



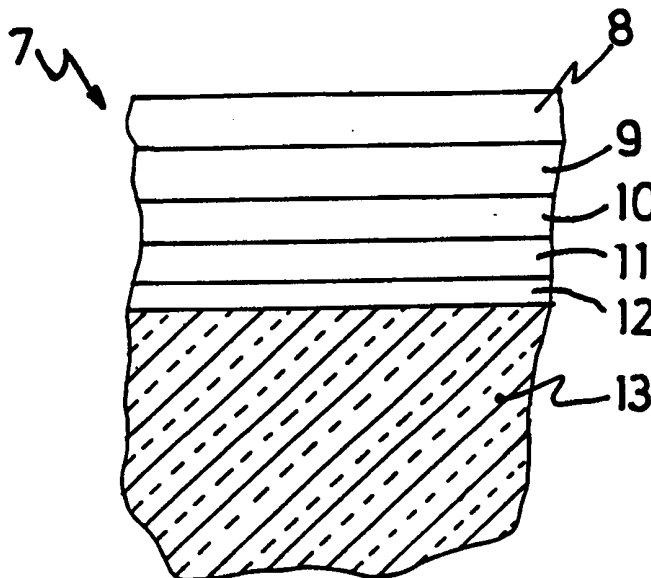
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: MULTILAYER ELECTRICALLY CONDUCTIVE ANTI-REFLECTIVE COATING

## (57) Abstract

The present invention comprises a multilayer inorganic anti-reflective coating with predetermined optical properties, for application on a flexible substrate. The coating comprises a stack consisting of five material layers, whereby the third layer is a dummy layer consisting of an electrically conductive material, preferably indium-tin oxide, which provides the coating with an adjustable electrical sheet resistance of between 25 and 2000  $\Omega/\text{sq}$  without thereby influencing its optical properties. The anti-reflective coating can be applied onto a flexible substrate (e.g. a polymer film) by means of a single or double pass vacuum magnetron sputtering operation.



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MULTILAYER ELECTRICALLY CONDUCTIVE ANTI-REFLECTIVE COATING

5 The invention relates to a multilayer anti-reflective coating for application on a flexible substrate.

State of the art

10 The performance of a multilayer anti-reflective coating can be evaluated from its admittance diagram and corresponding reflectance diagram.

15 In an admittance plot, the locus of the complex optical admittance  $Y$  of the stack constituting the anti-reflective coating is plotted in the complex plane, starting at the substrate and ending at the front surface of the stack - as if the admittance of the stack was plotted during the entire deposition process. For each dielectric layer being part of the stack, this locus is an arc of a circle centered on the real axis, and traced out clock-wise. Optimum anti-reflection properties of the full coating stack are obtained if  
20 the end of the admittance plot is near the point (1,0), which is the optical admittance of air, the entrance medium.

25 In a reflectance diagram, the percentage reflection of the incident light (hereafter called reflectance) is plotted as a function of its wave-length. The reflectance should be as low as possible over the visual wave-length range, roughly from about 400 to about 700 nm.

The so-called broadened V-coat, flattened V-coat or Vermeulen coat, as illustrated in Figure 1, is a generally well known anti-

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reflective coating. This coating 6 comprises a stack consisting of four material layers. The first layer 1 which is situated farthest from the substrate, is a quarterwave layer, which means that it has a thickness of about  $\lambda_0/4$ ,  $\lambda_0$  being the design wave-length of about 510 nm, which is the reciprocal mean visual wave-length. The second layer 2 is a halfwave layer, with a thickness of about  $\lambda_0/2$ . The third and fourth layers 3 and 4 which are situated closest to the substrate, are very thin material layers, typically with thicknesses of about  $\lambda_0/12$  and  $\lambda_0/16$  respectively. An example of such a coating is described in the patent US 5450238.

In order to obtain optimum optical properties such as low reflectance and large band-width, the four-layer stack should combine materials with very low and very high refractive indices. Practically, silicon dioxide is used as material with very low refractive index (of about 1.46), and titanium dioxide is used as material with very high refractive index (of about 2.35).

The admittance plot of such a four-layer Vermeulen anti-reflective glass coating is shown in Figure 2, relating to a stack consisting of a silicon dioxide layer with an optical thickness of  $0.25\lambda_0$  situated farthest from the substrate, followed by a titanium dioxide layer with a thickness of  $0.52\lambda_0$ , a silicon dioxide layer with a thickness of  $0.09\lambda_0$ , and finally, closest to the substrate, a titanium dioxide layer with a thickness of  $0.06\lambda_0$ ,  $\lambda_0$  being about 510 nm. The corresponding reflectance diagram is shown as plot A in Figure 7. As can be seen from these diagrams, the optical properties of this Vermeulen type coating are very good: a low reflectance over the visual wave-length range and a high band-width; the latter being

defined as the ratio of the long wave-length  $\lambda_L$  to the short wave-length  $\lambda_S$  at a reflectance level of 1%.

5 A very important drawback of such coatings however, is their high electrical resistance (typically more than 20000  $\Omega$ /sq), making the coating not suitable for anti-static or EMI (Electro-Magnetic Interference) shielding applications, e.g. as coating for cathode ray tubes (CRT).

10 In order to improve the electrical conductivity of the coating, it is common to replace the titaniumdioxide layers by electrically conductive material layers such as e.g. In- or Al-doped zincoxyde, Sb- or F-doped tinoxyde, Sn doped cadmiumoxyde, or indium-tinoxyde layers.

15 The optical properties of such modified Vermeulen coatings are however worse than those of the afore-mentioned Vermeulen coating, since the modified coatings comprise a stack which combines silicondioxide with an electrically conductive material with lower refractive index than titaniumdioxide (typically 2.0 -  
20 2.1). The reflectance of the incident light is therefore higher, and the band-width lower. This can be seen from the reflectance plot B of Figure 7, which is related to a modified Vermeulen glass coating comprising a stack consisting of a silicondioxide layer with an optical thickness of  $0.24\lambda_0$  which is situated farthest from  
25 the substrate, followed by an indium-tinoxyde layer with a thickness of  $0.39\lambda_0$ , a silicondioxide layer with a thickness of  $0.06\lambda_0$ , and an indium-tinoxyde layer with a thickness of  $0.07\lambda_0$  closest to the substrate. The corresponding admittance plot is illustrated in Figure 3.

In the patent US 5270858 a multilayer anti-reflective coating is described wherein the intermediate titaniumdioxide layer of the Vermeulen coating is partially replaced by an electrically  
5 conductive material layer such as a doped zincoxyde or indium-tin  
tin-oxido layer, leading to a coating comprising a stack consisting of five material layers.

Although this coating has the advantage of being somewhat electrically conductive, it still has important drawbacks.

10 Since part of the titaniumdioxide has been replaced by an electrically conductive material (with lower refractive index), the optical properties of the coating are worse than those of the Vermeulen coating described before. This can be seen from the reflectance plot C of Figure 7, relating to a coating on glass  
15 comprising a stack consisting of a silicondioxyde layer with an optical thickness of  $0.28\lambda_0$  farthest from the substrate, followed by a titaniumdioxide layer with an optical thickness of  $0.13\lambda_0$ , followed by a zincoxyde layer with an optical thickness of  $0.37\lambda_0$ , followed by a silicondioxyde layer with an optical thickness of  
20  $0.12\lambda_0$ , and finally followed by a titaniumdioxide layer with an optical thickness of  $0.03\lambda_0$  closest to the substrate.

