(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 January 2002 (17.01.2002)

PCT

(10) International Publication Number
WO 02/04995 A1

(51) International Patent Classification[7]: G02B 5/08

(21) International Application Number: PCT/EP01/07170

(22) International Filing Date: 25 June 2001 (25.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00114611.7 7 July 2000 (07.07.2000) EP

(71) Applicant (*for all designated States except US*): **SOLA INTERNATIONAL HOLDINGS LIMITED** [AU/AU]; Sherriffs Road, Lonsdale, S.A. 5160 (AU).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **MACCHI, Marco** [IT/IT]; Via Albisetti, 29, I-21049 Tradate (IT). **MALNATI, Sabrina** [IT/IT]; Via dei Cavalli, 87, I-21100 Varese (IT).

(74) Agent: **BOTTERO, Claudio**; Porta Checcacci & Associati S.p.A., Viale Sabotino, 19/2, I-20135 Milano (IT).

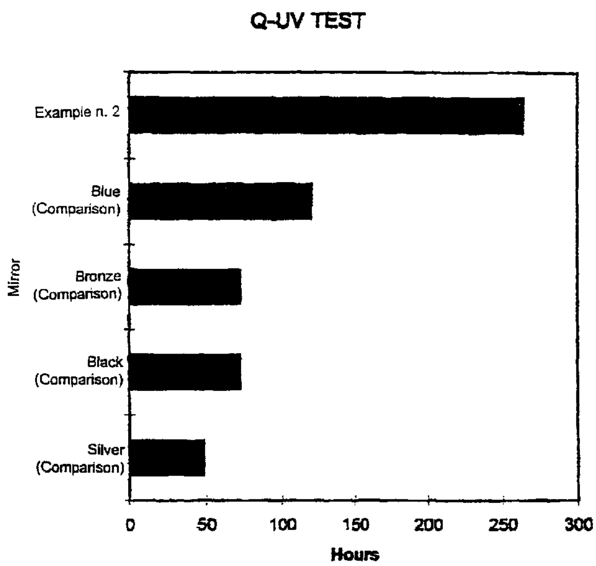
(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: OPTICAL ELEMENT COMPRISING A SUPERFICIAL MIRROR COATING AND METHOD FOR FORMING SAID COATING



(57) Abstract: The invention relates to an optical element comprising a transparent substrate provided with a superficial mirror coating having improved characteristics of adhesion to the substrate and of resistance to abrasion, and to a method for forming the coating. The superficial mirror coating includes a plurality of superimposed layers, namely: an adhesion layer including a first material adapted to firmly adhere to the substrate; a reflection layer including a second material having a high refraction index selected from the group comprising: Cr_xO_y, TiO_2, ZnSe, Zns and mixtures thereof, wherein x is a number comprised between 1 and 2 and y is a number comprised between 1 and 3; a coloring and optionally abrasion-resistance layer, including a third material having a refraction index lower than the refraction index of the second material.

WO 02/04995 A1

Optical element comprising a superficial mirror coating and method for forming said coating

DESCRIPTION

Field of invention

The present invention relates to an optical element comprising a transparent substrate provided with a superficial mirror coating, and to a method for forming said coating.

In the following description and in the appended claims, the expression "optical element" is used to indicate any substantially transparent element capable of allowing vision through the same, such as for example ophthalmic and non-ophthalmic lenses for glasses, visors, slabs, protective shields, etc.

In the following description and in the appended claims, the expression "transparent substrate" is used to indicate any transparent substrate, made of glass or of plastics, in particular of polycarbonate or diethylenglycol-bis-allyl-carbonate, commercially available as CR 39™ (PPG Industries Inc.), both commonly used for manufacturing ophthalmic and non-ophthalmic lenses for glasses.

Prior art

As is known, in the field of optical elements and in particular of lenses for glasses, one of the most difficult problems to be solved is that of providing a superficial mirror coating exhibiting, at the same time, a suitable adhesion to the substrate, a good resistance to abrasion, a good reflectance, a low absorbance and, finally, an aesthetically pleasant color.

According to the teaching of the prior art, the desired characteristics of coloring and mirroring of the optical element are obtained by forming a coating including at least two layers of suitable materials on the transparent substrate of the optical element.

