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

(19) World Intellectual Property
Organization
International Bureau

(43) International Publication Date
16 September 2004 (16.09.2004)

PCT

(10) International Publication Number
WO 2004/079278 A1

(72) Inventor; and
(75) Inventor/Applicant (for US only): **SCHÜLER, Andreas** [DE/CH]; c/o Ecole Polytechnique Fédérale de Lausanne, Ecublens, CH-1015 Lausanne (CH).

(74) Agent: **ROLAND, André**; Avenue Tissot 15, CH-1001 Lausanne (CH).
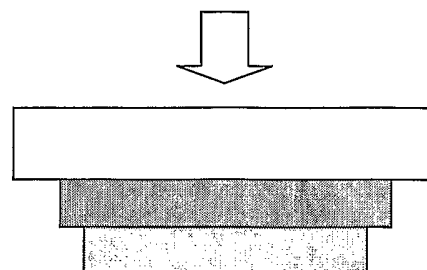
(54) Title: GLAZING

air   n = 1

glass n = 1.52

TiO$_2$ n = 2.2 , varying thickness
SiO$_2$ n = 1.46 , 140 nm

air   n = 1

(57) Abstract: The invention relates to a glazing designed to reflect a narrow spectral band of visible light while being transparent for the rest of the solar spectrum. The glazing is particularly, but not exclusively, suitable for solar collectors.

GLAZING

Field of the invention

The present invention relates to glazings which, in particular, may be used in solar collectors.

In the present text, the term "glazing" means any material, e.g. glass or polycarbonate, transparent to visible electromagnetic radiation.

State of the art

Architectural integration of solar energy systems into buildings is becoming more and more important. Thermal solar collectors, typically equipped with black, optical selective absorbers sheets, exhibit in general good energy conversion efficiencies. However, the black color, and sometimes the visibility of tubes and corrugations of the metal sheets, limits the architectural integration into buildings. Various attempts have been made to overcome this drawback. One way out is to color the absorber sheets. Optical selective absorber coatings are usually deposited by processes such as magnetron sputtering, vacuum evaporation, electrochemical processes, SolGel technology, or as selective paint (thickness-sensitive or thickness-insensitive). These processes are optimised for high solar absorption, yielding typically black or dark blue surfaces. Modifying the process parameters can result in a colored appearance of the solar absorber sheet. Selective paints can be prepared to exhibit blue, green, and brownish red colors. By varying the layer thickness, sputtered absorber coatings can also be colored in a large variety of shades. Following this approach, the absorber surface combines the functions of optical selectivity (high solar absorption/low thermal emission) and colored reflection.

Tripanagnostopoulos et. al. (Y. Tripanagnostopoulos, M. Souliotis, Th. Nousia, Sol. Energy 68, (2000), 343) proposed a different solution, i.e. the use of non-selective colorful paints as absorber coatings for glazed and unglazed collectors, and compensated the energy losses by additional booster reflectors.

1

BESTÄTIGUNGSKOPIE

Summary of the invention

An object of the present invention is to provide a colored reflection from a glazing, e.g. from the cover glass of a solar collector. This approach has the advantage to separate the functions of optical selectivity and colored reflection, providing thereby more freedom to layer optimization. In addition, if the invention is used in a solar collector, the black, sometimes ugly absorber sheet is hidden by the colored reflection of the glazing.

The principle of the invention is summarised in Figure 1 which schematically shows a thermal solar collector wtih a colored coating applied to the glazing. The coating reflects a color, thus hiding the corrugated absorber sheet,. However the complementary spectrum is transmitted. No absorption occurs in the coating. The coating can be deposited onto the inner of the glazing, as shown in the drawing, but also on the outer side, or on both. Also, a colored coating on the inner side can be combined with a mat outer surface (or with a diffusing substrate).The glazing can consist e.g. of white glass (low iron content), or of organic material such as polycarbonate.

No energy should be lost by absorption in the coating. All non-reflected energy should be transmitted.

Those objectives are achieved with the glazing according to the present invention which, preferably but not exclusively, comprises multilayer interference stacks of transparent materials.

Multilayer interference stacks for various optics and laser applications are known in other fields , see e.g. H. Angus Macleod "Thin-Film Optical Filters", 3rd Ed., Institute of Physics Publishing, Bristol, ISBN 0-7503-0688-2 (2001) (2nd Ed. with Adam Hilger Ltd, Bristol, ISBN 0-85274-784-5 (1986)).

For the present invention the material choice must be realistic, and the considered refractive indices have consequently to be within a certain range. In addition to that, the maximum number of layers is limited. In contrast to applications such as laser interference filters, solar applications employ typically large surfaces to be coated at low price, which implies that production costs limit the number of individual layers building up the multilayer stack.

2

One possible way to color the reflected light is the use of thin film interference which is a well known phenomena which can be observed with soap bubbles, thin oil films on water, etc.. The cover glass of a solar collector can be coated, either on one side, or on both. Because of the constraint that no absorption must occur, we preferably use thin films built up of dielectric, transparent materials like e.g. SiO_2, Al_2O_3, TiO_2, composite silicon titanium oxide, or MgF_2. Preferably the glass to be coated is practically iron-free ('white' solar glass).

In contrast to photovoltaics, solar thermal collectors can convert the full solar spectrum including the infrared. Thus, in solar collectors, the fraction of invisible but usable solar radiation is much higher than for photovoltaics.

List of figures

Detailed description of the invention

For the calculation of the solar absorbance of thermal solar collectors, the solar spectrum at air mass 1.5 (AM1.5) is used conventionally. For the calculation of the solar transmittance T_{sol} of the colored cover glasses, we also adapt the use of the spectrum AM1.5.

Regarding colorimetry, the Commission Internationale d'Eclairage (CIE) describes standard illuminants (like A, B, C, D65, E). For the determination of the color coordinates of an illuminated surface, we use the standard illuminant D65, that corresponds to a daylight illumination taking into account the diffuse radiation of the sky.

The spectra of D65 and AM1.5 are quite close to each other, but not identical (see Fig. 2).

In order to get an idea of the potential of the envisaged colored glazing with high solar transmission, we calculate the performance of an idealized system that reflects just an extremely narrow spectral band (represented by a δ-distribution) and is perfectly transparent for the rest of the solar spectrum. Calculated are the visible reflectance R_{VIS} under daylight illumination D65, and the solar energy losses by reflection R_{sol} (%) (based on the solar global spectrum at air mass 1.5). In absence of absorption in films and glass, reflection and transmission are complementary: R_{sol} (%) + T_{sol} (%) = 100 %.

