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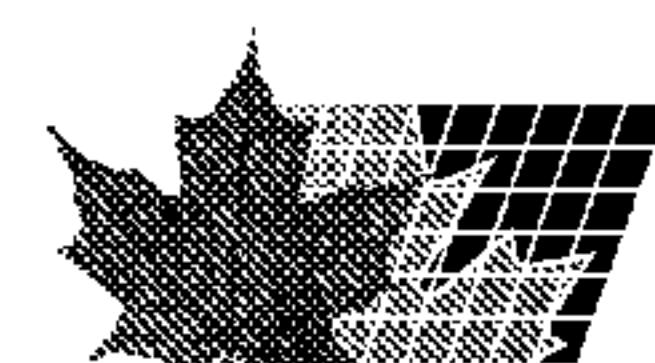
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(54) Titre : SUBSTRAT AVEC REVETEMENT DE PROTECTION SOLAIRE A REFLECTANCE ELEVEE
(54) Title: SOLAR CONTROL COATED SUBSTRATE WITH HIGH REFLECTANCE

(57) **Abrégé/Abstract:**

A solar control coated substrate with high reflectance (RL) and comprises a pyrolytically-formed coating layer containing oxides of tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, characterised in that the coating layer further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, whereby the so-coated substrate has a reflectance of at least 10 %. The invention covers a process for making such a coated substrate and a glazing panel incorporating such a coated substrate.



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(54) Title: SOLAR CONTROL COATED SUBSTRATE WITH HIGH REFLECTANCE (57) Abstract A solar control coated substrate with high reflectance (RL) and comprises a pyrolytically-formed coating layer containing oxides of tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, characterised in that the coating layer further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, whereby the so-coated substrate has a reflectance of at least 10 %. The invention covers a process for making such a coated substrate and a glazing panel incorporating such a coated substrate.		

Solar control coated substrate with high reflectance.

The present invention relates to a solar control coated substrate with high reflectance and to a process for making such a coated substrate.

Transparent solar control panels have become much in demand for use as exterior glazing for buildings. In addition to having aesthetic appeal
5 they offer advantages in providing protection against solar radiation and its dazzling effects, giving occupants of the building a screen against overheating and glare.

The panels comprise at least one sheet of a transparent substrate material, typically soda-lime glass, carrying a coating to provide the specific
10 properties required. The solar control requirement is that the panel shall not pass too great a proportion of total incident solar radiation, thereby resisting overheating of the building interior. The transmission of total incident solar radiation may be expressed in terms of the "solar factor" (FS). As used herein, the term "solar factor" means the sum of the total energy directly transmitted
15 and the energy which is absorbed and re-radiated on the side away from the energy source, as a proportion of the total radiant energy incident on the coated substrate.

Although architects seeking glazing panels for use in buildings have traditionally tended to favour panels with low levels of reflection, a
20 changing perception of the aesthetic appeal has led to increasing demands for panels with high levels of reflection, while retaining a low solar factor.

Properties of the coated substrate discussed herein are based on the standard definitions of the International Commission on Illumination - Commission Internationale de l'Eclairage ("CIE").

25 The "luminous transmittance" (TL) is the luminous flux transmitted through a substrate as a percentage of the incident luminous flux.

The "luminous reflectance" (RL) is the luminous flux reflected from a substrate as a percentage of the incident luminous flux.

The "selectivity" of a coated substrate for use in a building
30 glazing panel is the ratio of the luminous transmittance to the solar factor (TL/FS).

The "purity" (p) of the colour of the substrate refers to the

excitation purity in transmission or reflection measured with Illuminant C. It is specified according to a linear scale on which a defined white light source has a purity of zero and the pure colour has a purity of 100%. Illuminant C represents average daylight having a colour temperature of 6700°K.

5 The term "refractive index" (n) is defined in the CIE International Lighting Vocabulary, 1987, page 138.

The "dominant wavelength" (λ_D) is the peak wavelength in the range transmitted or reflected by the coated substrate.

A number of techniques are known for forming coatings on a
10 vitreous substrate, including pyrolysis. Pyrolysis generally has the advantage of producing a hard coating, precluding the need for a protective layer. The coatings formed by pyrolysis have durable abrasive- and corrosion-resistant properties. It is believed that this is due in particular to the fact the process involves deposition of coating material on to a substrate which is hot. Pyrolysis
15 is also generally cheaper than alternative coating processes such as sputtering, particularly in terms of the investment in plant.