In the case of a mirror coating consisting of two layers only - which nowadays is the most widespread on the market due to its low-cost features - each layer has one or more specific functions.

The first layer, generally consisting of chromium or aluminium, in fact, exerts both the function of adhering the coating to the substrate and of evenly reflecting the light in the visible spectrum (400-700 nm).

The second layer, generally consisting of silicon oxide, exerts on the other hand both the function of imparting the desired color to the lens and of imparting a certain resistance to abrasion to the coating.

The technologies used for manufacturing these low-cost two-layered coatings are those of physical vapor deposition, or PVD, based on a thermal evaporation mechanism wherein the heating of the material to be evaporated is substantially carried out by Joule effect.

Although two-layered mirror coatings of the known type substantially meet the purpose and have a reasonable cost, nonetheless they possess the drawback of having properties of adhesion to the substrate and of resistance to abrasion which are not entirely satisfactory.

Summary of the invention

Accordingly, the technical problem underlying the present invention is that of providing an optical element comprising a superficial mirror coating which would allow to achieve improved characteristics of adhesion to the substrate and of resistance to abrasion with respect to those of the two-layered coatings of the prior art currently on the market.

According to the present invention, it has been surprisingly found that the desired improvement of the characteristics of adhesion and of resistance to abrasion of the mirror coating may be achieved by realizing the coating with a new combination of layers of suitable materials.

Thus, according to a first aspect thereof, the present invention provides an optical element comprising a superficial mirror coating as defined in the attached claim 1.

In a preferred embodiment, the mirror coating of the invention comprises a sequence of three superimposed layers respectively consisting of a first material, which is mainly intended for carrying out the function of adhesion to the substrate; of a second material, which is mainly intended for carrying out the function of reflection, that is, of mirroring; and of a third material, which is mainly intended for carrying out the function of imparting to the coating the desired coloring and, optionally, the desired resistance to abrasion.

Advantageously, thanks to said combination of layers, it is also possible to obtain a wider range of colors and a greater variety of shades with respect to those obtainable with the conventional two-layered coatings.

The mirror-coated substrate of the invention is also easier to clean than the two-layered coatings of known type. Said advantageous feature may be attributed to the lower superficial roughness of the coating of the invention.

Advantageously, the mirroring layer of the present invention exhibits a greater transmittance with respect to that of two-layered coatings, which allows to coat dark substrates in a wider and more flexible way with respect to the prior art, while falling within the minimum transmittance limits possibly required by the applicable standards. This advantage is particularly appreciated in the case of lenses for sunglasses, since it is possible to widen the range of colors of the lens complying, at the same time, with the minimum transmittance limit of the coated lens, which limit is provided in the case of lenses to worn when driving motor vehicles, and is fixed to 8% by the standards EN 1836, ANSI Z80.3 and AS 1067.1.

Advantageously, the lower stiffness of the coating allows to achieve better properties of adhesion to the substrate, always with reference to those possessed by the two-layered coatings of comparable cost.

In a preferred embodiment, and as it will better appear hereinafter, the optical element of the invention may be manufactured at a reasonable cost using the equipment and the technology of vapor deposition used so far for forming the aforementioned two-layered coatings.

Preferably, the layer including the first material has a thickness comprised between 0.5 and 5 nm and most preferably between 0.5 and 2 nm. For the purposes of the invention, the first material is preferably selected from the group comprising: Cr, Ti, SiO, SiO_2, In_2O_3, SnO_2 and mixtures thereof. Among them, chromium is particularly preferred.

Preferably, the layer including the second material has a thickness comprised between 3 and 80 nm and most preferably between 8 and 50 nm. For the purposes of the invention, the second material is preferably selected from the group comprising: Cr_xO_y, TiO_2, ZnSe, ZnS and mixtures thereof, wherein x is a number comprised between 1 and 2, and y is a number comprised between 1 and 3. Among them, Cr_2O_3 is particularly preferred.

According to a preferred embodiment, the second material has a refraction index comprised between 1.7 and 2.7. More preferably, the refraction index of the second material is comprised between 1.9 and 2.4.