By straightforward integration, the ratio R_{VIS} (%) / R_{sol} (%) is found to be independent of the amplitude of the narrow spectral band, and depends therefore on the wavelength only (see fig. 3).

In the region from 480 nm to 640 nm, the ratio R_{VIS} (%) / R_{sol} (%) is greater than 1. The absolute maximum amounts 6.3 and is reached at 550 nm, which corresponds to a color of yellowish green. This means, that at this wavelength, a visible reflectance of e.g. 12.6 % would just induce solar losses of only 2 %.

Obviously, the ratio R_{VIS} (%) / R_{sol} (%) has the character of a figure of merit.

The substrate to be coated is preferably glass. Solar glazing is nearly iron-free, which ensures low absorption in the bulk glass. Typical refractive indices exhibit normal

4

dispersion in the range of $1.51 \leq n \leq 1.58$ (at 500 nm: n=1.52 for BK7, n = 1.54 for AF45).

Some commonly used thin film materials are listed below :

material	deposition technique	refractive index n
Al_2O_3	e - beam evaporation, magnetron sputtering, SolGel?	1.62 at 600 nm, 1.59 at 1600 nm
MgF_2	evaporation from tantalum boat	1.38 at 550 nm, 1.35 at 2000 nm
SiO_2	e - beam evaporation, magnetron sputtering, SolGel	1.46 at 500 nm, 1.445 at 1600 nm
Si_3N_4	low voltage reactive ion plating, magnetron sputtering	2.06 at 500 nm
TiO_2	e - beam evaporation, magnetron sputtering, SolGel	2.2 – 2.7 at 550 nm depending on structure

Of course there exists many more. Intermediate refractive indices can be achieved by mixing materials to composites (e.g. by mixing SiO_2 and TiO_2 to composite silicon titanium oxide). In many cases the refractive indices depend to a large extend on the deposition conditions.

Numerical simulation of multilayered interference stacks

The optical behavior of multilayered thin film stacks is described by well-known but complicated formulae. Each individual layer is represented by a 2 x 2 matrix, the multilayered stack by their matrix product. Multiple reflections from back and front side of the glass have to be taken into account. Due to the complexity of the equations, numerical simulations are usually performed with the aid of a computer. Software performing these calculations is already commercially available. Spectra-Ray Advanced Fit (SENTECH) is a software originally designed for evaluating ellipsometry data, but it is also capable of straightforward simulation of reflectance and transmittance spectra. A professional tool for designing interference filters is Tfcalc, which also includes the features of refining an existing design and even a global search for optimal designs.

In large area deposition, it is always advantageous to find a solution with the least number of individual layers possible.

Example 1 : Refractive Indices 1.46 and 2.2

These refractive indices correspond roughly to SiO_2 and TiO_2, both durable materials accessible by the sol-gel technique as well as by the vacuum techniques of magnetron sputtering or e - beam evaporation. Therefore it is worthwhile to use their combination.

In this example, one side of the glass, which may be the inner side, is coated (see Figure 4).

The effect of varying just a single parameter, the TiO_2 thickness t2.2 , has been studied.

The graph illustrated in Figure 5 shows the reflectance spectra under variation of the TiO_2 thickness t2.2 from 0 nm to 80 nm, in steps of 10 nm. The SiO_2 thickness t1.46 is kept as a constant (140 nm).

The black solid line represents the spectrum for a TiO_2 thickness t2.2 = 30 nm. It shows a sharp maximum at 370 nm, giving rise to a blue-violet color and even a

region of antireflection around 650 nm. Exhibiting acceptable color saturation (x = y = 0.22) and a relative luminosity of 8.1 %, the spectrum yields a solar transmission as high as 89.8%.

The locus (x. y) in color space can be plotted with the TiO_2 thickness t2.2 as curve parameter. In Figure 6 the TiO_2 thickness t2.2 has been running from 0 nm to 1000 nm - point 'A' corresponds to the start at t2.2 = 0 nm.

Starting not far from white (point 'D65'), the response of the system is of oscillatory nature. The resulting trajectory is in a certain sense beautiful but illustrates the complexity of the problem: extrema of saturation are of local character (compare points 'B' and 'D').

Color coordinates, visible reflectance and solar transmission for some representative points are given in Table 1.

TABLE 1

point	t2.2 (nm)	x	y	approx. color	R_{VIS} (%)	T_{sol} (%)
A	0	0.3	0.32	white	7.5	92.7
B	30	0.22	0.22	blue	8.1	89.8
C	106	0.36	0.39	yellow	14.2	86.9
D	152	0.2	0.19	blue	8.5	88.2
E	300	0.22	0.37	green	14	88.5
glass		0.31	0.33		8.2	91.8

(t1.46 = 140 nm)

A variety of colors can be achieved, keeping the solar transmission above 86 %.

Point 'B' is characterized by excellent solar transmission, only 2 % worse than that of uncoated glass.

Example 2 : Refractive indices 1.38 and 2.2

If a low-index material like MgF_2 is available (n = 1.38), the coloration can be combined with a better partial anti-reflection. Conventionally, this material is deposited by vacuum evaporation. However it is less tough and stable than SiO_2.

At one wavelength, the so-called design-wavelength λ_0, the reflection can made to be zero. Due to the shape of the reflection minimum, this 2-layer design is called "V-coat". This is achieved by choosing the appropriate film thicknesses t1.38 and t2.2.

Coating both sides of the glass enhances color saturation and the effect of anti-reflection (see Figure 7).

Figure 8 visualizes the reflectance spectra for design-wavelengths λ_0 = 650 nm and 1300 nm.

By scaling the film thickness, interference minima and maxima can be shifted easily in wavelength, thus giving rise to a variety of colors (see TABLE 2).

TABLE 2

λ_0	t2.2 (nm)	t1.38 (nm)	x	y	approx. color	R_{VIS} (%)	T_{sol}(%)
600	16	140	0.15	0.1	violet	1.44	94
650	17	151	0.16	0.15	blue	3.64	93.4
700	19	163	0.19	0.2	blue	7.7	92.2
800	21	186	0.23	0.27	blue-green	16	90.7
900	24	209	0.28	0.34	green	23.4	88.9
1000	27	233	0.35	0.41	yellow-green	26.1	87.5
1200	32	279	0.39	0.32	white	16.8	82.2
1300	35	302	0.3	0.2	purple	11.5	83.9
1400	37	326	0.22	0.18	violet	11.4	82.9
	glass		0.313	0.329		8.17	91.8

The solar transmission T_{sol} can even be made higher than the one of uncoated glass, nevertheless keeping considerable luminosities in the violet and blue, up to nearly 8 %! In the yellow-green, a luminosity of 26.1 % is achieved, the losses are only 4.4 % worse compared to the uncoated glass!