A wide variety of coating materials have been proposed for modifying the optical properties of glazing panels. Tin oxide (SnO_2) has been widely used, often in combination with other materials such as other metal
20 oxides.

Our GB patent 1455148 teaches a method for pyrolytically forming a coating of one or more oxides (e.g. ZrO_2 , SnO_2 , Sb_2O_3 , TiO_2 , Co_3O_4 , Cr_2O_3 , SiO_2) on a substrate, primarily by spraying compounds of a metal or silicon, so as to modify the light transmission and/or light reflection of the
25 substrate. Our GB patent 2078213, which relates to a method for pyrolytically forming a coating by two separate sprays to achieve high rates of coating build-up, discloses tin oxide coatings doped with fluorine or antimony. Our GB patent 2200139 relates to forming a pyrolytic tin oxide coating from a precursor containing at least two additives such as oxidising agents, sources of
30 fluorine and sources of metal.

The use of a tin oxide coating with a small proportion of antimony oxide has been found to offer several advantageous combinations of optical properties. Our GB patent applications 2302101 ('101) and 2302102 ('102) describe anti-solar glazing panels comprising a pyrolytic coating layer of
35 oxides of tin and antimony in which the Sb/Sn molar ratio is from 0.01 to 0.5. The '101 coating is applied by liquid spray and has a thickness of at least 400 nm, a luminous transmittance of less than 35% and a selectivity of at least 1.3. The '102 coating is applied by chemical vapour deposition (CVD) and has a

solar factor below 70%.

It is an object of the present invention to provide a pyrolytically formed coated substrate which imparts solar screening properties and a high reflectance.

5 We have discovered that this and other useful objectives can be achieved by including certain defined additives when applying to a substrate a pyrolytic coating comprising tin and antimony oxides.

Thus, according to a first aspect of the present invention, there is provided a transparent substrate carrying a pyrolytically-formed coating layer
10 containing oxides of tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, characterised in that the coating layer further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, whereby the so-coated substrate has a reflectance (RL) of at least 10%.

15 The invention further provides a method of forming a transparent coated substrate comprising the pyrolytic deposition from a reactant mixture onto the substrate of a coating layer containing tin oxide and antimony in a Sb/Sn molar ratio from 0.01 to 0.5, said reactant mixture comprising a source of tin and a source of antimony, characterised in that the
20 reactant mixture further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, whereby the so-coated substrate has a reflectance (RL) of at least 10%.

It has been found that a coating of oxides of tin and antimony
25 modified by an additive as described above (referred to herein as a "modified tin oxide/antimony coating") retains the anti-solar properties of the coating without the additive but also can display a much higher level of reflectance.

A coated substrate according to the invention may be employed as a single-sheet glazing panel or alternatively in a multiple-glazed or laminated
30 panel assembly. In a multiple glazing or laminated assembly it is preferred that just one of the constituent sheets carries the coating.

Although the invention is described herein primarily with reference to glazing panels for buildings, panels according to the invention are suitable for other applications such as vehicle windows, in particular vehicle
35 sunroofs.

Because coatings produced by pyrolysis generally have a greater mechanical resistance than coatings produced by other methods the choice of location of the coating can be made according to the obtained properties of the

panel rather than for reasons of protecting the coated surface against exposure to wear or corrosion.

Coated substrate sheets according to the invention preferably have a low solar factor of around 70% or less, more preferably at most 65%. In the case of multiple glazing, locating the coating on the outer face, i.e. towards the energy source, generally improves the solar factor over that achieved with the coating facing away from the energy source.

The Sb/Sn molar ratio in the coating layer is preferably at least 0.03, most preferably at least 0.05. This assists in ensuring a high level of absorption. On the other hand the said ratio is preferably less than 0.21, with a view to achieving a high level of luminous transmittance (TL). Most preferably the ratio is less than 0.16, since above this level the coating layer displays an unduly high level of absorption, coupled with poor selectivity.