In the present description, the refraction indexes of the different materials are intended as indexes measured at the wavelengths at which the respective materials are transparent or only weakly absorbent.

Preferably, the layer including the third material has a thickness comprised between 5 and 400 nm and most preferably between 10 and 200 nm. For the purposes of the invention, the third material is preferably selected from the group comprising: SiO, SiO_2, MgF_2, $Na_5Al_3F_{14}$, and mixtures thereof.

Preferably, the third material has a refraction index comprised between 1.32 and 1.8 and more preferably between 1.4 and 1.7.

Preferably, the substrate essentially consists of a transparent element of glass or plastics having a refraction index at 500 nm comprised between 1.38 and 1.75.

If the substrate is made of plastics, it may be coated with a polisiloxane resin or other suitable material having the double function of imparting scratch-proof properties to the finished product, and of increasing the adhesion degree of the mirroring coating to the same substrate.

For the purposes of the invention, the plastics is preferably selected from the group comprising: acrylic-based polymers and copolymers, polymethylmethacrylate, polycarbonate, polyol-allyl-carbonates, cellulose esters, polyacrylates, polystyrene, polyurethanes.

Among them, an acrylic-based copolymer commercially available as Spectralite ™ (Sola Optical), diethylenglycol-bis-allyl-carbonate, commercially available as CR 39™ (PPG Industries Inc.), and polycarbonate, commonly used for manufacturing ophthalmic and non-ophthalmic lenses for glasses, are preferred.

Preferably, the optical element is manufactured in the shape of lens or visor for glasses, or in the shape of slab or protective shield.

According to a second aspect thereof, the present invention provides a method for forming on a transparent substrate of an optical element a superficial mirror coating, as is defined in the attached claim 13.

In a preferred embodiment of the method according to the invention, the superficial mirror coating of the substrate is formed by means of a process of physical vapor deposition carried out using the low-cost equipment and technologies usually employed in the manufacture of the two-layered superficial mirror coatings.

The Applicant has surprisingly noted that it is advantageously possible in this way to attain the desired improved adhesion properties at a cost comparable to that reached so far by the methods for forming two-layered mirroring coatings.

In fact, even by using the low-cost coating equipment and technologies usually employed in the manufacture of the two-layered superficial mirror coatings, the method of the present invention advantageously allows to improve the quality of mirroring, which is comparable to the quality of multi-layered coatings which are much more expensive and produced with sophisticated techniques, such as those based on the use of electronic guns, but at the same time to limit the costs, maintaining them comparable to those of two-layered coatings.

Moreover, this preferred manufacturing method of the present invention allows to increase the productivity with respect to the methods of the prior art employed for the manufacture of multi-layer coatings thanks to the reduced process time of this less sophisticated equipment.

The coating equipment of most preferred use comprises, in particular:

- a sealed chamber provided with an outer coil for heating/cooling the same,

- a dome serving as a support for the blanks of the optical element to be coated,

- a plurality of metallic crucibles suitably connected to a current source which is adapted to heat the crucibles by Joule effect and, along therewith, to heat the material to be deposited onto the substrate of the optical element housed therein,

- a vacuum system in fluid communication with the sealed chamber,

- an adjusting device for feeding optional reactive gases (for example oxygen) and a ion discharge device for cleaning the substrate to be coated.

According to a preferred embodiment, the crucibles are preferably made of molybdenum and are provided on top by a removable shutter which closes the crucibles until the material to be evaporated reaches the desired evaporation temperature.

Preferably, the substrate is positioned in a sealed chamber wherein a vacuum degree comprised between $2*10^{-5}$ e $1.5*10^{-4}$ mbar is reached.

In a preferred embodiment, the method of the invention provides for forming a metal adhesion layer on the substrate followed by depositing on this adhesion layer a reflection layer essentially consisting of an oxide of the same metal or, alternatively, of a different metal.

In the former case, it is preferable and advantageous to form the reflection layer by evaporating said metal in an oxygen-containing environment, so as to form the desired oxide layer "*in situ*", i.e., directly onto the underlying adhesion layer.

Preferably, the reflection layer is formed in this case by adjusting the deposition rate of the second material on the substrate in a range comprised between 0.05 and 0.15 nm/s.