Example 3 : V-coat or W-coat

For two-layered systems, the nicknames "V-coat" and "W-coat" indicate special anti-reflection designs. The names are derived from the form of the spectra: a V-coat has one minimum, a W-coat two ones. For the latter one, the region of low reflection is broader.

model: air//LH//glass//HL//air

With "design-wavelength" λ_0 : n x t(H) = $\lambda_0/2$ n x t(L) = $\lambda_0/4$

n(H) = 1.8,   2.2
n(L) = 1.38, 1.47

Figure 9 shows the reflection spectra for a design-wavelength of 800 nm.

For the shown examples, the resulting colors are in the region of bluish green. Due to the partial antireflection, the achieved color saturation and as well the solar transmission are remarkable (see Table 3).

TABLE 3

n(H)	n(L)	t(H)	t(L)	x	y	R_{VIS} (%)	T_{sol} (%)
1.8	1.47	222	136	0.18	0.27	9.1	92.5
2.2	1.47	182	136	0.21	0.32	21.1	86.2
1.8	1.38	222	145	0.19	0.29	9.4	93.4
2.2	1.38	182	145	0.23	0.34	23.3	85.7

Example 4 : Three-layered system

Adding an additional layer to a V-design results in a strong enhancement of the colored reflection (see Figure 10).

The reflectivity is computed for normal incidence (see Figure 11).

The spectrum corresponding to the case of a 30 nm thick top layer exhibits a strong enhancement of the reflection peak and still a region of partial anti-reflection at a wavelength of 1000 nm. For the top layer being 50 nm thick, the region of anti-reflection is already less pronounced.

The table 4 shows the numerical results in dependence on the thickness t3 of the third layer (the topmost one).

TABLE 4

t3 (nm)	x	y	R_{vis} (%)	Rsol(%)	Tsol(%)
0	0.22	0.22	8.1	10	90
10	0.24	0.27	17	12	88
20	0.27	0.31	28	16	84
30	0.29	0.34	37	20	80
40	0.31	0.36	43	24	76
50	0.34	0.38	46	27	73

Also from the point of view of the solar transmission Tsol(%), the region between 10 nm and 40 nm appears most interesting.

Towards shorter wavelengths, the reflectance spectra for dielectric thin film stacks exhibit rapid oscillations between the maxima and minima of higher order. By using high enough thickness of the individual layers, these maxima can be chosen to be located in the visible spectral region.

Here, the computation of color coordinates is based on the CIE illuminant C. Fortunately, the materials SiO_2 and TiO_2 are included, assuming the refractive indices listed in table 5.

TABLE 5

wavelength (nm)	TiO2	SiO2
300	2.6	1.48
400	2.52	1.47
500	2.42	1.46
600	2.35	1.45
700	2.33	1.45
800	2.3	1.44

Figure 12 illustrates an example showing the rapid oscillations in the high wavelength region and the peaks in the visible which are used for the coloration: for a color of pink, two peaks in the blue and in the red, are necessary.

In this case, color coordinates of x = 0.39 , y = 0.24 are found, with a visible reflectance of 9.8 % - the solar transmission amounts 84.6 %. Layer thickness of 213 nm and 258 nm are assumed for the TiO_2 and the SiO_2 layers, respectively. Only one side of the glass is assumed to be coated.

Some more examples are listed in Table 6. The selection comprises two, three and four layered systems.

TABLE 6

design	layer				color coordinates		approx. Color	R_{VIS} (%)	T_{sol} (%)
	1 TiO_2 (nm)	2 SiO_2 (nm)	3 TiO_2 (nm)	4 SiO_2 (nm)	x	y			
A	213	258			0.39	0.24	pink	9.8	84.6
B	126	304.34			0.22	0.14	blue	6.7	83.6
C	15	410			0.35	0.42	yellow	13.9	90.4
D	88	224			0.48	0.38	orange	16.1	82.7
E	11.5	378	11.5		0.35	0.41	yellow	16.9	88.5
F	21	45	259	109	0.22	0.15	blue	6.3	88.4
G	11.5	378	11.5	378	0.29	0.39	green	14	89.7
H	104	37	103	231	0.52	0.35	orange	15.5	80.3

Layer 1 is the next to the glass. Refractive index for the glass : n = 1.52 , coating only on one side.

Often, quarter wave interference stacks are designed as broadband reflection filters, consisting of numerous individual layers and exhibiting a nearly perfect reflection over a broad frequency range. In contrast to this, we focus on filters reflecting just a narrow frequency band, and we will show how it is possible to achieve reasonable results with only a few of individual layers.

Example 5 : Narrow peak by many λ/4 layers

Stacks of λ/4 layers are frequently used to generate high reflectivity mirrors exhibiting a broad band of reflection.
However, by choosing the refractive indices of the two involved materials close to each other, narrow reflection peaks can be produced. If the refractive indices are really close, a lot of layers are however needed to produce a reasonable amplitude.

The present example refers to a system consisting of 40 individual layers. As shown further in the text, such a great number of layers is not preferred for the present invention and should therefore be considered like a comparative example.

We consider (see Figure 13) the reflection of just one coated surface, which corresponds to the situation where the other surface of the glazing is perfectly "anti-reflected".

The resulting reflectance (see Figure 14) spectrum exhibits a sharp peak at $\lambda = 550$ nm.

The FWHM amounts 21 nm, the spectrum yielding

$x = 0.31$ $y = 0.47$ $R_{VIS} = 9.1\ \%$

If one assumes that the other side of substrate is neither anti-reflected nor coated, the resulting color is a little less saturated:

$x = 0.31$ $y = 0.41$ $R_{VIS} = 12.7\ \%$

12

The peak position can be chosen freely and is controlled by the scale of the optical thicknesses of the individual layers : $n \times t = \lambda/4$

The position of the peak depends on the angle of reflection, therefore also the color is angular-dependent (see Figure 15).

For angles of 0°, 20°, 40° and 60° one gets a different position of the maximum, 550 nm, 535 nm, 496 nm and 447 nm, respectively. The background level rises for high angles, leading to less saturated colors.

Example 6 : System with a few layers

For a large area application, it is advisable to reduce the number of individual layers. In order to achieve a reasonable peak height, the refractive indices must exceed a minimum of difference (see Figure 16). However, if they are too different, the peak is too broad.

Refractive indices correspond to SiO_2 (L) and Al_2O_3 (H).
To achieve a nice peak with this choice of refractive indices, it is important that the first and the last layers consist of the high index material (phase shifts).

