited between the first layer of dielectric material and the first reflective layer and at least a second absorbent layer must be deposited between the last reflective layer and the last layer of dielectric material, each reflective layer being separated from the following one by an intermediate layer, in particular a layer of dielectric material, and/or possibly a barrier layer. Hence, all the reflective layers are sandwiched between the 2 absorbent layers. Therefore, in the above sequence of layers, it is the intermediate layer, which can be replaced by an alternating arrangement of intermediate / reflective / intermediate layers.

It is also possible to deposit more than two absorbent layers. Therefore, the possibility is not excluded to deposit one or more absorbent layers between two layers of infrared reflective materials.
The total thickness of the infrared reflective layer or layers is generally greater than 10 nm, preferably in the range of between 13 and 40 nm, and further preferred between 18 and 35 nm. In the special case where the stack comprises two layers of silver, the total thickness of the two layers is preferably greater than 25 nm, and further preferred greater than 27 nm.

In particular, the stack according to the invention comprises a sacrificial layer disposed between the infrared reflective layer and the following dielectric layer.

According to a preferred embodiment of the invention, the stack essentially consists of a succession of the following layers, starting from the substrate:

a) a layer of dielectric material,
b) an absorbent layer,
c) an infrared reflective layer,
d) a sacrificial barrier,
e) a layer of dielectric material,
f) an infrared reflective layer,
g) an absorbent layer also having the function of a barrier,
h) a layer of dielectric material.

The dielectric materials of the layers can be selected from metal oxides, nitrides and oxynitrides, e.g. aluminium oxide (Al₂O₃), aluminium nitride (AlN), aluminium oxynitride (AlNₓOᵧ), magnesium oxide (MgO), niobium oxide (Nb₂O₅), silicon dioxide (SiO₂), silicon nitride (SiNₓ), titanium dioxide (TiO₂), bismuth oxide (Bi₂O₃), yttrium oxide (Y₂O₃), tin oxide (SnO₂), tantalum oxide (Ta₂O₅), zinc oxide (ZnO), zirconium oxide (ZrO₂), zinc stannate (ZnSn₃O₈) or from sulphides such as zinc sulphide (ZnSₓ). These compounds can be in stoichiometric or non-stoichiometric form. In general, these compounds have a spectral absorption index k over the entire visible spectrum of lower than 0.1.

These compounds can be used alone or in mixture. They constitute transparent, non-absorbent materials, which allow the light reflection LR to be
adjusted and colours reflected by optical interference effects to be neutralised. A
dielectric layer can comprise two or more layers of different material.

The materials of the absorbent layers are selected from materials
having a spectral absorption index on the wavelength of 580 nm (k_{580}) higher than
0.8, in particular higher than 1, and further preferred higher than 1.2. Such materials
are, for example, metals such as titanium, zirconium, stainless steel, niobium, zinc,
chromium, nickel, and alloys of these metals, or metal nitrides such as titanium or
zirconium nitride.

The materials of the infrared reflective layers generally comprise silver
or alloys of silver with other metals such as platinum or palladium.

When the substrate is a clear soda-lime sheet of glass with a thickness
of 6 mm, the light transmission of the coated substrate is preferably higher than 25%,
and further preferred higher than 30%, and is preferably lower than 60%, preferably
lower than 55%, and further preferred lower than 50%. The light reflection both with
respect to the layer (LR_{r}) and with respect to the substrate (LR_{s}) of the coated
substrate is preferably lower than 30%, more preferred lower than 23%, and further
preferred lower than 20%, and is generally higher than 8%, and in particular higher
than 10%. The LR values with respect to the layer or with respect to the substrate
are, of course, not necessarily identical.

In a preferred manner, the coated substrate according to the invention
has an aesthetically pleasing reflected colour, i.e. which is neither pink nor yellow,
but neutral or bluish or turquoise. In particular, the reflected colour, with respect to
the glass, has a colorimetric index a_{*} in the range of between 0 and -10, preferably
in the range of between -1 and -8, and a colorimetric index b_{*} in the range of
between 0 and -20, preferably in the range of between -1 and -15, and further
preferred between -2 and -10. b_{*} is preferably lower than a_{*}. These values are
expected for the finished products, either heat treated or not.

The coated substrates according to the invention can be incorporated
in particular into single or multiple glazing units in buildings, in particular double
8
glazing units, but also in laminated glazing units, and used for automotive
applications such as the roofs of vehicles, side rear windows or rear windows.

In a double glazing, the sun protection coating according to the
invention could be deposited in position 2 or possibly in position 3, the faces of each
of the two glass sheets being numbered from the outside of the buildings inwards.

Advantageously, the solar factor of a double glazing (6 mm sheet -
space of 15 mm - 6 mm sheet) is lower than 35%, preferably lower than 30%, and
further preferred lower than 26%. The selectivity of the double glazing (LT/SF) is
preferably higher than 1.3, preferably higher than 1.5.