In this way, it is advantageously possible to obtain an oxide layer having the desired stoichiometric ratio between metal and oxygen.

According to a preferred embodiment of the method of the invention, each deposition step of the first, second and third material is carried out by evaporation and is preceded by a pre-heating step of the respective material.

Conveniently, the pre-heating steps are adapted to bring each material to a pre-heating temperature close to that most suitable for effecting the evaporation and are carried out while maintaining the removable shutter of the crucibles in its closed position.

Preferably, both the pre-heating and evaporation steps are carried out by means of Joule effect so as to reach a temperature, which may easily determined by those skilled in the art, that allows to carry out the deposition at the desired rate.

According to a preferred embodiment, the pre-heating steps are carried out when the crucibles are made of molybdenum by feeding thereto a current having a value preferably comprised between 200 and 390 A.

Still more preferably, the current fed to the crucibles during the pre-heating steps has the following values:

i) of from 330 A and 370 A, most preferably equal to about 350 A, when pre-heating the first material;

ii) of from 360 A and 400 A, most preferably equal to about 380 A, when pre-heating the second material;

iii) of from 200 A and 240 A, most preferably equal to about 220 A, when pre-heating the third material.

According to a preferred embodiment, the evaporation steps are carried out when the crucibles are made of molybdenum by feeding thereto a current having a value preferably comprised between 280 and 400 A.

Still more preferably, the current fed to the crucibles during the evaporation steps has the following values:

i) of from 360 A and 400 A, most preferably equal to about 380 A, when evaporating the first material;

ii) of from 360 A and 400 A, most preferably equal to about 380 A, when evaporating the second material;

iii) of from 270 A and 310 A, most preferably equal to about 290 A, when evaporating the third material.

Advantageously, using the equipment briefly described hereinabove, it is possible to carry out the coating method of the invention in an overall time comprised between 15 and 35 minutes.

Preferably, said time is divided among the main operative steps as follows:

- vacuum time: 8 - 10 min;
- time for activating the surface of the substrate: 3 - 5 min;
- pre-heating time of the first material: about 180 s;
- deposition time of the first material: 2.5 - 10 s;
- pre-heating time of the second material: about 180 s;
- deposition time of the second material: 40 - 300 s;
- pre-heating time of the third material: about 180 s;
- deposition time of the third material: 7 - 300 s;
- time for restoring the ambient pressure: about 180 s.

In this preferred embodiment, thanks to the relatively low fixed cost of said equipment and to the reduced process times, it is possible to form a mirror coating on the optical element at a cost which is comparable, as a whole, to that of the optical elements provided with a two-layered coating of the prior art, obtaining at the same time the desired improvement of the properties of adhesion and of abrasion resistance of the coating.

In the alternative, it is clearly possible to carry out the method of the present invention by using more sophisticated equipment, such as those commonly employed for manufacturing multi-layered coatings, thus obtaining as good results in terms of mechanical resistance and of adhesion of the coating to the substrate, but to the detriment of the cost of the optical element thus produced, which in this case is much higher.

Brief description of the drawing

Additional features and advantages of the invention will become more readily apparent from the following description of some preferred embodiments of the invention, given hereinbelow by way of non-limitative examples with reference to the accompanying drawing.

In the drawing, figure 1 illustrates, in the form of a histogram, the results of the Q-UV test for determining the adhesion properties of the coating to the support.

EXAMPLE 1

On 100 lenses for glasses made of CR 39™ (PPG Industries Inc.), a mirror coating according to the invention was realized, comprising:

- an adhesion layer of Cr;

- a reflection layer of TiO_2 (refraction index = 2.25 at 500 nm);

- a coloring and abrasion-resistance layer of SiO_2 (refraction index = 1.47 at 500 nm).

The formation of the coating layers was carried out by means of a Satis 1200 DLS coater (Satis Vacuum AG), commercially available, equipped with an electronic gun having a 15 kW power supply, an ion gun having a 9.5 kW power supply and an oxygen flow regulator.

The adhesion layer of the coating was deposited by evaporating under vacuum metallic Cr after having activated the surface of the lens by ion discharge in oxygen environment for a period of time equal to 180 s.