Let us consider the evolution of the reflectance peak, while successive layers are added (increasing m).

Figure 17 shows the calculated reflectance spectra for 3 to 15 layers (m from 1 to 7).

Increasing the number of layers leads to increasing color saturation and visible reflectance. Values for color coordinates x, y, R_{VIS} (%), and height and width of reflection peak R_{max} , FWHM (full width at half maximum) are given in TABLE 7.

13

TABLE 7

m	x	y	R_{VIS} (%)	R_{max}	FWHM (nm)
7	0.33	0.56	40.4	0.64	76
6	0.33	0.55	37.7	0.57	81
5	0.34	0.54	34.5	0.49	90
4	0.35	0.53	30.6	0.41	102
3	0.36	0.5	25.9	0.32	124
2	0.35	0.45	20.4	0.23	156
1	0.33	0.38	14.2	0.15	234

For five layers (m = 2), the values seem already to be reasonable.

Figure 18 shows the case of a 5 layer object where the refractive index of material H is changed, keeping its optical thickness n(H) x t(H) always to $\lambda/4$ (λ= 550 nm).

The spectrum for n(H) = 1.65 has already been known from the last calculation and is again represented by the black solid line.

By changing the difference of the refractive indices n(H) - n(L), the peak height can be easily controlled. Considerable peak heights can be achieved without too excessive peak broadening (see Table 8).

TABLE 8

n(H)	t(H) (nm)	x	y	R_{VIS} (%)	R_{max}	FWHM (nm)
1.55	89	0.34	0.42	9.4	0.1	144
1.6	86	0.35	0.44	14.6	0.16	152
1.65	83	0.35	0.45	20.4	0.23	156
1.7	81	0.36	0.46	26.5	0.3	164
1.75	79	0.36	0.46	32.7	0.36	174
1.8	76	0.35	0.45	38.7	0.43	180

(n(L) = 1.47, t(L) = 93 nm)

Example 6 : Full system

The full system includes the two surfaces of the glass: one or both could be coated.

one side coated: air//glass//HLHLH //air

combination with AR: air//AR//glass//HLHLH //air

In a SolGel dip - coating process, both sides of the glass can be coated symmetrically at the same time (see Figure 19) as follows : air//HLHLH//glass//HLHLH //air

As expected, coating both sides of the substrate identically leads to much higher peaks (see Figure 20).

The black solid line represents again the system with n(H) = 1.65.

The peaks get slightly broader, but not much. For n(H) = 1.65 this means a FWHM of 167 nm instead of 156 nm. However, this does not harm the color saturation considerably (see Table 9).

TABLE 9

n(H)	t(H) (nm)	R_{max}	FWHM (nm)	x	y	R_{VIS} (%)	T_{sol} (%)
1.55	89	0.19	152	0.34	0.41	17.2	89.7
1.65	83	0.37	167	0.35	0.44	33.7	84.2
1.75	79	0.53	186	0.36	0.44	49	78.3

For n(H) = 1.55, the glass has only lost 2.1 % of solar transmission relative to an uncoated glass (T_{sol} = 91.7 %), yielding a visible reflectance of 17.2 %. Even higher visible reflectance of 33.7 % is found for n(H) = 1.65, the losses relative to the uncoated glass amount just 7.6 %.

The peak position and thus the color can be controlled by scaling the optical film thicknesses to a quarter of the design wavelength λ_0.

With n(H) = 1.65, n(L) = 1.47 we obtain the representative spectra depicted at Figure 21.

The chosen peak positions correspond to colors of blue, green and orange, respectively (see Table 10).

TABLE 10

λ_0	t(H) (nm)	t(L) (nm)	x	y	approx. Color	R_{VIS} (%)	T_{sol} (%)
450	68	77	0.2	0.24	blue	17.1	86.1
550	83	93	0.35	0.44	green	33.7	84.2
650	98	111	0.44	0.36	orange	20	83.8

Figure 22 shows the angular dependence of the spectra for the system with n(H) = 1.65, n(L) = 1.47, λ_0 = 550 nm.

The quantification is presented in the Table 11.

TABLE 11

angle	pos. of max. (nm)	x	y	R_{VIS} (%)	T_{sol} (%)	T_{glass} (%)	loss rel. to glass (%)
0°	548	0.35	0.44	33.7	84.2	91.8	7.6
20°	534	0.32	0.42	33	84.4	91.8	7.4
40°	499	0.27	0.35	28.5	84.2	91	6.8
60°	456	0.25	0.29	24	79.8	84.4	4.6
80°		0.3	0.33	55.6	44.6	45.7	1.1

For raising angles, one notes a blue shift of the maximum. The losses relative to the uncoated glass (solar transmission T_{glass}) tend to decrease, the color saturation, however, too (increasing level of background).

Now, we would like to lower the level of background oscillation. Therefore we choose both indices of refraction n(H) and n(L) to be lower than the one of glass.

model: air//(HL)^3//glass//(HL)^3//air

L: MgF$_2$ n(L) = 1.38
H: SiO$_2$ n(H) = 1.47

To take into account the phase jump relations, the coating is of the form (HL)^m.

The resulting spectra is illustrated on Figure23.

For normal incidence, the level of oscillation could indeed be lowered to a value of 6% instead of 9 %, thus gaining some percent in solar transmission.

The quantification is shown on Table 12.

TABLE 12

angle	pos. of max. (nm)	x	y	R_{VIS} (%)	T_{sol} (%)	T_{glass} (%)	loss rel. to glass (%)
0°	549	0.36	0.48	20.8	90.6	91.8	1.2
20°	534	0.32	0.47	20	90.7	91.8	1.1
40°	490	0.22	0.33	14.6	90.2	91	0.8
60°	436	0.25	0.23	13.1	84.7	84.4	-0.3
80°	397	0.31	0.32	52.5	46.5	45.7	-0.8

In this example, the transmission losses relative to the uncoated glass are really small or even negative (which means gains) – in spite of considerable relative luminance.

The numerical simulation can also be used to monitor the different preparation stages of a multilayered coating. If samples are produced with e.g. 1, 2, 3, 4 & 5 individual layers, the measured spectra can be compared to the theoretical targets. Refractive indices are taken here as measured by experimental methods such as ellipsometry and *in situ* laser reflectometry.

model :

# of layer	material	ref. index	thickness (nm)
0	glass	1.52	
1	Al_2O_3	1.6	93
2	SiO_2	1.48	86
3	Al_2O_3	1.6	93
4	SiO_2	1.48	86
5	Al_2O_3	1.6	93

Figure 24 shows the theoretical normal reflection as the successive layers are added .