Furthermore, the thickness of the electrically conductive material layer constituting the stack is very critical, and it should obey exactly the design specifications, since it has a direct influence on  
25 the optical properties of the coating. The electrical conductivity of the coating is therefore not adjustable at all and often not high enough to render the coating suitable for EMI shielding applications.

### Object of the invention

5 It is an object of the invention to provide an anti-reflective coating which is suitable for application on flexible substrates, and which has optimum optical properties, such as a low reflectance of incident light within the visual wave-length range and a high bandwidth.

10 It is also an object of the invention to provide an anti-reflective coating which is electrically conductive, and suitable for anti-static and EMI shielding applications.

It is a further object of the invention to provide an anti-reflective coating with an electrical conductivity that is adjustable, independently from the optical properties of the coating.

15 It is still a further object of the invention to provide a method for coating a substrate with an anti-reflective coating at a reasonable speed, making the coating process suitable for industrial application.

### Summary of the invention

20 The present invention comprises a multilayer inorganic anti-reflective coating with predetermined optical properties, for application on a flexible substrate. The coating comprises a stack consisting of five material layers, whereby the third layer is a dummy layer consisting of an electrically conductive material, preferably indium-tin oxide, which provides the coating with an adjustable electrical sheet resistance (i.e. the resistance of one square of the coating ) of between 25 and 2000  $\Omega/\text{sq}$  without thereby influencing its optical properties. A dummy layer is defined

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as a layer of which the thickness has no or very little influence on the optical properties of the coating.

The first layer, situated farthest from the substrate, has a refractive index less than the refractive index of the substrate, and an optical thickness which is comprised between  $0.2$  and  $0.3\lambda_0$ , this means about  $0.25\lambda_0$  (a quarterwave). The second layer has a refractive index greater than about  $2.2$  and an optical thickness which is comprised between  $0.4$  and  $0.6\lambda_0$ , i.e. of about  $0.5\lambda_0$  (a halfwave). The fourth layer has a refractive index which is about the same as the refractive index of the first layer, and an optical thickness of less than about  $0.1\lambda_0$ , i.e. in any event less than  $0.15\lambda_0$ . The fifth layer has a refractive index which is about the same as the refractive index of said second layer, and an optical thickness which is comprised between  $0.025$  and  $0.1\lambda_0$ , i.e. of about  $0.04\lambda_0$ ,  $\lambda_0$  being the design wave-length which is comprised between  $480$  and  $560$  nm, i.e. which is about  $510$  nm.

The anti-reflective coating according to the invention can be applied onto a flexible substrate (e.g. a polymer film) by means of a single or double pass vacuum magnetron sputtering operation which can be performed in a vacuum chamber comprising:

- (1) a section for unwinding and rewinding the flexible substrate;
- (2) deposition sections wherein the material layers constituting the coating are sputtered onto the substrate;
- (3) a central cooling drum, on the surface of which the substrate moves through the deposition sections.

In case a single pass operation is performed, minimum five deposition sections are required; in case a double pass operation is applied, only minimum three deposition sections are needed.



The invention will now be described in more detail, referring to the following drawings.

5        Brief description of the drawings

Figure 1 schematically illustrates the constitution of a four-layer Vermeulen coating (state of the art).

10       Figure 2 shows the admittance plot of a four-layer Vermeulen coating (state of the art).

Figure 3 graphically illustrates the admittance plot of a modified four-layer Vermeulen coating (state of the art).

Figure 4 illustrates the admittance plot of a conductive five-layer coating (state of the art).

15       Figure 5 schematically illustrates the constitution of an anti-reflective five-layer coating according to the invention.

Figure 6 shows the admittance plot of an anti-reflective five-layer coating according to the invention.

20       Figure 7 represents the reflectance plots of a four-layer Vermeulen coating (A), a modified four-layer Vermeulen coating (B), and a five-layer conductive coating (C), all being part of the state of the art, and of a five-layer coating according to the invention (D).

25       Figure 8 shows the reflectance plots of four 5-layer conductive coatings (on a transparent PET-film as substrate) according to the invention, comprising a dummy indium-tin-oxide layer with a physical thickness of 25 nm (E), 30 nm (F), 35 nm (G) and 40 nm (H) respectively.

Figure 9 illustrates schematically a single pass sputtering process for coating a flexible substrate with an anti-reflective coating according to the invention.

5 Figure 10 illustrates schematically a double pass sputtering process for coating a flexible substrate with an anti-reflective coating according to the invention made on a wide web coater or roll coater.

10 Figure 11 shows the reflectance plot of a five-layer conductive coating according to the invention in which a dummy indium-tin oxide layer with a physical thickness of about 25 nm is used and deposited on a hard-coated PET-substrate. This coating has been made on a wide web coater or roll-coater (substrate width 1200 mm) with five deposition chambers.

15 Detailed description of the invention

In the description below the "optical properties" includes especially the reflectance, i.e. the percentage reflection of incident light, and the band-width BW, i.e. the ratio of the long wave-length  $\lambda_L$  to the  
20 short wave-length  $\lambda_S$  at a reflectance level of 1% ( $BW = \lambda_L / \lambda_S$ ), as e.g. indicated on the reflectance plot D of Figure 7.

25 According to the invention, a multilayer anti-reflective coating 7 for flexible substrates is proposed, comprising a stack consisting of five material layers, as shown in Figure 5.

The first layer 8 is situated farthest from the substrate, consists of a material with a refractive index less than the refractive index of the substrate, and has an optical thickness which is comprised between  $0.2$  and  $0.3\lambda_0$ , typically of about  $0.25\lambda_0$  (a quarterwave).

The thickness is expressed as a fraction of  $\lambda_0$ , about 510 nm, the reciprocal mean of the boundary wave-lengths limiting the visual wave-length region, viz. from 400 nm to 700 nm.

5 The second layer 9 which is comprised in the coating, consists of a material with a refractive index which is greater than about 2.2, and has an optical thickness which is comprised between 0.4 and  $0.6\lambda_0$ , typically of about  $0.5\lambda_0$  (a halfwave).

The third layer 10 consists of an electrically conductive material, and will be characterised in detail furtheron.

10 The fourth layer 11 consists of a material with a refractive index which is about the same as the refractive index of the first layer 8, and has an optical thickness of less than about  $0.1\lambda_0$ , typically comprised between  $0.05$  and  $0.15\lambda_0$ .

15 The fifth layer 12, closest to the substrate 13, consists of a material with a refractive index which is about the same as the refractive index of the second layer 9, and has an optical thickness which is comprised between  $0.025$  and  $0.1\lambda_0$ , typically of about  $0.05\lambda_0$ .

20 The stack preferably combines titaniumdioxide and silicon dioxide as materials with respectively very high and low refractive indices, providing the coating with good optical properties, which are comparable to those of the afore-mentioned four-layer Vermeulen coating. This can be seen from the reflectance plot D of Figure 7,  
25 which is related to a coating according to the invention, as characterised in Example 2 below.