It is desirable that the glazing panel shall transmit a reasonable proportion of visible light in order to allow both good natural illumination inwards into the building or vehicle and good visibility outwards. Thus it is desirable to increase the selectivity of the coating, i.e. to increase the ratio of the transmittance to the solar factor. Indeed it is preferred that the selectivity be as high as possible. The light transmission (TL) of a coated substrate according to the invention is typically in the range 35 to 76%, depending upon the specific additive employed.

Preferably, the modified tin oxide/antimony coating has a thickness of from 100 to 500 nm.

As mentioned above with reference to prior documents such as GB patent 2078213 one previously proposed constituent element in tin/antimony oxide coatings was fluorine, formed for example from reactants containing tin, antimony and fluorine in the ratios $Sb/Sn = 0.028$, $F/Sn = 0.04$. However we have discovered that the presence of fluorine tends to hinder the incorporation of antimony into the coating. For example reactants containing antimony and tin in the ratio $Sb/Sn = 0.028$ gave a coating with an Sb/Sn ratio of about 0.057, whilst the same reactants plus a fluorine-containing reactant in an amount such that $F/Sn = 0.04$ gave a coating with an Sb/Sn ratio of about 0.038. Fluorine is therefore specifically excluded from the coatings of the present invention.

Preferably, to ensure high optical quality, any haze in the product should be less than 2%. The possibility of reducing haze by using an undercoat is discussed later in this description.

One preferred group of metals from which to select the additive

comprises aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, and zinc. Using these additives permits the production of coatings presenting low levels of haze.

Another preferred group of metals from which to select the additive comprises aluminium, chromium, cobalt, iron, magnesium and zinc. These additives have the most favourable effect on the reflectance of the product.

Thus to form a coating having high reflectance and low haze, the additive is preferably selected from aluminium, chromium, cobalt, iron, magnesium, and zinc, more preferably from chromium, iron and magnesium. Chromium is most preferred: it permits the achievement of a product with high reflectance and very low haze, and which can have a neutral aspect in reflection.

As described and claimed in our copending patent application of the same date as the present application, the reflectance of the coating may be further improved by the application of an outer reflective layer having a geometric thickness in the range 30 to 150 nm and a refractive index in the range 2.0 to 2.8.

Application of a pyrolytic coating to flat glass is best achieved when the glass is newly formed, e.g. as it leaves a float glass line. This provides economic benefits in avoiding the need to reheat the glass for the pyrolytic reactions to take place, and in the quality of the coating, since the newly formed glass surface is in pristine condition.

Preferably the source of tin is selected from one or both of SnCl_4 and monobutyl trichloro tin ("MBTC"). The source of antimony may be selected from one or more of SbCl_5 , SbCl_3 , organo antimony compounds such as $\text{Sb}(\text{OCH}_2\text{CH}_3)_3$, $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$, $\text{Cl}_2\text{SbOCHClCH}_3$, $\text{Cl}_2\text{SbOCH}_2\text{CHCH}_3\text{Cl}$ and $\text{Cl}_2\text{SbOCH}_2\text{C}(\text{CH}_3)_2\text{Cl}$. The source of the additive may similarly be a suitable chloride or organo-metallic compound of the respective element.

The sources of tin, antimony and additive are preferably formed into a single starting solution, described herein as the "reactant mixture", so as to be applied simultaneously to the substrate.

The reactant mixture may be applied to the substrate by chemical vapour deposition (CVD or "vapour pyrolysis") or as a liquid spray ("liquid pyrolysis"). Especially for liquid spray deposition, the proportions of tin, antimony and additive in the formed coating can differ significantly from those in the reactant mixture solution such that it is necessary to alter the

relative concentrations of reactants to obtain layers with the desired proportions in the coating.

In the reactant mixture the proportion of tin is typically in the range 20 to 45% by weight and the proportion of antimony is typically in the range 0.5 to 2.5% by weight of the total mixture. The proportion of additive is preferably in the range 0.2 to 3.6% by weight. Because it may be difficult to establish the proportion of the additive in the finished coating the quantity of additive to be employed is determined at the stage of forming the reactant mixture.

To form the modified tin oxide/antimony coating by CVD, the substrate is brought into contact, in a coating chamber, with the reactant mixture comprising the sources of tin, antimony and additive. The reactant mixture is typically supplied through a first nozzle. Where this mixture comprises chlorides which are liquid at ambient temperature, it is vaporised in a heated current of anhydrous carrier gas such as nitrogen. Vaporisation is facilitated by the atomization of these reagents in the carrier gas. To produce the oxides, the chlorides are brought into the presence of water vapour conducted through a second nozzle.