The deposition parameters were the following:

- initial vacuum: $3 \cdot 10^{-5}$ mbar;
- temperature at the beginning of the deposition*: 60°C;
- vacuum time: 20 min;
- time for activating the surface of the substrate by ion discharge: 180 s;
- pre-heating time of Cr: 180 s;
- deposition time of Cr: about 5 s;
- pre-heating time of TiO_2: 180 s;
- deposition time of TiO_2: about 120 s;
- pre-heating time of SiO_2: 180 s;
- deposition time of SiO_2: about 180 s;
- time for restoring the ambient pressure: 15 min.

* measured on the lens.

The TiO_2 layer was deposited by evaporating metallic Ti and introducing an O_2 flow equal to about 35 sccm (standard cubic centimetres per minute), whereas the final layer of SiO_2 was deposited in the absence of O_2.

At the end of the deposition operations, a mirror coating, having the characteristics illustrated in the following Table I, was obtained on each lens.

EXAMPLE 2

On 100 lenses made of polycarbonate, a mirror coating according to the invention was realized, comprising:

- an adhesion layer of Cr;

- a reflection layer consisting of a non-stoichiometric chromium oxide of empirical formula Cr_xO_y, wherein x is a number comprised between 1 and 2 and y is a number comprised between 1 and 3, having a refraction index comprised between 1.9 and 2.4 at 500 nm;

- a coloring and abrasion-resistance layer of SiO (refraction index = 1.7 at 500 nm).

The formation of the coating layers was carried out by means of a Satis 150/S coater (Satis Vacuum AG), commercially available, comprising a plurality of crucibles provided with electrical resistors adapted to heat the material by Joule effect.

The deposition parameters were the following:

- initial vacuum: $1.1 \cdot 10^{-4}$ mbar;

- temperature at the beginning of the deposition*: 50°C;

- vacuum time: 10 min;

- time for activating the surface of the substrate by ion discharge: 180 s;

- pre-heating time of Cr: 180 s;

- deposition time of Cr: about 5 s;

- pre-heating time of Cr before deposition of Cr_xO_y: 180 s;

- deposition time of Cr_xO_y: about 45 s;

- pre-heating time of Si before deposition of SiO: 180 s;

- deposition time of SiO: about 150 s;

- time for restoring the ambient pressure: 180 s.

* measured on the lens.

The Cr_xO_y layer was deposited by evaporating metallic Cr and introducing an O_2 flow equal to about 46 sccm, whereas the layer of SiO was deposited by evaporating Si and introducing an O_2 flow equal to about 32.8 sccm.

At the end of the deposition operations, a mirror coating, having the characteristics illustrated in the following Table II, was obtained on each lens.

EXAMPLE 3

On 100 lenses made of polycarbonate, a mirror coating according to the invention was realized, comprising:

- an adhesion layer of SiO (refraction index = 1.7 at 500 nm);

- a reflection layer consisting of non-stoichiometric chromium oxide of empirical formula Cr_xO_y, wherein x is a number comprised between 1 and 2 and y is a number comprised between 1 and 3, having a refraction index comprised between 1.9 and 2.4 at 500 nm;

- a coloring and abrasion-resistance layer of SiO (refraction index = 1.7 at 500 nm).

The formation of the layers of the coating was carried out by means of a Satis 150/S coater (Satis Vacuum AG).

The deposition parameters were the following:

- initial vacuum: $1,1\cdot10^{-4}$ mbar;

- temperature at the beginning of the deposition*: 50°C;

- vacuum time: 10 min;

- time for activating the surface of the substrate by ion discharge: 180 s;

- pre-heating time of SiO: 180 s;

- deposition time of SiO: about 8 s;

- pre-heating time of Cr before deposition of Cr_xO_y: 180 s;

- deposition time of Cr_xO_y: about 55 s;

- pre-heating time of Si before deposition of SiO: 180 s;

- deposition time of SiO: about 10 s;

- time for restoring the ambient pressure: 180 s.

* measured on the lens.

The Cr_xO_y layer was deposited by evaporating metallic Cr and introducing an O_2 flow equal to about 46 sccm, whereas the layer of SiO was deposited by evaporating Si and introducing an O_2 flow equal to about 32.8 sccm.