The use of titaniumdioxide for the fifth layer 12 closest to the substrate 13, has the additional advantage that it gives said layer

moisture barrier properties, preventing moisture from outside to penetrate through the interface between the substrate and the fifth layer 12, and so preventing coating stack degradation such as crack formation.

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The anti-reflective coating according to the invention yields a photopic reflectance that does not exceed 0.15%, when applied on transparent PET-films or 0.25% on substrates having a hardcoat, e.g. consisting of highly cross-linked UV-cured acrylates. The photopic reflection is the convolution of the eye sensitivity and the reflectance plot, and is measured in the wavelength region from 380 to 780 nm using a standard illuminant D65 and the 2° observer defined by the Commission Internationale de l'Eclairage in 1931.

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Furthermore, the coating has a band-width (as defined above) of more than about 1.60, which is larger than the band width of most conventional coatings for flexible substrates. In reality however, small and/or local deviations in layer thicknesses or in refractive indexes (as a consequence of small deviations in layer compositions) may result in an increase of the photopic reflection values. These values may rise up to about 0.60% when applied onto a flexible and transparent substrate or up to about 0.70% when applied onto a hardcoated flexible substrate. Preferably the values should not exceed 0.60% resp. 0.70% and most preferably they should not exceed 0.45% resp. 0.55%.

The third material layer 10 in the coating stack according to the invention, consists of an electrically conductive material, giving the anti-reflective coating the desired electrical conductivity.

This layer is a so-called "dummy layer", which means that its thickness has no or very little influence on the optical properties of the coating. By changing the thickness of this dummy layer, the electrical conductivity of the coating can be adjusted within a broad range, without influencing the optical properties of the coating.

5 A layer acts as dummy layer if it is inserted in the stack at a position where the complex optical admittance  $Y$  of the stack takes a real value, and if the refractive index of the inserted layer is equal to said real value.

10 After depositing the fifth and fourth stack layers 11 and 12 onto the substrate, the nascent stack has a real admittance of about two, as can be seen from the admittance diagram of Figure 6. If at this point a layer is inserted of a material with a refractive index of about two, the admittance diagram continues as a circle with extremely small radius (or ideally a point), meaning that the optical properties of the coating remain virtually unchanged. As indium-tin-oxide (ITO) has a refractive index of about two, it is very suitable for the above-said purpose. An ITO layer inserted as third layer in the stack constituting the anti-reflective coating according to the invention, acts therefore as a dummy layer.

15 The ITO dummy layer is electrically conductive, and provides the coating with an adjustable electrical conductivity. Indeed, by varying the thickness of the ITO dummy layer between 5 and 50 nm, and preferably between 20 and 40 nm, the electrical sheet resistance of the coating can be adjusted between 25 and 2000  $\Omega/\text{sq}$ , without influencing the optical properties of the coating. For application e.g. on cathode ray tubes, the electrical

sheet resistance of the coating is preferably very low, between 25 and 500  $\Omega$ /sq.

The electrical sheet resistance is defined as the resistance of a conductor with a surface area of one square (length = width), which can be calculated as the ratio of the resistivity of the  
5 conductive layer and the thickness of the conductive coating layer.

It is an additional advantage of the coating according to the invention that its colour is adjustable and reproducible. Since the  
10 optical properties of the proposed coating are not very sensitive to small changes in thickness of its constituting stack layers and/or in the stoichiometry of the materials, fine-tuning of the colour is possible.

#### 15 Exemplary embodiments of the invention

Some non-limiting embodiments of the anti-reflective coating according to the invention are given below.

#### 20 Example 1

An anti-reflective coating comprising a stack with a composition as given in Table 1, has a band-width of 1.75 and leads to a photopic reflection (as defined above) of 0.094% when applied onto a (transparent) polyethyleneterephthalate (PET) film as substrate,  
25 and to a photopic reflection of 0.175% when applied onto a hardcoated PET film as substrate. The hardcoat consists of highly cross-linked UV-cured acrylates, and has a thickness of about 3.5  $\mu$ m. The reflectance plot relating to this coating is shown as plot E in Figure 8.

The coating has an electrical sheet resistance of less than about 250  $\Omega$ /sq, depending on the exact composition of the deposited ITO material.

Table 1.

Layer	Material	Refractive Index	Optical Thickness
	< Air >		
1	SiO <sub>2</sub>	1.46	0.26 $\lambda_0$
2	TiO <sub>2</sub>	2.35	0.50 $\lambda_0$
3	ITO	2.03	0.10 $\lambda_0$
4	SiO <sub>2</sub>	1.46	0.09 $\lambda_0$
5	TiO <sub>2</sub>	2.35	0.05 $\lambda_0$
	< Substrate >		

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Example 2

An anti-reflective coating comprising a stack with a composition as given in Table 2, has a band-width of 1.65 and leads to a photopic reflection (as defined above) of 0.094% when applied onto a polyethyleneterephthalate (PET) film as substrate, and to a photopic reflection of 0.172% when applied onto a hardcoated PET film as substrate. The hardcoat consists of highly cross-linked UV-cured acrylates, and has a thickness of about 3.5  $\mu$ m. The reflectance plot relating to this coating is shown as plot F in Figure 8, or plot D in Figure 7.

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The coating has an electrical sheet resistance of less than about 200  $\Omega$ /sq, depending on the exact composition of the deposited ITO material.

Table 2.

Layer	Material	Refractive Index	Optical Thickness
	< Air >		
1	SiO <sub>2</sub>	1.46	0.26λ <sub>0</sub>
2	TiO <sub>2</sub>	2.35	0.49λ <sub>0</sub>
3	ITO	2.03	0.12λ <sub>0</sub>
4	SiO <sub>2</sub>	1.46	0.09λ <sub>0</sub>
5	TiO <sub>2</sub>	2.35	0.05λ <sub>0</sub>
	< Substrate >		

Example 3.

5 The anti-reflective coating comprising a stack with a composition as given in Table 3, has a band-width of 1.64 and leads to a photopic reflection (as defined above) of 0.087% when applied onto a polyethyleneterephthalate (PET) film as substrate, and to a photopic reflection of 0.166% when applied onto a hardcoated

10 PET film as substrate. The hardcoat consists of highly cross-linked UV-cured acrylates, and has a thickness of about 3.5 μm. The reflectance plot relating to this coating is shown as plot G in Figure 8.

15 The coating has an electrical sheet resistance of 175 Ω/sq, depending on the exact composition of the deposited ITO material.



Table 3.

Layer	Material	Refractive Index	Optical Thickness
	< Air >		
1	SiO <sub>2</sub>	1.46	0.26λ <sub>0</sub>
2	TiO <sub>2</sub>	2.35	0.46λ <sub>0</sub>
3	ITO	2.03	0.14λ <sub>0</sub>
4	SiO <sub>2</sub>	1.46	0.09λ <sub>0</sub>
5	TiO <sub>2</sub>	2.35	0.04λ <sub>0</sub>
	< Substrate >		

Example 4

5 The anti-reflective coating comprising a stack with a composition as given in Table 4, has a band width of 1.6 and leads to a photopic reflection (as defined above) of 0.081% when applied onto a polyethyleneterephthalate (PET) film as substrate, and to a photopic reflection of 0.161% when applied onto a hardcoated PET film as substrate. The hardcoat consists of highly cross-

10 linked UV-cured acrylates, and has a thickness of about 3.5 μm. The reflectance plot relating to this coating is shown as plot H in Figure 8.