The glazing according to the invention advantageously has a reflected
colour, with respect to the outside, wherein the colorimetric index a* is in the range
of between 0 and -10, preferably in the range of between -1 and -8, and the
colorimetric index b* is in the range of between 0 and -20, preferably between -1
and -15, and further preferred between -2 and -10.

Moreover, the glazing according to the invention has an angular
stability such that, when the angle of incidence varies from 60°, the variation in the
colorimetric indexes a* and b* is less than 6, preferably less than 4, and further
preferred less than 2.

In a preferred embodiment, the glazing according to the invention
comprises a coated substrate which combines the following characteristics : a LT
comprised between 30 and 55%, preferably between 31 and 46%, a LR, with respect
to the non coated side, comprised between 8 and 25%, preferably between 9 and
24%, and colorimetric indexes with respect to the non coated side : a* comprised
between 0 and -8, preferably between 0 and -5, and b* comprised between 0 and
-20, preferably between -2 and -18.

The present invention is described in more detail in a non-restrictive
manner in the following examples.
Examples:

Each of the examples corresponds to a product formed from a substrate sheet of clear soda-lime glass with a thickness of 6 mm, which is introduced into a coating line comprising successive vacuum deposition chambers (at a pressure of about 0.3 Pa) containing magnetron-assisted sputtering cathodes.

Example 1:

The following stack of successive layers is manufactured as follows:

- a first dielectric layer of zinc oxide with a thickness of 39 nm is deposited by sputtering a metal target of zinc in a reactive atmosphere of oxygen.

- a first absorbent layer of titanium with a thickness of 4.5 nm is deposited by sputtering a metal target of titanium in an inert atmosphere of argon.

- a first layer of silver with a thickness of 17 nm is deposited by sputtering a metal target of silver in an inert atmosphere of argon.

- a 2nm barrier layer of titanium is deposited by sputtering a titanium target in an inert atmosphere of argon. This layer will in fact oxidise during deposit of the following layer over most of its thickness. It should be noted that once oxidised, the layer has a greater thickness than the one it would have had in a metallic state.

- a second dielectric layer of zinc oxide with a thickness of 84 nm is deposited by sputtering a metal target of zinc in a reactive atmosphere of oxygen.

- a second layer of silver with a thickness of 14 nm is deposited by sputtering a metal target of silver in an inert atmosphere of argon.

- a second absorbent 4 nm layer of titanium is deposited by sputtering a metal target in an inert atmosphere. This layer has a dual function:
it constitutes a sacrificial protective barrier for the silver layer by preventing all contact of the silver layer with the reactive atmosphere of the following layer, but it is sufficiently thick for a substantial portion of its thickness to remain metallic. Of the 4 nm thickness deposited, it is estimated that half the titanium deposited will oxidise and that 2 nm of the thickness will remain metallic. In the completed stack, therefore, there will be 2 nm of metallic Ti and approximately 4 nm of TiO₂.

- a third dielectric layer of zinc oxide 28 nm thick is deposited by sputtering a metal target of zinc in a reactive atmosphere of oxygen.

The optical properties of the substrate coated with this stack are collated in Table II below.

**Examples 2 to 14:**

The stacks of examples 2 to 14 can be deposited using the same operating method as in example 1. Table I below indicates the nature and thickness of the different layers deposited in each of the examples. The thicknesses are given in nm and are the thicknesses of the layers as deposited before any oxidation stage.
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The optical properties of each of the coated substrates are collated in Table II below. The solar factor (SF) values are calculated according to the En 410 standard.
Table II:

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CLAIMS

1. Transparent substrate coated with a stack of layers comprising, in succession starting from the substrate, at least:

   a) a first layer of dielectric material,
   b) a first absorbent layer,
   c) an infrared reflective layer,
   d) a second absorbent layer,
   e) a last layer of dielectric material,

   the thickness and the nature of the layers being selected such that the stack of layers would provide a 6 mm clear soda-lime glass with:

   i) a light absorption in the range of between 35 and 67%, preferably in the range of between 37 and 60%, and further preferred between 39 and 55%, and

   ii) a reflected colour, with respect to the glass, having a colorimetric index a* in the range of between 0 and -10, preferably in the range of between -1 and -8, and a colorimetric index b* in the range of between 0 and -20, preferably in the range of between -1 and -15, and further preferred between -1 and -10.

2. Coated substrate according to the preceding claim, characterised in that it comprises at least two infrared reflective layers disposed in the stack in the following sequence, starting from the substrate:

   a) a first layer of dielectric material,
   b) a first absorbent layer,
   c) a first infrared reflective layer,
   d) an intermediate layer,
   e) a last infrared reflective layer,
   f) a last absorbent layer,
g) a last layer of dielectric material.