Methods and devices for forming such a coating are described for example in French patent No 2348166 or in French patent application No 2 648 453 A1. These methods and devices lead to the formation of particularly strong coatings with advantageous optical properties.

To form the coating by a spray method, the substrate may be brought into contact with a spray of droplets containing the sources of tin, antimony and additive. The spray is applied by one or more spray nozzles arranged to follow a path which provides the coating across the width of the ribbon to be coated.

CVD offers benefits over sprayed liquids in providing coatings of regular thickness and composition, such uniformity of the coating being important where the product is to cover a large area. A spray coating also tends to retain traces of the sprayed droplets and of the path of the spray gun. Moreover, the pyrolysis of sprayed liquids is essentially limited to the manufacture of oxide coatings, such as SnO_2 and TiO_2 . It is also difficult to make multi-layer coatings using sprayed liquids because every coating deposition produces a significant cooling of the substrate. Furthermore, CVD is more economic in terms of raw materials, leading to lower wastage.

However despite such disadvantages of the spray method it is nevertheless convenient and inexpensive to apply and employs simple

equipment. It is thus often adopted, especially for formation of thick coating layers.

If desired an intermediate coating layer may be positioned between the substrate and the modified tin oxide/antimony coating layer, as an
5 "undercoat" for the modified layer, to adjust the optical properties of the coating. For example, it has been found that in the pyrolytic deposition of a tin oxide coating from tin chloride on a soda-lime glass substrate, sodium chloride tends to become incorporated into the coating as a result of reaction of the glass with the coating precursor material or its reaction products, leading to
10 haze in the coating. The presence of an undercoat can reduce or eliminate the haze. One effect of the undercoat layer is to inhibit the migration of sodium ions from a soda-lime glass substrate, whether by diffusion or otherwise into the modified tin oxide/antimony coating. Such diffusion may occur during formation of the coating or during a subsequent high temperature treatment.

15 We have also noted that for a tin oxide/antimony coating a selected undercoat layer can give a more neutral tint in reflection, which is widely considered to add to the aesthetic appeal of the coating.

In one embodiment of the invention the undercoat layer may be pyrolytically formed in an incompletely oxidized state by contacting the
20 substrate in an undercoating chamber with undercoat precursor material in the presence of oxygen in insufficient quantity for full oxidation of the undercoat material on the substrate. The expression "incompletely oxidized material" is used herein to denote a true sub-oxide, that is to say an oxide of a lower valency state of a multivalent element (for example VO_2 or TiO), and also to
25 denote an oxide material which contains oxygen gaps in its structure: an example of the latter material is SiO_x where x is less than 2, which may have the general structure of SiO_2 but has a proportion of gaps which would be filled with oxygen in the dioxide.

A preferred example of the material for the undercoat layer is
30 alumina with a small proportion of vanadium oxide. Such an alumina/vanadium material is described in GB 2248243. The preferred geometric thickness of an undercoat layer of this material is between 40 and 100 nm, for example about 80 nm.

If a glass substrate bearing an incompletely oxidised coating is
35 exposed to an oxidizing atmosphere for a sufficiently long period of time, it may be expected that the coating will tend to become fully oxidized so that its desired properties are lost. Therefore, such undercoat is over-coated with the modified tin oxide/antimony coating layer while it is still in an incompletely

oxidized state, and while the substrate is still hot, thereby to preserve such undercoat in an incompletely oxidized state. The time during which the freshly undercoated glass substrate may be exposed to an oxidizing atmosphere such as air and before the undercoat is over-coated, without
5 damaging the properties of the undercoat, will depend on the temperature of the glass during such exposure and on the nature of the undercoat.

Advantageously, said undercoating chamber is surrounded by a reducing atmosphere. This assists in preventing ambient oxygen from entering the chamber and accordingly allows better control of the oxidizing conditions.
10 The oxygen required for the undercoating reaction need not be pure oxygen and can accordingly be supplied from a controlled source of air.