The coating has an electrical sheet resistance of 150 Ω/sq, depending on the exact composition of the deposited ITO

15 material.

Table 4.

Layer	Material	Refractive Index	Optical Thickness
	< Air >		
1	SiO <sub>2</sub>	1.46	0.26λ <sub>0</sub>
2	TiO <sub>2</sub>	2.35	0.46λ <sub>0</sub>
3	ITO	2.03	0.16λ <sub>0</sub>
4	SiO <sub>2</sub>	1.46	0.10λ <sub>0</sub>
5	TiO <sub>2</sub>	2.35	0.04λ <sub>0</sub>
	< Substrate >		

5 The exemplary coating stacks mentioned in Tables 1 to 4, differ from each other in the thickness of the ITO dummy layer; the proposed coatings comprise an ITO layer with a physical thickness of 25, 30, 35 and 40 nm respectively. Figure 8, which combines the reflectance plots of these four coatings, demonstrates that the thickness of the ITO layer does virtually not

10 influence the reflectance properties of the coating, confirming the statement that the ITO layer is a dummy layer. On the other hand, the thickness of the ITO layer has a direct influence on the electrical sheet resistance of the coating; the electrical sheet resistance of the coating comprising an ITO layer with a physical

15 thickness of 40 nm is about 1.6 times lower than that of the coating with an ITO layer of 25 nm.

Example 5

An anti-reflective coating stack according to the present invention comprising a stack with a composition as given in Table 5 was deposited in two passes on a large web coater or roll-coater with three deposition sections. The coating stack was uniform over a width of about 1000 mm and had the following characteristics :

- average spectral reflection in the range 450 - 650 nm : 0.30 - 0.36%
- maximum reflectance in the wave-length range 450 - 650 nm : 0.51 - 1.62%
- band-width : 1.55 - 1.58
- photopic reflectance : 0.33%
- The sheet resistance of this coating was about 500  $\Omega$ /sq

Table 5.

Layer	Material	Refractive Index	Optical Thickness
	< Air >		
1	SiO <sub>2</sub>	1.50	0.25 $\lambda_0$
2	TiO <sub>2</sub>	2.41	0.51 $\lambda_0$
3	ITO	2.03	0.13 $\lambda_0$
4	SiO <sub>2</sub>	1.50	0.06 $\lambda_0$
5	TiO <sub>2</sub>	2.41	0.04 $\lambda_0$
	< Substrate >		

15

According to the invention, there is also proposed a method for coating a flexible substrate with an anti-reflective coating, whereby

the coating is applied onto the substrate by means of a single or double pass vacuum magnetron sputtering operation in a vacuum web coater. This sputtering operation can be performed in a vacuum chamber 20 comprising:

- 5 (1) a section 30 for unwinding and rewinding the flexible substrate;
  - (2) deposition sections wherein the material layers constituting the coating are consecutively sputtered onto the substrate;
  - (3) a central cooling drum 24, on the surface of which the substrate moves through the deposition sections. The vacuum
- 10 web coater can be a large web coater or a roll coater with e.g. three or five deposition sections.

Different sputter magnetrons can be used for obtaining the coating according to the invention. For example, rotatable or planar

15 magnetrons using silicon, titanium and In/Sn-alloy (90/10, wt%) targets can be used for reactive sputtering in an Ar/O<sub>2</sub> atmosphere.

It is however preferred to sputter the titaniumdioxide layers from a

20 (oxygen deficient) TiO<sub>x</sub> (x<2) rotatable ceramic target fixed on a cylindrical support.

In the prior art it is avoided to sputter from titaniumdioxide (TiO<sub>2</sub>) targets, because the sputter rate from a conventional planar titaniumdioxide target is very low, and also because the power

25 applied to the target has to be kept low, making the process not suitable for industrial application. In DC-mode, the power density on the target has to be low to prevent arcing due to the low conductivity of the titaniumdioxide target. In RF-mode the power

density on the target should be kept low for shielding reasons, to avoid electromagnetic interference around the sputter web coater. As titaniumdioxide leads to better optical properties than other materials because of its very high refractive index, it is however  
5 desirable to use titaniumdioxide instead of any other substitute material.

Theoretically, titaniumdioxide can be deposited by DC (or RF) reactive sputtering in an oxygen rich plasma from planar or rotatable titanium targets. It has however been shown that this  
10 way of operating makes it very difficult to obtain stoichiometric titaniumdioxide material layers, even when high oxygen flow rates are applied (which can lead to arcing and low deposition rates). Using an understoichiometric rotatable  $TiO_x$  ( $x < 2$ ) target the sputter rate is however enhanced, and stoichiometric  
15 titaniumdioxide layers are obtained, with little addition of oxygen to the plasma.

Furthermore, starting from an understoichiometric target material, titaniumdioxide is deposited as rutile rather than as anatase, yielding better optical properties, as the refractive index of rutile is  
20 even somewhat higher than that of anatase.

Using a single pass operation, the five layers 8 to 12 constituting the stack ( $TiO_2$ - $SiO_2$ -ITO- $TiO_2$ - $SiO_2$ , starting from the substrate) are sputtered consecutively onto the substrate, in five separate  
25 and adjacent deposition sections.

A possible single pass operation is illustrated in Figure 9. Vacuum pumps create a vacuum in the chamber 20 comprising the unwinding roll 21 and the rewinding roll 22 for the flexible substrate 23, the sputtering sources or targets 25 to 29, and the

cooling drum 24. The flexible substrate 23 is unwound from the unwinding roll 21, and moves on the surface of the cooling drum 24 through the deposition sections, and is finally rewound on the rewinding roll 22. The material layer which has to be closest to the substrate, the fifth layer, is sputtered first from a rotatable  $TiO_x$  target 25. In the next deposition sections, the fourth, third, second and first layers of the stack are consecutively sputtered, respectively from a rotatable silicon target 26, a planar indium/tin or ITO target 27, a rotatable  $TiO_x$  target 28, and a rotatable silicon target 29.

Using a double pass operation, the two material layers to be deposited closest to the substrate ( $TiO_2$ - $SiO_2$ ) are sputtered during the first pass of the substrate through the deposition sections, and the remaining three material layers (ITO- $TiO_2$ - $SiO_2$ ) are sputtered during the second pass. This implies that a double pass operation requires only three deposition sections.

Figure 10 illustrates a possible double pass operation. The fifth and fourth layers of the stack constituting the coating are sputtered during the first pass of the flexible substrate 23 through the deposition sections, from a rotatable  $TiO_x$  target 32 and a rotatable silicon target 33 respectively. During a second pass, material layers are sputtered from a planar indium/tin or ITO target 31, a rotatable  $TiO_x$  target 32 and a rotatable silicon target 33 consecutively onto the substrate 23.

It will be clear from the above description that each of the rotatable magnetrons can be replaced by a planar magnetron and vice-versa.