At the end of the deposition operations, a mirror coating, having the characteristics illustrated in the following Table III, was obtained on each lens.

EXAMPLE 4

(Determination of the adhesion properties of the coating)

The lenses of example 2 were subjected to a standard test for determining the adhesion properties of the coating.

In particular, the comparative test commonly known as Q-UV test was carried out on a set of lenses with the purpose of assessing the relative lifetime of the lenses examined in an outer environment.

Such a test, aims at simulating in laboratory the harmful effects exerted by the exposition to atmospheric agents in conformity with standards ASTM G53, D-4329, SAE J2020 and ISO 4892.

The results of the measures carried out, graphically represented in figure 1 in which the mean lifetime expressed in hours of the lenses of example 2 compared with the lifetimes of comparative lenses, is illustrated.

In the aforementioned figure, the bars labeled Blue, Bronze, Black and Silver are referred to polycarbonate lenses provided with a Cr- and SiO-based two-layered coating such as to impart to each of them the corresponding color; said lenses are commercially available with the respective technical denominations of Blue Mirror, Bronze Mirror, Black Mirror and Silver Mirror (Sola Optical Italia S.p.A.).

As it can be noted from the histogram reported in Fig. 1, the coating of the invention has significantly improved adhesion properties with respect to those of the two-layered coatings of known type.

EXAMPLE 5

(Determination of the abrasion resistance properties of the coating)

For the purpose of evaluating the abrasion resistance of the coating according to the previous Example 2 with respect to that of two-layered coatings of known type, another comparative test - known in the field with the name of Steel Wool test - was carried out.

Such a test is carried out by rubbing steel wool on the surface of the lens: the damage caused by the abrasion is evaluated in terms of increase of scratches on the lens.

The Steel Wool Test was carried out by means of a modified Sutherland ink-rub tester (James River Corp. - Kalamazoo, Michigan, U.S.A.), wherein the rubber pad was replaced by a flake of standard steel wool grade 000. The steel wool flake was subject to a 2-kg weight placed in oscillation for a predetermined number of abrasion cycles. The lenses were examined at the microscope and with the naked eye against an illuminated black panel after having been subject to 25 abrasion cycles.

The results, in terms of relative data, are reported in Table IV, and they fall within a range of values whose upper limit is defined by the abrasion resistance of glass, to which an evaluation equal to 5 stars is attributed, and whose lower limit corresponds to the abrasion resistance of uncoated polycarbonate, to which an evaluation equal to 0 stars is attributed.

From the comparison data reported in Table IV, it is possible to note that the plastics lenses of example 2 exhibit a higher resistance to abrasion with respect to that of the comparison lenses provided with a conventional two-layered coating, and just lower than that of the glass.

TABLE I

layer	deposition rate [nm/s]	thickness [nm]	optical thickness at 500 nm [nm]
Cr	0.1	0.50	-
TiO_2	0.35	42.00	94.50
SiO_2	0.96	173.11	254.47

TABLE II

layer	deposition rate [nm/s]	thickness [nm]	optical thickness at 500 nm [nm]
Cr	0.1	0.50	-
Cr_xO_y	0.18	8.00	17.2*
SiO	1.3	200.00	340.00

* = value obtained considering a mean value of the refraction index equal to 2.15

TABLE III

layer	deposition rate [nm/s]	thickness [nm]	optical thickness at 500 nm [nm]
SiO	0.5	4.00	-
Cr_xO_y	0.18	10.00	21.5*
SiO	0.5	5.00	8.5

* = value obtained considering a mean value of the refraction index equal to 2.15

TABLE IV

Silver (comparison)	**
Black (comparison)	**
Bronze (comparison)	***
Blue (comparison)	***
Example 2	****

CLAIMS

1. Optical element comprising a transparent substrate provided with a superficial mirror coating including a plurality of superimposed layers, wherein the coating comprises:

- an adhesion layer including a first material adapted to firmly adhere to said substrate;

- a reflection layer including a second material having a high refraction index selected from the group comprising: Cr_xO_y, TiO_2, ZnSe, ZnS and mixtures thereof, wherein x is a number comprised between 1 and 2 and y is a number comprised between 1 and 3;

- a coloring and optionally abrasion-resistance layer, including a third material having a refraction index lower than the refraction index of said second material.