At the design wavelength (here 550 nm), adding the individual layers successively results in alternating enhanced reflection or anti-reflection.

Other experimental results are listed below :

sample I :

glass substrate // 30 nm TiO2 // 140 nm SiO2

sample II :

glass substrate // 30 nm TiO2 // 140 nm SiO2 // 30 nm TiO2

sample III :

glass substrate // 30 nm TiO2 // 140 nm SiO2 // 30 nm TiO2 // 140 nm SiO2 // 30 nm TiO2

sample IV :

glass substrate // 45 nm TiO2 // 210 nm SiO2

sample V :

glass substrate // 45 nm TiO2 // 210 nm SiO2 // 45 nm TiO2

sample VI :

glass substrate // 45 nm TiO2 // 210 nm SiO2 // 45 nm TiO2 // 210 nm SiO2 // 45 nm TiO2

TABLE 13

sample	color x	color y	R(vis)[%]	T(sol)[%]	loss[%]	M=R(vis)/loss
I	0.26	0.25	9	92	8	1.13
II	0.24	0.26	16	89	11	1.45
III	0.2	0.22	18	87	13	1.38
IV	0.28	0.33	20	90	10	2.00
V	0.38	0.41	26	85	15	1.73
VI	0.32	0.29	15	82	18	0.83

The table shows the CIE color coordinates x, y, the visible reflectance R_{VIS} under daylight illumination D65, the solar transmission T_{sol} for a solar spectrum AM1.5 global, the solar energy loss, and the figure of merit M = R_{VIS} / loss, as determined for the samples I to VI by spectrophotometry.

The colored thin film interference stack can also be located between two "thick" layers (e.g. a substrate and "thick" transparent top layer). "Thick" means here a thickness larger than the coherence length of the light. This will reduce the color change induced by water droplets condensing eventually on the inner side of the collector glazing or being formed on the outer side, respectively.

The following procedure illustrates a general approach which can be used in order to define the most appropriate glazing for a specific use :

i. rough concept of coating design by theoretical calculation with assumed values for the index of refraction

ii. literature data of material properties $\Rightarrow$ choice of materials

iii. deposition of individual layers of chosen materials

iv. experimental determination of optical properties (n, k) and film thicknesses (t) of real samples (individual layers): spectroscopic ellipsometry, spectrophotometry

v. optimization of coating design for the real material properties taking into account the dispersion of refractive index - recommended software Tfcalc

19

vi.   finding process parameters for the right film thicknesses (magnetron sputtering: e.g. deposition time, input power // SolGel dip - coating: e.g. withdrawing speed, viscosity)

loop: coating deposition
          ⇓   ⇑
optical measurement of thickness

vii.   deposition of multilayered coating

viii.   measurement of reflection and transmission spectra of multilayered coating, comparison with predictions of theory

ix.   in case of deviations: adaptation of the process

Other References

1. Alfred Thelen "Design of Optical Interference Coatings", McGraw-Hill, New York, ISBN 0-0-063786-5 (1989)

2. Alfred Thelen "Design of Multilayer Interference Filters", in "Physics of Thin Films", ed. by Georg Hass and Rudolf E. Thun, Academic Press, New York, Vol. 5, p. 47 (1969)

3. Oliver S. Heavens "Optical Properties of Thin Solid Films", Butterworths, London (1955)

4. Kurt Nassau, "The Physics and Chemistry of Color – The Fifteen Causes of Color",John Wiley & Sons, New York, ISBN 0-471-86776-4 (1983)

5. Robert Sève, "Physique de la couleur – de l'apparence colorée à la technique colorimétrique", Masson, Paris, ISBN 2-225-85119-0 (1996)

6. International Commission on Illumination CIE, Colorimetry, CIE Publication 15.2., 2nd Ed., ISBN 3-900-734-00-3, Vienna, (1986)

Claims

1.   Glazing characterized by the fact that it is comprises selective reflecting means adapted to exclusively reflect a narrow spectral band of visible light while being transparent for the rest of the solar spectrum.

2.   Glazing according to claim 1 wherein said selective reflective means comprise an interference filter.

3.   Glazing according to any of the previous claims wherein said selective reflective means comprise multi-layer interference stacks.

4.   Glazing according to any the previous claim wherein said selective reflective means are located between two layers having each a thickness larger than the coherence length of the light.

5.   Glazing according to any of the previous claims wherein said selective reflective means are located at the inner side of the glazing.

6.   Glazing according to any of the previous claims 1 to 5 wherein said selective reflective means are located at the outer side of the glazing.

7.   Glazing according to any of the previous claims comprising a light-diffusing layer, or a light-diffusing rough surface, or a light-diffusing rough interface

8.   Glazing according to any of the previous claims designed in a such a way that said narrow spectral band corresponds to a ratio "visible reflectance R_{vis} / solar energy loss R_{sol}" which is higher than 1.2.

9.   Solar collector comprising a glazing according to any of the previous claims.
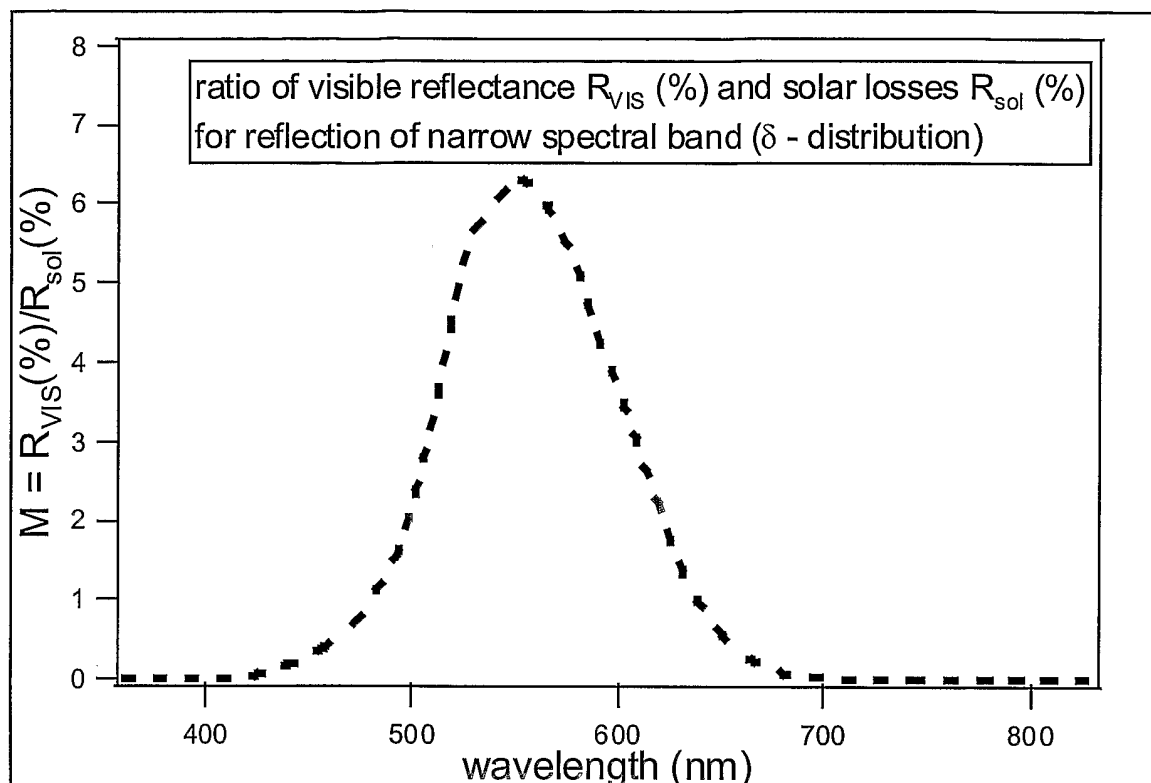
FIG. 1