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5 The anti-reflective coating according to the invention can be successfully used as a coating for a polymer film which constitutes the front surface of a cathode ray tube (both in television applications or computer monitors), or of a liquid crystal display.

Claims

- 1        A multilayer inorganic anti-reflective coating (7) with  
5        predetermined optical properties for application on a  
flexible substrate (13), whereby said coating comprises a  
stack consisting of five material layers, respectively  
designated as the first, second, third, fourth, and fifth layer,  
starting from the layer situated farthest from the substrate,  
10        and whereby said first layer (8) has a refractive index less  
than the refractive index of said substrate and an optical  
thickness of about a quarterwave ( $\lambda_0/4$ ), and whereby said  
second layer (9) has a refractive index greater than about  
2.2 and an optical thickness of about a halfwave ( $\lambda_0/2$ ), and  
15        whereby said fourth layer (11) has a refractive index which  
is about the same as the refractive index of said first layer  
and an optical thickness of less than about  $0.1\lambda_0$ , and  
whereby said fifth layer (12) has a refractive index which is  
about the same as the refractive index of said second layer  
20        and has an optical thickness of about  $0.04\lambda_0$ ,  $\lambda_0$  being  
about 510 nm, characterised in that said third layer (10) is a  
dummy layer consisting of an electrically conductive  
material which provides said coating with an adjustable  
electrical sheet resistance of between 25 and 2000  $\Omega/\text{sq}$   
25        without thereby influencing the optical properties of said  
coating.
- 2        Anti-reflective coating according to claim 1, having an  
electrical sheet resistance between 25 and 500  $\Omega/\text{sq}$ .



- 3 Anti-reflective coating according to claim 1, whereby said dummy layer consists of indium-tin-oxyde.
- 5 4 Anti-reflective coating according to claim 1, whereby the thickness of said dummy layer is comprised between 5 and 50 nm.
- 10 5 Anti-reflective coating according to claim 4, whereby the thickness of said dummy layer is comprised between 20 and 40 nm.
- 15 6 Anti-reflective coating according to claim 1, whereby said first and fourth layers consist of silicondioxyde, and whereby said second and fifth layers consist of titaniumdioxide.
- 20 7 Anti-reflective coating according to claim 1, yielding a photopic reflectance of incident light that does not exceed 0.60% in a wave-length region of from 380 to 780 nm when applied onto a flexible substrate.
- 25 8 Anti-reflective coating according to claim 1, yielding a photopic reflectance of incident light that does not exceed 0.70% in a wave-length region of from 380 to 780 nm when applied onto a hardcoated flexible substrate.
- 9 Anti-reflective coating according to claim 1, having a bandwidth of more than about 1.50.



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- 5
- (2) three deposition sections wherein the material layers constituting said coating are consecutively sputtered onto the substrate;
  - (3) a central cooling drum (24), on the surface of which the substrate (23) moves through said target sections.

14 A method according to claim 12 or 13, whereby use is made of a rotatable or planar  $\text{TiO}_x$  target.

10

15 Use of an anti-reflective coating according to claim 1, as coating for a polymer film which constitutes the front surface of a cathode ray tube (CRT).

15

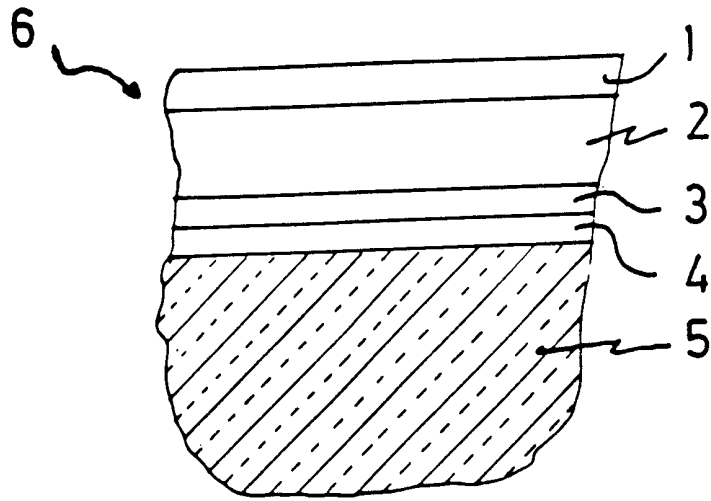


FIG. 1

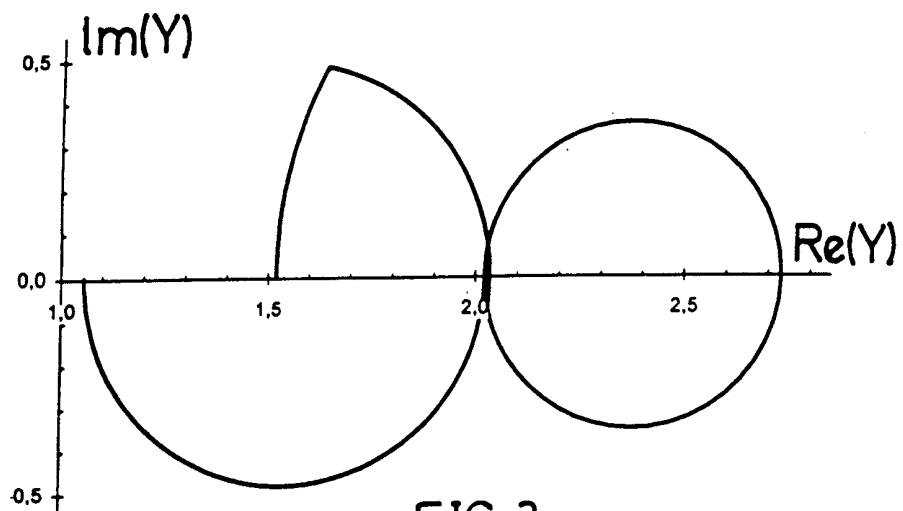
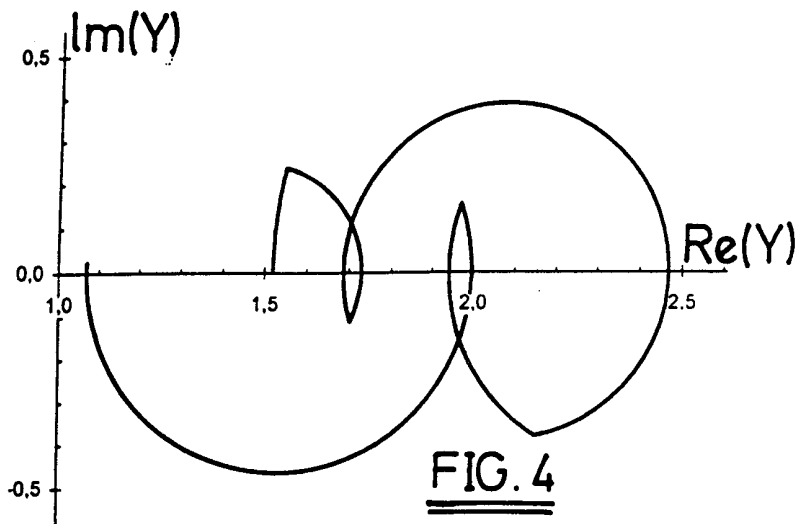
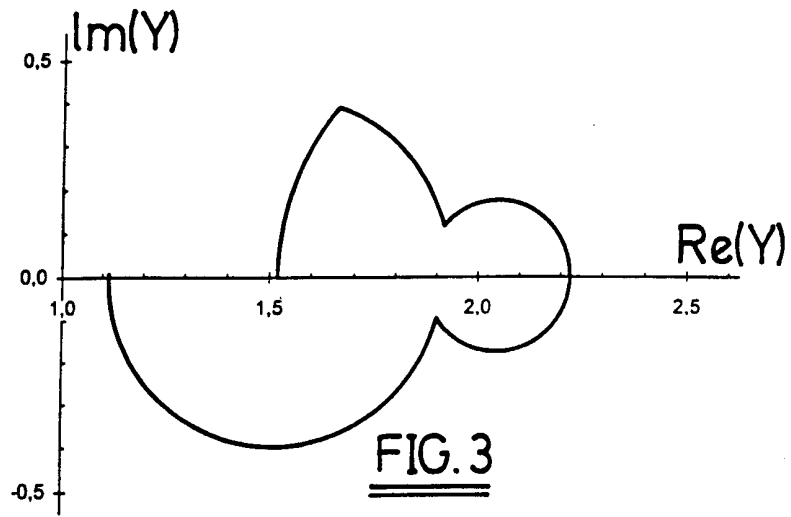