Glazing panels incorporating coated substrates according to the invention may be manufactured as follows. Each pyrolytic coating step may be carried out at a temperature of at least 400°C, ideally from 550°C to 750°C.
15 The coatings can be formed on a sheet of glass which moves in a tunnel oven or on a glass ribbon during formation, whilst it is still hot. The coatings can be formed inside the lehr which follows the glass ribbon forming device or inside the float tank on the top face of the glass ribbon whilst the latter is floating on a bath of molten tin.

20 The invention will now be described in more detail, with reference to the following non-limiting examples.

In the Examples the Sb/Sn molar ratio in the coating layers was determined by an X-ray analysis technique in which the number of X-ray counts of the respective elements was compared. While this technique is not as
25 precise as if a calibration by chemical dosage were made, the similarity of antimony and tin means that they respond similarly to X-rays. The ratio of the measured number of observed counts of the respective elements thus provides a close approximation to their molar ratio.

The initials in the headings in the accompanying tables (TL, TE
30 etc.) have the meanings described above.

Examples 1 to 13

A coating was applied to clear soda-lime float glass of 6 mm thickness at a coating station located at a position in a float chamber where the glass was at a temperature in excess of 550°C. A reactant mixture solution
35 comprising, monobutyl trichloro tin ("MBTC"), $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$, a chromium precursor and 4% by weight of a stabiliser methylisobutyl ketone $\text{C}_4\text{H}_9\text{COCH}_3$ was sprayed on to the glass through a reciprocating spray head to form a coating comprising an oxidised mixture of tin, antimony and chromium.

The proportions of Sn, Sb and Cr in the solution were respectively 37.35%, 0.783% and 0.5% by weight, i.e. a Sb/Sn ratio in the solution of 0.02. The accompanying Table 1 shows the thickness of the resultant coated substrate and its Sb/Sn ratio, together with its reflectance and other optical properties.

5 For the other examples, the procedure of Example 1 was followed but with variations in the choice of additive and its proportion in the reactant mixture as shown in Table 2 below. The proportions of the respective components were percentages by weight of the whole mixture.

10 It should be borne in mind that comparisons of the respective reflectance values between different examples can only be made for similar thicknesses and Sb/Sn ratios because these parameters are of great importance for the reflectance value. For example, two coatings of the same composition will show differences in reflectance as a function of their thickness.

15 Examples 1 to 4 show that chromium as the additive gives a coating with low haze and with increased reflectance. Haze is sometimes present but is very low if an SiO_2 undercoat is deposited between the glass and coating (see example 4).

Examples with Fe and examples with Mg as the additive show high reflectance values.

TABLE 1

Example	Additive element	Additive in solution	TL	RL	TE	FS	TL/FS	TL/TE	Haze (Haze with undercoat)	Thickness	[Sb]/[Sn]
		%	%	%	%	%				nm	
1	Cr	0.5	69	15.7	58	65	1.06	1.19	1.5	368	0.05
2	Cr	1	67	16.5	61	67	1.00	1.10	3	364	0.05
3	Cr	2	61	16	60	66	0.92	1.02	1	319	0.06
4	Cr	1	53	17	43	54	0.98	1.23	1.6 (0.26)	392	0.12
5	Fe	0.5	69	17	62	68	1.01	1.11	1.5	310	0.17
6	Fe	1	53	11	42	54	0.98	1.26	1.5	345	0.17
7	Fe	2.4	62	20	58	64	0.97	1.07	6.7	331	0.21
8	Mg	0.5	69	14	59	67	1.03	1.17	3.5	337	0.09
9	Zn	1	53	15	46	57	0.93	1.15	1.3	307	0.09
10	Al	0.9	55	14	48	58	0.95	1.15	1.2	323	0.22
11	Co	3.55	48	14	40	52	0.92	1.20	6.4 (1.27)	307	0.24
12	Mn	0.5	46	10	37	51	0.90	1.24	1.6	331	0.17
13	Ni	0.35*	39	10	36	49	0.80	1.08	0.47	241	0.20
14	V	5	49	11	41	53	0.92	1.20	0.68	329	0.24
15	Zr	2	58	12	44	55	1.05	1.32	6.5	389	0.06
16	Zr	2	44	11	32	47	0.94	1.38	20.5 (12.4)	573	0.06
Comp1	<i>Sb alone</i>	0.07	34	10	32	46	0.74	1.06	0.54	337	0.21
Comp2	<i>Sb alone</i>	0.02	71	12	57	65	1.09	1.25	0.4	264	0.06
Comp3	<i>Sb alone</i>	0.04	41	12	32	47	0.87	1.28	0.78	350	0.11