incident radiation

colored reflection

glazing

coating

black absorber

transmitted radiation

SUBSTITUTE SHEET (RULE 26)

FIG. 2

FIG. 3

ratio of visible reflectance R_{VIS} (%) and solar losses R_{sol} (%) for reflection of narrow spectral band (δ - distribution)
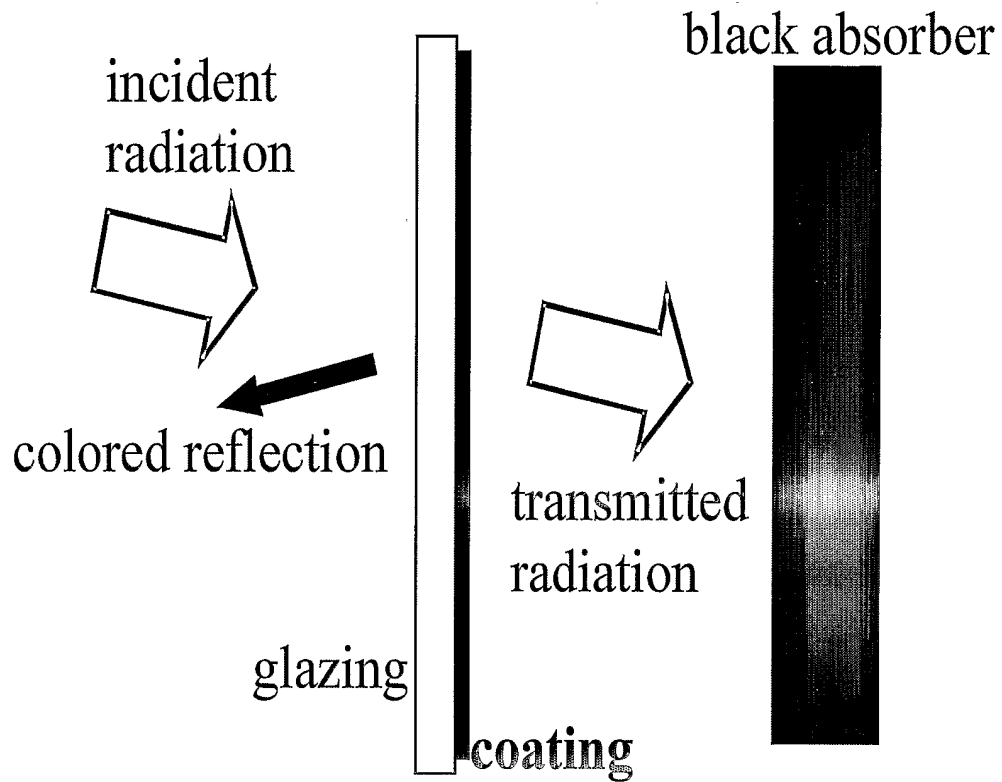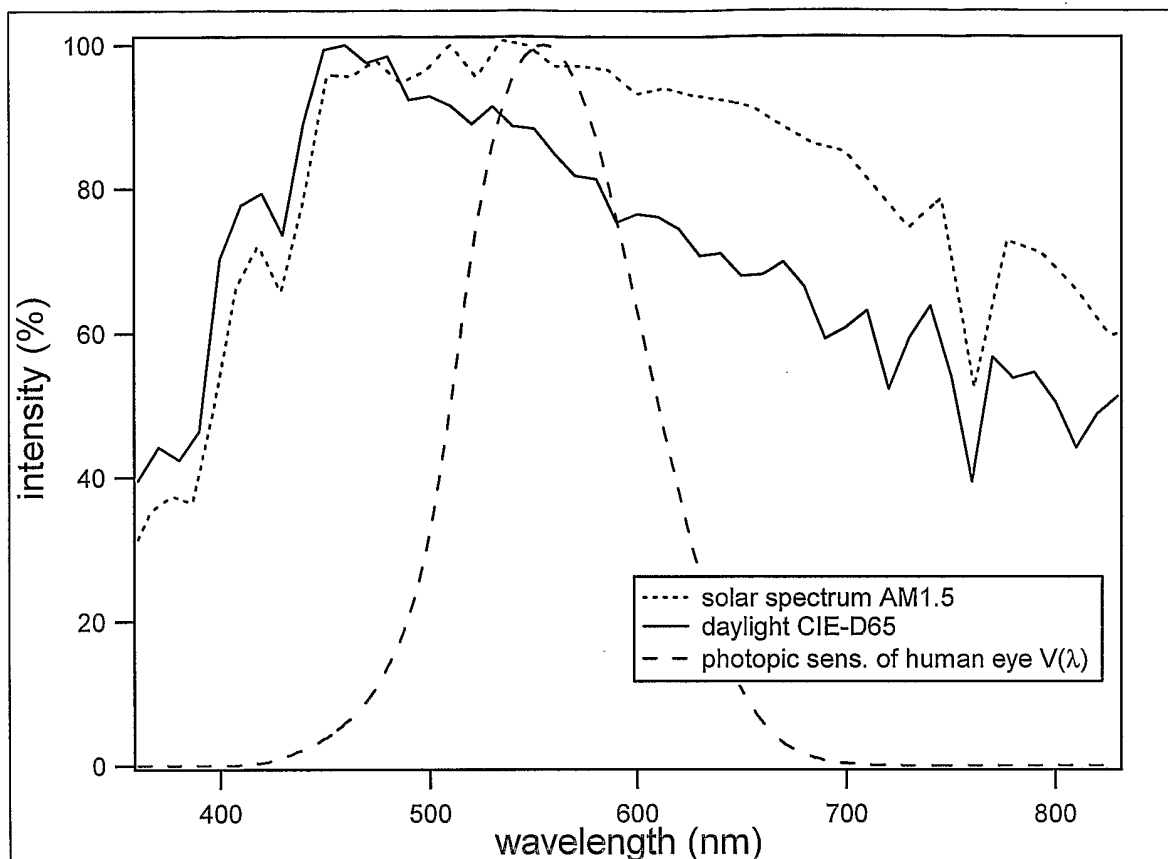
FIG. 4