FIG. 2



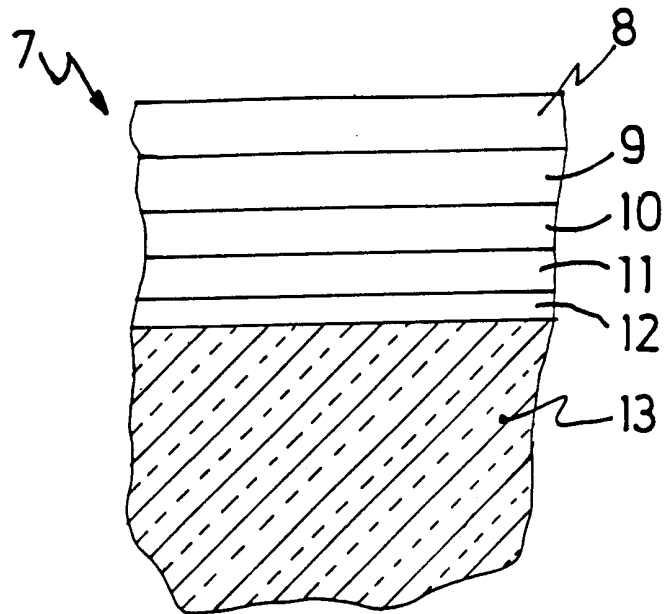


FIG. 5

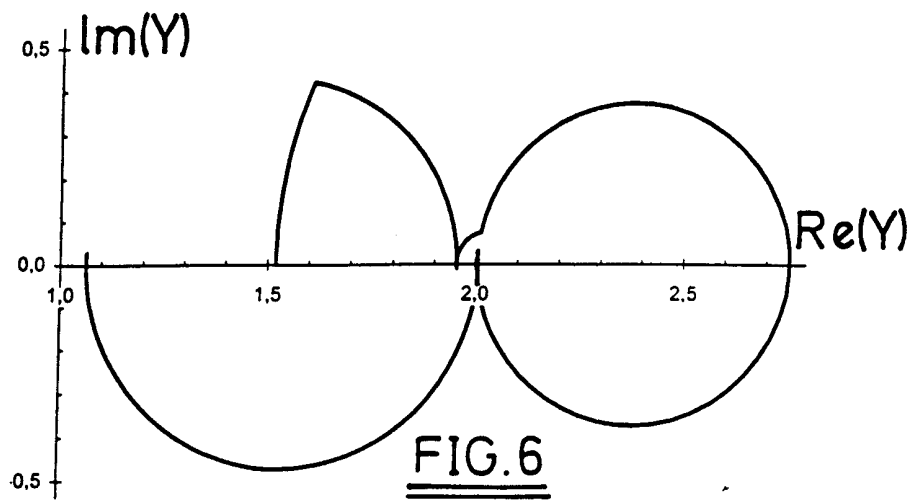
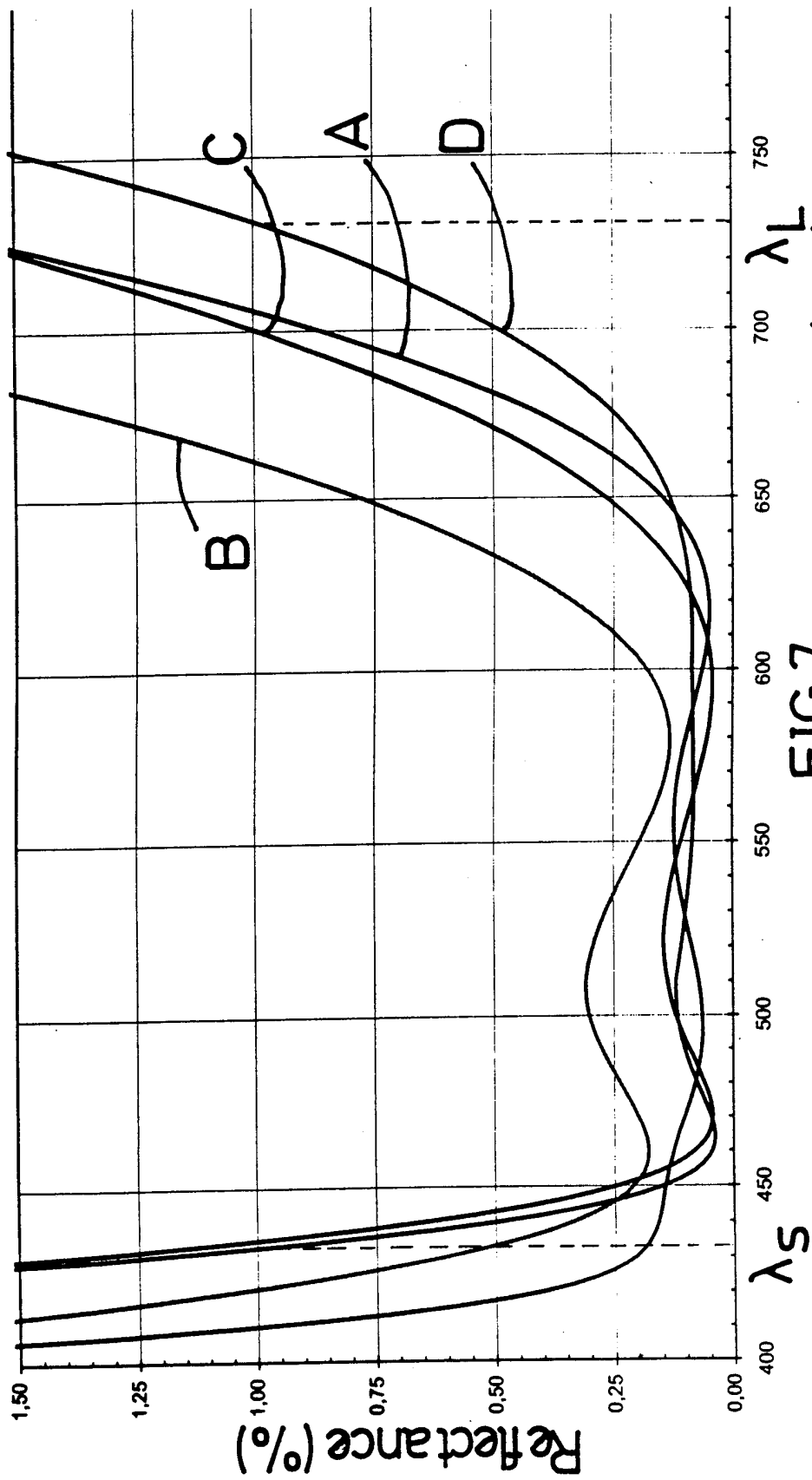