3. Coated substrate according to the preceding claim, characterised in that the intermediate layer comprises a sequence of layers as follows:
   a) a first dielectric layer,
   b) an infrared reflective layer,
   c) a second layer of dielectric material.

4. Coated substrate according to any one of the preceding claims, characterised in that it comprises at least one sacrificial layer disposed between an infrared reflective layer and a following layer of dielectric material.

5. Coated substrate according to any one of the preceding claims, characterised in that the material of the dielectric layers comprises one or more compounds selected from among the following: aluminium oxide (AlO₃), aluminium nitride (AlN₃), aluminium oxynitride (AlNₓOᵧ), magnesium oxide (MgO₃), niobium oxide (NbO₃), silicon dioxide (SiO₂), silicon nitride (SiNₓ), titanium dioxide (TiO₂), bismuth oxide (BiO₃), yttrium oxide (YO₃), tin oxide (SnO₂), tantalum oxide (TaO₃), zinc oxide (ZnO₂), zirconium oxide (ZrO₂), zinc stannate (ZnSnO₃) or zinc sulphide (ZnS₂).

6. Coated substrate according to any one of the preceding claims, characterised in that the infrared reflective layer or layers comprises/comprise silver or an alloy of silver with other metals.

7. Coated substrate according to any one of the preceding claims, characterised in that the material of the absorbent layers is selected from materials having a spectral absorption index on the wavelength of 580 nm (k₅₈₀) higher than 0.8, in particular higher than 1, and further preferred higher than 1.2.

8. Coated substrate according to any one of the preceding claims, characterised in that the material of the absorbent layers is selected from metals such as titanium, zirconium, stainless steel, niobium, zinc, chromium, nickel, and alloys of these metals or from metal nitrides such as titanium or zirconium nitride.
9. Coated substrate according to any one of the preceding claims, characterised in that the light transmission of the coated substrate is in the range of between 25 and 60%, preferably between 30 and 55%, when the substrate is a 6 mm clear soda-lime glass.

10. Coated substrate according to any one of the preceding claims, characterised in that the light reflection with respect to the layer side (LR₁) of the coated substrate is less than 30%, preferably in the range of between 8 and 25%, and further preferred between 10 and 20%.

11. Coated substrate according to any one of the preceding claims, characterised in that the light reflection with respect to the non coated side (LR₂) of the coated substrate is lower than 30%, preferably in the range of between 8 and 23%, and further preferred between 10 and 18%.

12. Coated substrate according to any one of the preceding claims, characterised in that the total thickness of the infrared reflective layer or layers is greater than 10 nm, preferably in the range of between 13 and 40 nm, and further preferred between 18 and 35 nm.

13. Coated substrate according to any one of the preceding claims, characterised in that the reflected colour, with respect to the glass, has a colorimetric index a* in the range of between 0 and -10, preferably in the range of between -1 and -8, and a colorimetric index b* in the range of between 0 and -20, preferably in the range of between -1 and -15, and further preferred between -1 and -10.

14. Glazing comprising a coated substrate according to any one of the preceding claims, characterised in that it has a solar factor of less than 35%, preferably less than 30%, and further preferred less than 26%.

15. Glazing according to the preceding claim, characterised in that the selectivity (LT/SF) is higher than 1.3, preferably higher than 1.5.
16. Glazing according to either one of Claims 15 and 16, characterised in that the reflected colour with respect to the outside has a colorimetric index $a^*$ in the range of between 0 and -10, preferably in the range of between -1 and -8, and a colorimetric index $b^*$ in the range of between 0 and -20, preferably in the range of between -1 and -15, and further preferred between -1 and -10.

17. Glazing according to any one of claim 14 to 16, characterized in that it comprises a coated substrate with a LT comprised between 30 and 55%, a LR, with respect to the non coated side, comprised between 8 and 25% and colorimetric indexes with respect to non coated side, $a^*$ comprised between 0 and -8 and $b^*$ comprised between 0 and -20.
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

| IPC7 | C03C17/36 |

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)

| IPC7 | C03C |

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 practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 6 190 776 B1 (TURKIYE SISE CAM) 20 February 2001 (2001-02-20) abstract figure 1,2 figure 6A column 3, line 16 - line 20 column 5, line 9 - line 31 column 8, line 10 - line 47 column 9, line 8 - line 14 example 3 examples T1372IG,-T1378IG claims 1,4,14</td>
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* Special categories of cited documents:

- **A** document defining the general state of the art which is not considered to be of particular relevance
- **E** earlier document but published on or after the international filing date
- **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- **O** document referring to an oral disclosure, use, exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed

- **T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- **X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- **Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- **G** document member of the same patent family

Date of the actual completion of the international search: 24 November 2004

Date of mailing of the international search report: 01/12/2004

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Authorized officer: Picard, S
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