*: Solution further contains 0.1% Ti to improve the nickel compound stability

TABLE 2

Example	Metal Content	Sn content (%)by weight	Sb content % by weight	Sb/Sn
1	0.5 % Cr	37.35	0.747	0.02
2	1.0% Cr	35.55	0.711	0.02
3	2.0% Cr	32	0.640	0.02
4	1.0% Cr	35.58	1.423	0.04
5	0.5 % Fe	36.23	2.53	0.07
6	1.0% Fe	34.57	2.42	0.07
7	2.4% Fe	31.14	2.18	0.07
8	0.5% Mg	35.31	2.47	0.07
9	1.0% Zn	35.69	2.50	0.07
10	0.90 % Al	32.29	2.26	0.07
11	3.55% Co	31.14	2.18	0.07
12	0.5% Mn	36.06	2.52	0.07
13	0.35% Ni	36.60	2.56	0.07

Example 14:

A reactant mixture solution comprising monobutyl trichloro tin ("MBTC"), SbCl_3 , a vanadium precursor (vanadium triacetylacetonate) and 4% by weight of a stabiliser (methylisobutyl ketone $\text{C}_4\text{H}_9\text{COCH}_3$) was sprayed on to the glass through a reciprocating spray head to form a coating comprising an oxidised mixture of tin, antimony and vanadium. The Sb/Sn ratio in the solution was 0.07. The reflectance value obtained for this example was low.

Examples 15 and 16:

The procedure of Example 1 was followed but with variations in the choice of additive and its proportion in the reactant mixture. The additive is zirconium.

These examples presented good reflectance but high haze, even with an undercoat.

Examples 17 to 27

An undercoat was applied to clear soda-lime float glass of 6 mm thickness at a coating station located at a position in a float chamber where the glass was at a temperature in excess of 550°C . A solution in glacial acetic acid of 220 g/l aluminium acetylacetonate and 12 g/l vanadium triacetylacetonate

was sprayed on to the glass through a reciprocating spray head to form an undercoat of about 80 nm thickness and comprising an oxidised mixture of aluminium and vanadium.

5 The undercoated glass substrate was passed to a second coating station at which a reactant mixture solution comprising, monobutyl trichloro tin ("MBTC"), $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$, and an additive precursor was sprayed on to the glass through a reciprocating spray head to form a coating comprising an oxidised mixture of tin, antimony and aluminium. The proportions of additive and the Sb/Sn ratio in the solution were as mentioned in the accompanying
10 Table 3, which also shows the thickness of the resultant coated substrate and its Sb/Sn ratio, together with its reflectance and other optical properties.

Examples 28 to 33

Coated glass substrates prepared as in Examples 17 and 18 were formed into double glazing panels comprising the coated substrate and a
15 similar but uncoated soda-lime glass sheet.

The reflectance and other optical properties of the so-formed panels are shown in the accompanying Table 4. The position of the coating is indicated by the designations P1, P2 or P3, in which P1 represents the outward facing surface of the external sheet, P2 represents the inward facing surface of
20 the external sheet and P3 represents the outward facing surface of the internal sheet. The results of Examples 17 and 18 (with a monolithic sheet) are repeated in Table 3 for ease of comparison with the double glazed panels.