FIG. 6



**FIG. 7** Wavelength (nm)

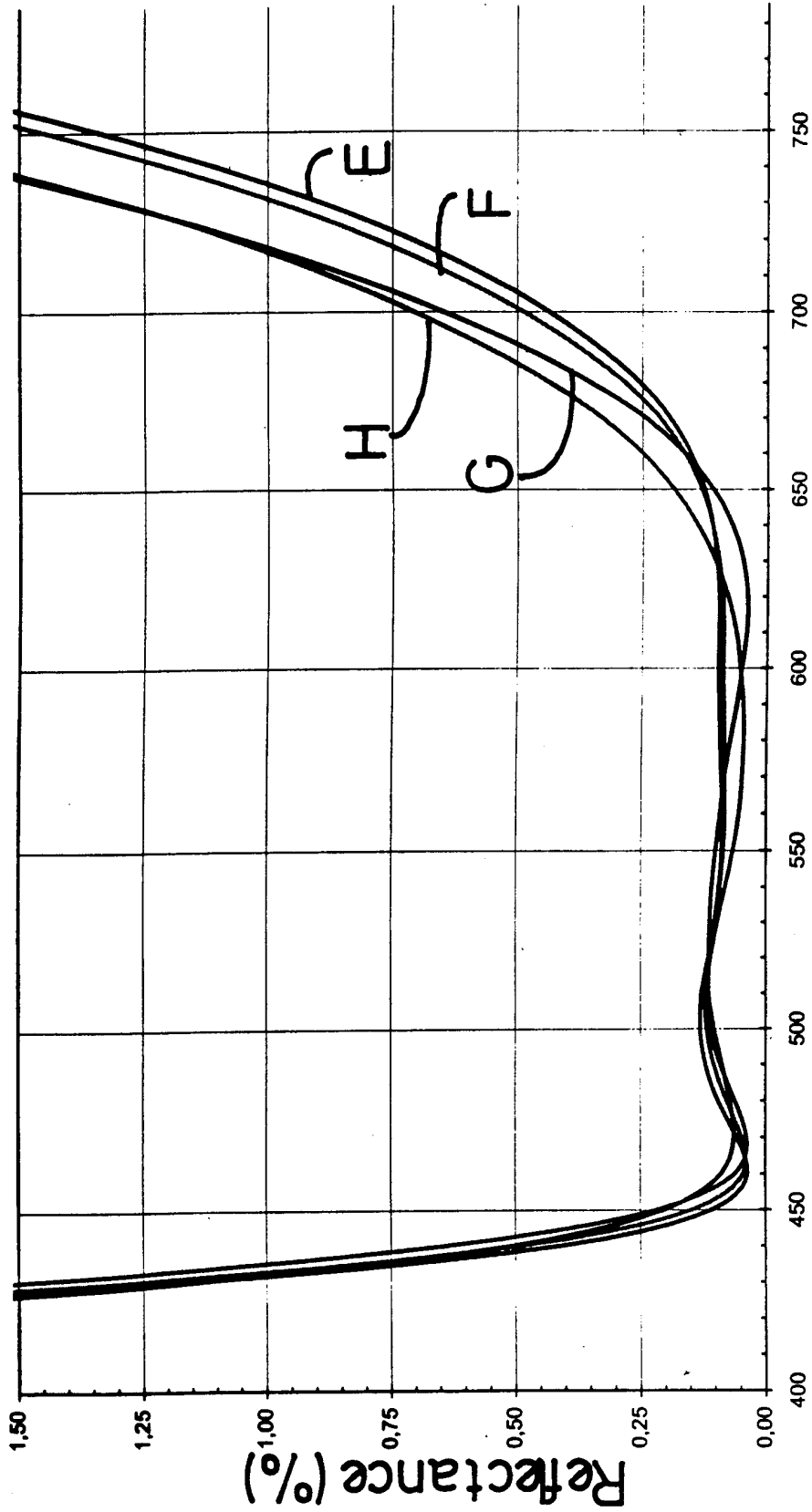


FIG. 8 Wavelength(nm)