2. Optical element according to claim 1, characterized in that the layer including said first material has a thickness comprised between 0.5 and 5 nm.

3. Optical element according to claim 1, characterized in that the layer including said second material has a thickness comprised between 3 and 80 nm.

4. Optical element according to claim 1, characterized in that the layer including said third material has a thickness comprised between 5 and 400 nm.

5. Optical element according to claim 1, characterized in that said first material is selected from the group comprising: Cr, Ti, SiO, SiO_2, In_2O_3, SnO_2 and mixtures thereof.

6. Optical element according to claim 1, characterized in

that said second material has a refraction index comprised between 1.7 and 2.7.

7. Optical element according to claim 1, characterized in that said third material has a refraction index comprised between 1.32 and 1.8.

8. Optical element according to claim 1, characterized in that said third material is selected from the group comprising: SiO, SiO_2, MgF_2, $Na_5Al_3F_{14}$, and mixtures thereof.

9. Optical element according to claim 1, characterized in that said transparent substrate essentially consists of glass or plastics having a refraction index at 500 nm comprised between 1.38 and 1.75.

10. Optical element according to claim 9, characterized in that said plastics is selected from the group comprising: acrylic-based polymers and copolymers, polymethylmethacrylate, polycarbonate, polyol-allyl-carbonates, cellulose esters, polyacrylates, polystyrene, polyurethanes.

11. Optical element according to anyone of the preceding claims, in the form of lens or visor for glasses.

12. Optical element according to anyone of claims 1-10, in the form of slab or protective shield.

13. Method for forming, on a transparent substrate of an optical element, a superficial mirror coating according to anyone of the preceding claims, comprising the steps of:

a) placing said substrate in a sealed chamber;

b) bringing said chamber to a predetermined vacuum degree;

c) activating the surface of said substrate by means of ion discharge in an oxygen-containing environment for a predetermined period of time;

d) depositing in substantial absence of oxygen said first material on the substrate so as to form an adhesion layer having a predetermined thickness;

e) depositing at a controlled rate, optionally in the presence of oxygen, said second material on said adhesion layer so as to form a reflection layer having a predetermined thickness;

f) depositing, optionally in the presence of oxygen, said third material having a refraction index lower than the refraction index of said second material on said reflection layer, so as to form a coloring and optionally abrasion-resistance layer having a predetermined thickness.

14. Method according to claim 13, wherein said steps d), e), f) are carried out by evaporating said first, second and third material by means of the Joule effect.

15. Method according to claim 14, wherein each of said steps d), e), f) is preceded by a step of pre-heating the materials to be evaporated at a predetermined temperature.

16. Method according to claim 13, wherein said step e) is carried out so as to have a deposition rate of said second material onto the substrate comprised between 0.05 and 0.15 nm/s.