air   n = 1

glass n = 1.52

TiO_2 n = 2.2 , varying thickness
SiO_2 n = 1.46 , 140 nm

air   n = 1

FIG. 5

SUBSTITUTE SHEET (RULE 26)

FIG. 6
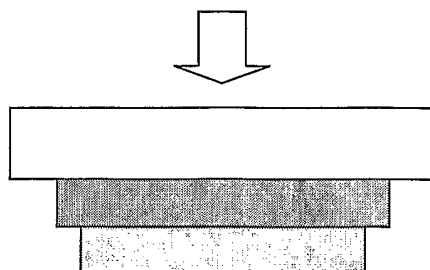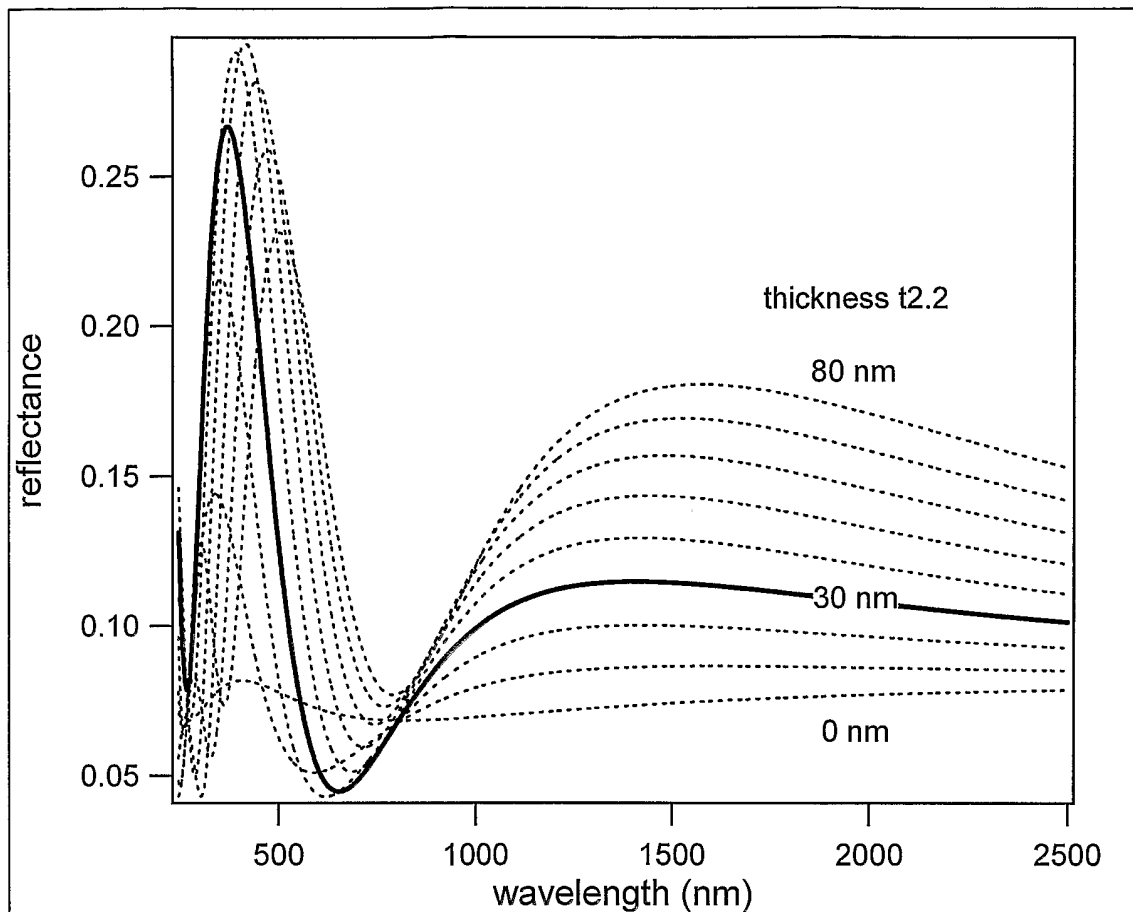
SUBSTITUTE SHEET (RULE 26)
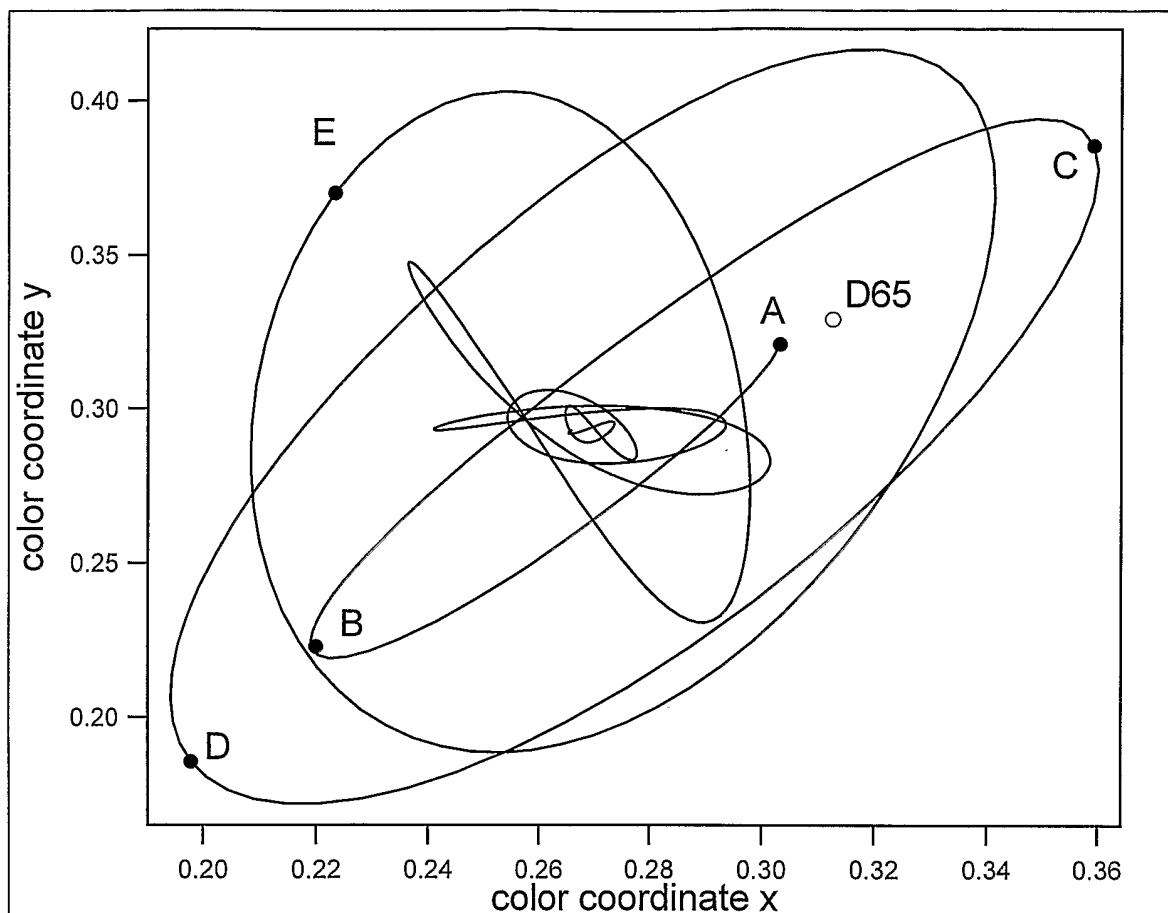
FIG. 7