TABLE 3

Example	Additive	Additive in solution	Sb/Sn in solution	TL	λ_D	Purity (TL)	RL (CS)	λ_D	Purity (RL)	TE	FS	TL/TE	TL/FS	Haze	Sb/Sn	Thickness
		%		%	nm	%	%	nm	%	%	%			%		nm
17	Cr	0.5	0.02	75.9	552	1.6	13	600	2.6	64.8	71.2	1.17	1.07	0.29	0.06	240
18	Cr	0.5	0.04	61.7	488	2.3	13.1	576	10	53.2	62.1	1.16	0.99	0.18	0.15	220
19	Cr	0.5	0.04	65	486	2.7	13.7	565	5.4	55.6	64.6	1.17	1.01	0.2	0.13	190
20	Cr	2	0.07	70	571	8.8	11.1	-566	15.7	61.6	68.7	1.14	1.02	1.47	0.15	240
21	Mg	0.5	0.07	74.3	569	2.5	14.1	574	7.4	67.4	73	1.10	1.02	1.04	0.10	220
22	Fe	0.5	0.07	68.8	568	8.8	14.3	-544	12.3	61.1	68.3	1.13	1.01	1.87	0.20	320
23	Fe	2.4	0.07	74.5	571	11.3	12.9	-567	18.5	66.6	71.9	1.12	1.04	0.59	0.23	240
24	Fe	1	0.07	64.4	543	2	11.9	-531	9.5	53.1	62.6	1.21	1.03	0.73	0.23	240
25	Al	0.9	0.07	66.6	570	6.8	11.1	-567	12.9	60	67.6	1.11	0.99	0.31	0.32	220
26	Zn	1	0.07	67.7	556	3.4	12.7	-555	12.3	57.2	65.5	1.18	1.03	1.38	0.24	250
27	Mn	0.5	0.07	51.9	484	6	10.1	-552	5.1	41.1	54.2	1.26	0.96	1.13	0.17	340
Comp	Sb <i>alone</i>	0	0.07	29.6	476	11.9	9.6	-500	4	32.5	47.9	0.91	0.62	0.55	0.24	240

TABLE 4

Example	Position	TL	λ_D	Purity (TL)	RL (CS)	λ_D	Purity (RL)	TE	FS	TL/TE	TL/FS	Haze	Sb/Sn	Thickness
		%	nm	%	%	nm	%	%	%			%		nm
17	monolit.	75.9	552	1.6	13	600	2.6	64.8	71.2	1.17	1.07	0.29	0.06	240
28	P1	69.6	552	1.9	17.8	584	2.4	58.1	63.6	1.20	1.09			
29	P2	69.6	551	1.8	17.1	575	7.1	58.1	63.8	1.20	1.09			
30	P3	69.6	551	1.8	18.6	585	1.3	58.1	70.7	1.20	0.98			
18	monolit.	61.7	488	2.3	13.1	576	10	53.2	62.1	1.16	0.99	0.18	0.15	220
31	P1	56.5	490	2.3	16.3	575	6.9	47.7	54.2	1.18	1.04			
32	P2	56.7	490	2.2	14.1	558	6.7	47.8	54.4	1.19	1.04			
33	P3	56.7	490	2.2	18.7	573	5.4	47.8	67.3	1.19	0.84			

CS = coated side

The embodiments of the invention, in which an exclusive property or privilege is claimed are defined as follows:

1. A transparent substrate carrying a pyrolytically-formed coating layer containing oxides of tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, characterised in that the coating layer has a thickness of from 100 to 500 nm and in that the coating layer further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, whereby the so-coated substrate has a reflectance (RL) of at least 10%.
2. A transparent substrate carrying a pyrolytically-formed coating layer containing oxides of tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, characterised in that the coating layer further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, and in that the coated substrate further comprises an undercoat positioned between the substrate and the said coating layer, whereby the so-coated substrate has a reflectance (RL) of at least 10%.
3. A coated transparent substrate as claimed in claim 1 or 2, wherein the Sb/Sn molar ratio in said coating layer is in the range 0.03 to 0.21.
4. A coated transparent substrate as claimed in claim 3, wherein the Sb/Sn molar ratio is in the range 0.03 to 0.16.
5. A coated transparent substrate as claimed in any one of claims 1 to 4, wherein the additive is selected from aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, and zinc.
6. A coated transparent substrate as claimed in any one of claims 1 to 5, wherein the additive is selected from aluminium, chromium, cobalt, iron, magnesium and zinc.
7. A coated transparent substrate as claimed in any one of claims 1 to 6, wherein the additive is selected from chromium, iron and magnesium.
8. A coated transparent substrate as claimed in any one of claims 1 to 7, wherein the reflectance (RL) is at least 13%.
9. A coated transparent substrate as claimed in claim 2, wherein said coating layer has a thickness of from 100 to 500 nm.
10. A coated transparent substrate as claimed in any one of claims 1 to 9, wherein the said coating layer has a thickness of from 220 to 500 nm.