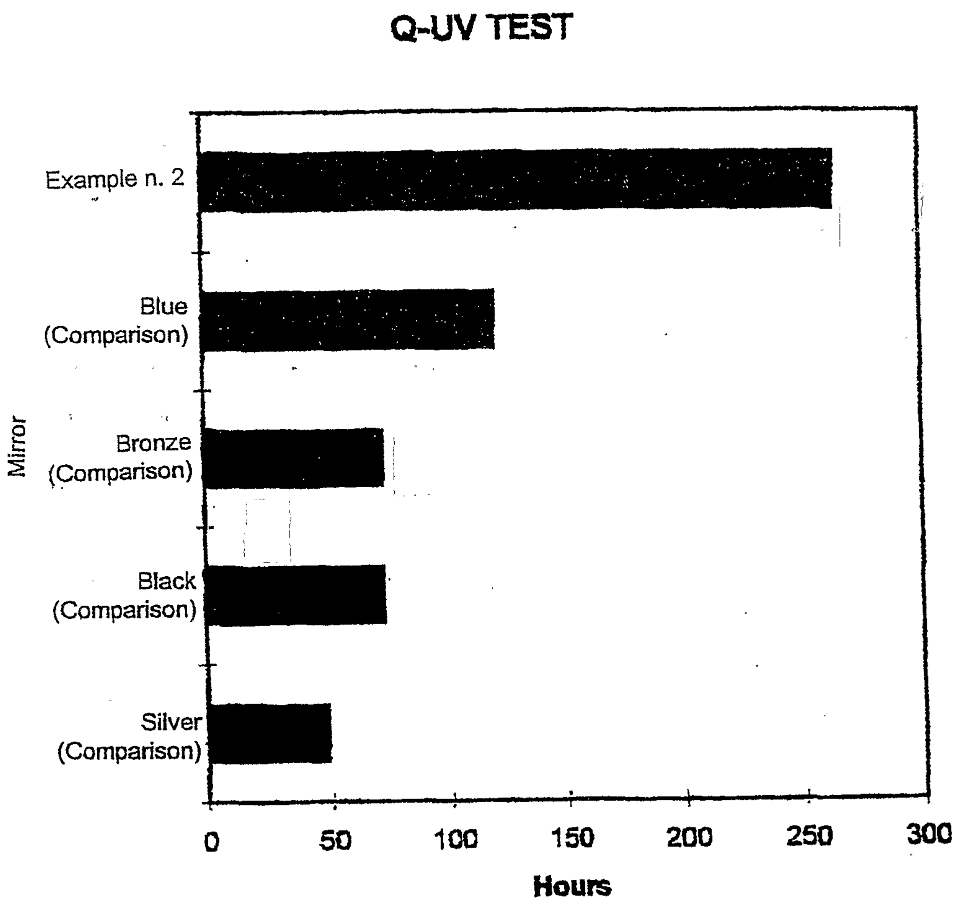

Q-UV TEST
Mirror
Example n. 2
Blue
(Comparison)
Bronze
(Comparison)
Black
(Comparison)
Silver
(Comparison)
0
50
100
150
200
250
300
Hours

Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/07170

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G02B5/08

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)
IPC 7 G02B

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, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 268 509 A (PILKINGTON UK LTD) 12 January 1994 (1994-01-12) page 18, paragraph 1 -page 19, paragraph 1; figures 1-3	1,13
A	DE 39 28 939 A (HOYA CORP) 1 March 1990 (1990-03-01) column 3, line 47 -column 5, line 52; figures 1A-1C	1,13
A	EP 0 456 488 A (BOC GROUP INC) 13 November 1991 (1991-11-13) page 3, line 9 - line 55; figures 2,3	1,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° 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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 September 2001	17/09/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Sarneel, A

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2268509 A	12-01-1994	AT 145195 T	15-11-1996
		AU 4152993 A	13-01-1994
		BR 9302815 A	22-02-1994
		CA 2099519 A	12-01-1994
		CN 1081657 A,B	09-02-1994
		CZ 9301318 A	16-02-1994
		DE 69305936 D	19-12-1996
		DE 69305936 T	17-04-1997
		DK 583871 T	21-04-1997
		EG 20125 A	31-07-1997
		EP 0583871 A	23-02-1994
		ES 2096864 T	16-03-1997
		FI 933164 A	12-01-1994
		GR 3022231 T	30-04-1997
		HU 70362 A	30-10-1995
		IL 106202 A	31-01-1996
		JP 6183787 A	05-07-1994
		MX 9304101 A	31-01-1994
		NZ 248032 A	24-02-1995
		PL 299635 A	21-03-1994
		RU 2120919 C	27-10-1998
		TR 26801 A	08-08-1994
		US 5505989 A	09-04-1996
		US 5580364 A	03-12-1996
		US 5745291 A	28-04-1998
		ZA 9304664 A	25-01-1994
DE 3928939 A	01-03-1990	JP 2064601 A	05-03-1990
		JP 2561946 B	11-12-1996
		GB 2222466 A,B	07-03-1990
		IT 1233190 B	16-03-1992
		US 4955705 A	11-09-1990
EP 0456488 A	13-11-1991	AU 7524091 A	14-11-1991
		CA 2041053 A	11-11-1991
		JP 4229804 A	19-08-1992
		ZA 9102915 A	29-04-1992