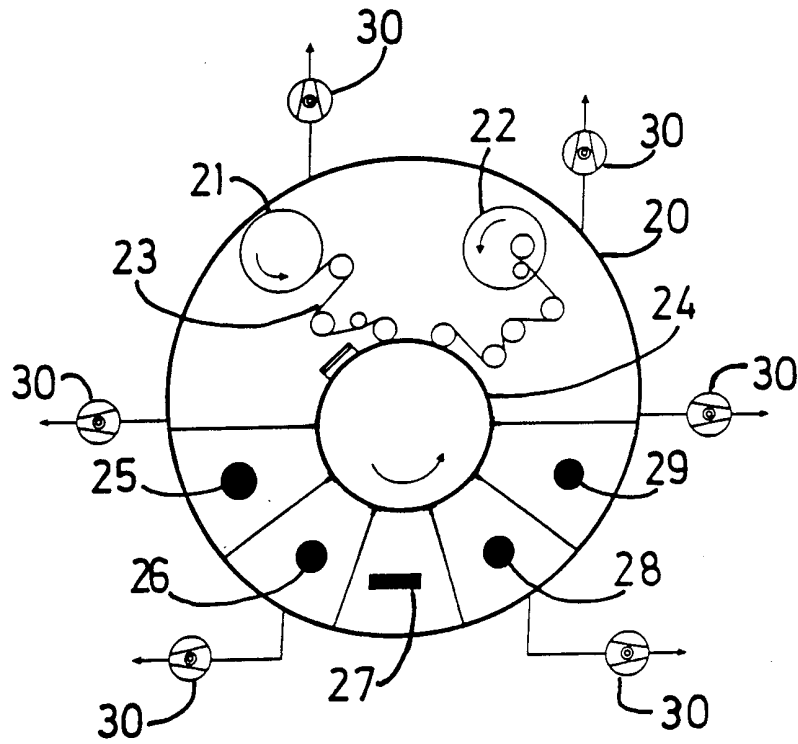


FIG. 9

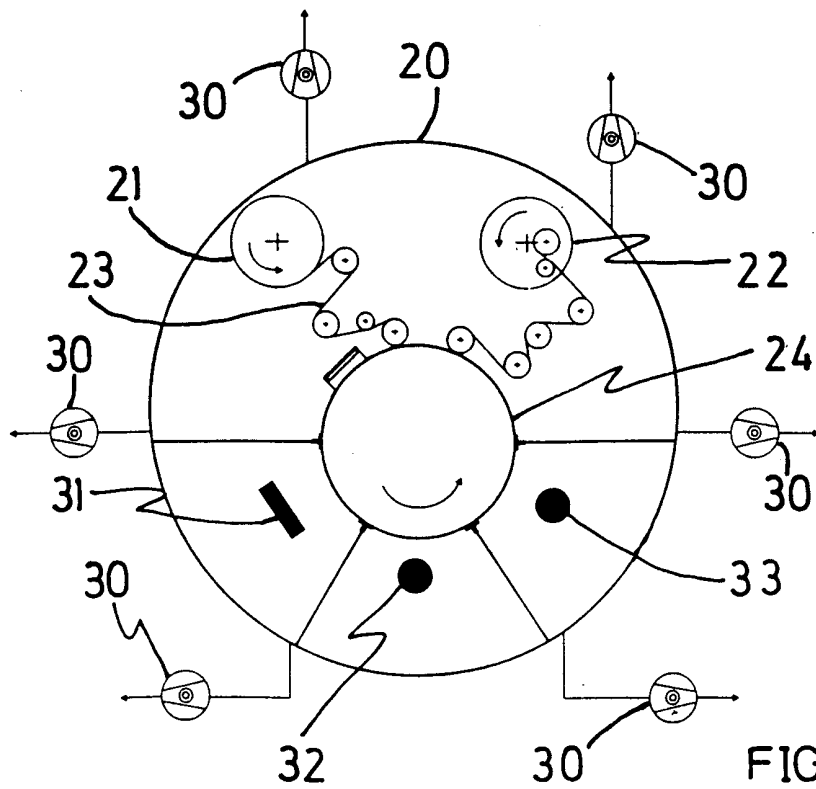
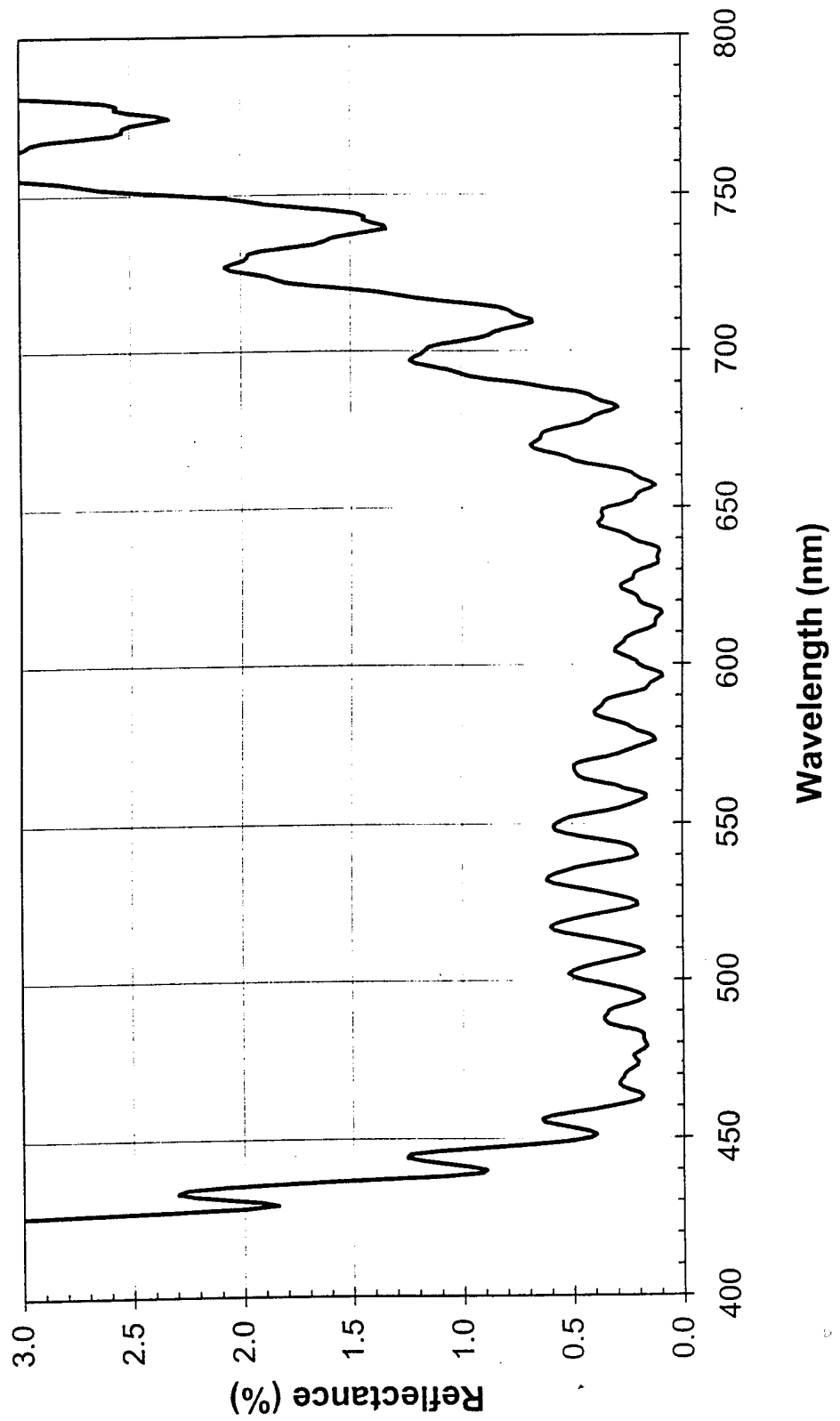


FIG. 10

Fig. 11



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 98/06996

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 G02B1/00 G02B1/11 C03C17/34

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 6 G02B 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)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 508 091 A (AUSTIN R RUSSEL) 16 April 1996 see column 6, line 12 - column 11, line 17; figures 1-6 ---	1-15
A	US 5 270 858 A (DICKEY ERIC R) 14 December 1993 cited in the application see column 5, line 11 - column 12, line 49; figures 2-8 ---	1-15
A	US 4 422 721 A (HAHN ROBERT E ET AL) 27 December 1983 see column 2, line 39 - column 3, line 21 see column 6, line 64 - column 8, line 29; claim 1; figures 1,6 ---	1-6,15
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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
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Date of the actual completion of the international search  <b>19 February 1999</b>	Date of mailing of the international search report  <b>02/03/1999</b>
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Name and mailing address of the ISA 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	Authorized officer   <b>THEOPISTOU, P</b>
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# INTERNATIONAL SEARCH REPORT

Inter. Appl. Application No  
PCT/EP 98/06996

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 667 880 A (OKANIWA MASAYUKI) 16 September 1997 see column 3, line 28 - column 5, line 53 see column 7, line 65 - column 8, line 55; figures 2-6,12-15; example 1; tables 6-9 -----	1-6, 12-15
A	US 5 450 238 A (BJORNARD ERIK J ET AL) 12 September 1995 cited in the application see column 3, line 55 - column 6, line 53; figures 1-4 -----	1-15

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Information on patent family members

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