11. A coated transparent substrate as claimed in any one of claims 1 to 10, wherein the source of tin for said coating layer is selected from SnCl_4 or monobutyl trichloro tin.
12. A coated transparent substrate as claimed in any one of claims 1 to 11, wherein the source of antimony for said coating layer is selected from SbCl_5 , SbCl_3 and organo antimony compounds.
13. A coated transparent substrate as claimed in claim 12, wherein the source of antimony for said coating layer is an organo antimony compound selected from the group consisting of $\text{Sb}(\text{OCH}_2\text{CH}_3)_3$, $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$, $\text{Cl}_2\text{SbOCHClCH}_3$, $\text{Cl}_2\text{SbOCH}_2\text{CHCH}_3\text{Cl}$ and $\text{Cl}_2\text{SbOCH}_2\text{C}(\text{CH}_3)_2\text{Cl}$.
14. A coated transparent substrate as claimed in any one of claims 1 to 13, wherein the source of the additive for said coating layer is selected from a chloride or organo-metallic compound of the respective element.
15. A coated transparent substrate as claimed in any one of claims 1 to 14, which further comprises an undercoat positioned between the substrate and the coating layer.
16. A coated transparent substrate as claimed in claim 15, wherein the undercoat comprises alumina with a small proportion of vanadium oxide.
17. A coated transparent substrate as claimed in claim 16, wherein the undercoat has a geometric thickness comprised between 40 and 100 nm.
18. A coated transparent substrate as claimed in any one of claims 15 to 17, wherein the undercoat gives to the coating a more neutral tint in reflection.
19. A coated transparent substrate as claimed in any one of claims 1 to 18, having a solar factor (FS) of at most 70%.
20. A coated transparent substrate as claimed in claim 19, wherein the solar factor (FS) which is at most 65%.
21. A coated transparent substrate as claimed in any one of claims 1 to 20, having a luminous transmittance (TL) of between 35 and 76%.
22. A coated transparent substrate as claimed in any one of claims 1 to 21, wherein the coating layer consists essentially of an oxidised mixture of tin, antimony and the additive.
23. A coated transparent substrate as claimed in any one of claims 1 to 22, wherein the coating layer consists of an oxidised mixture of tin, antimony and the additive.
24. A glazing panel comprising a coated transparent substrate as defined in any one of claims 1 to 23.

25. A glazing panel as claimed in claim 24, comprising two or more substrate sheets of which one is a coated transparent substrate as defined in any one of claims 1 to 23.
26. A glazing panel as claimed in claim 24 or 25, for use as a building glazing panel.
27. A glazing panel as claimed in claim 24 or 25, for use as a vehicle window.
28. A glazing panel as claimed in any one of claims 24 to 27, wherein the coating is located to face the exterior of the building or vehicle.
29. A glazing panel as claimed in claim 25, wherein the coating is located on the outer face of the outer sheet.
30. A method of forming a transparent coated substrate comprising the pyrolytic deposition from a reactant mixture onto the substrate by chemical vapour deposition (CVD) of a coating layer containing tin oxide and antimony in a Sb/Sn molar ratio from 0.01 to 0.5, said reactant mixture comprising a source of tin and a source of antimony, characterised in that the reactant mixture further contains an additive comprising one or more of aluminium, chromium, cobalt, iron, manganese, magnesium, nickel, vanadium, zinc and zirconium and is free from fluorine, said additive being present in the reactant mixture within the range 0.2-3.6% by weight, whereby the so-coated substrate has a reflectance (RL) of at least 10%.
31. A method as claimed in claim 30, wherein the coating layer is deposited at a temperature in the range 550° C to 750° C.
32. A method as claimed in claim 30 or 31, wherein the coating layer is formed on a sheet of glass in a tunnel oven or on a glass ribbon during formation, whilst it is still hot.
33. A method as claimed in any one of claims 30 to 32, wherein an undercoat is formed between the substrate and the said coating layer.
34. A method as claimed in claim 33, wherein the undercoat layer is pyrolytically formed in an incompletely oxidized state by contacting the substrate in an undercoating chamber with undercoat precursor material in the presence of oxygen in insufficient quantity for full oxidation of the undercoat material on the substrate.
35. A method as claimed in claim 33, wherein the undercoat layer is alumina with a small proportion of vanadium oxide.
36. A method as claimed in any one of claims 33 to 35, wherein the undercoat has a geometric thickness comprised between 40 and 100 nm.