air　　n = 1

MgF$_2$　n = 1.38
TiO$_2$　n = 2.2

glass　n = 1.52

TiO$_2$　n = 2.2
MgF$_2$　n = 1.38

air　　n = 1

FIG. 8

Legend:
- $\lambda_0 = 650$ nm: blue
  $R_{VIS} = 3.64$ %, $T_{sol} = 93.4$ %
- $\lambda_0 = 1300$ nm: purple
  $R_{VIS} = 11.5$ %, $T_{sol} = 83.9$ %
- solar spectrum AM1.5
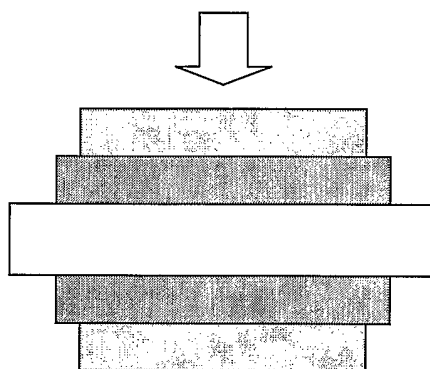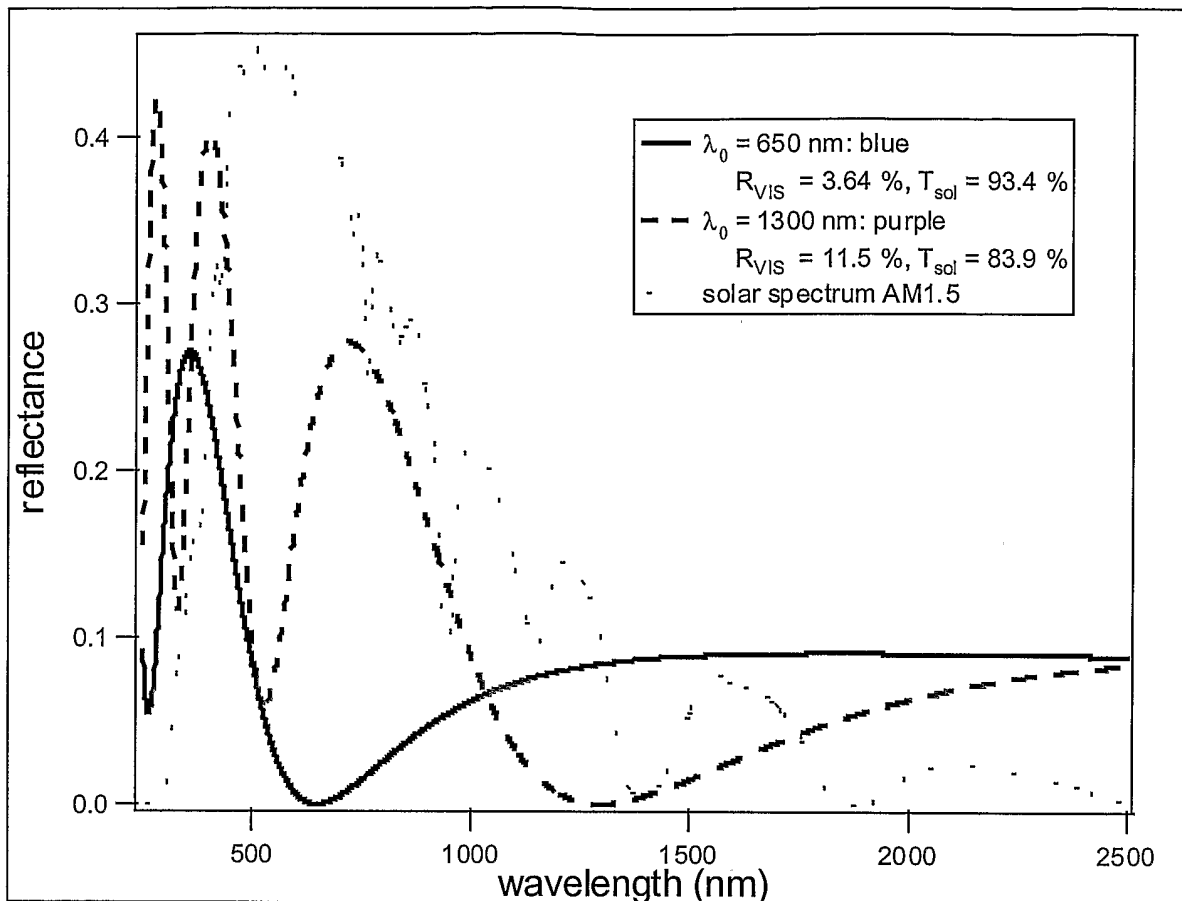
FIG. 9
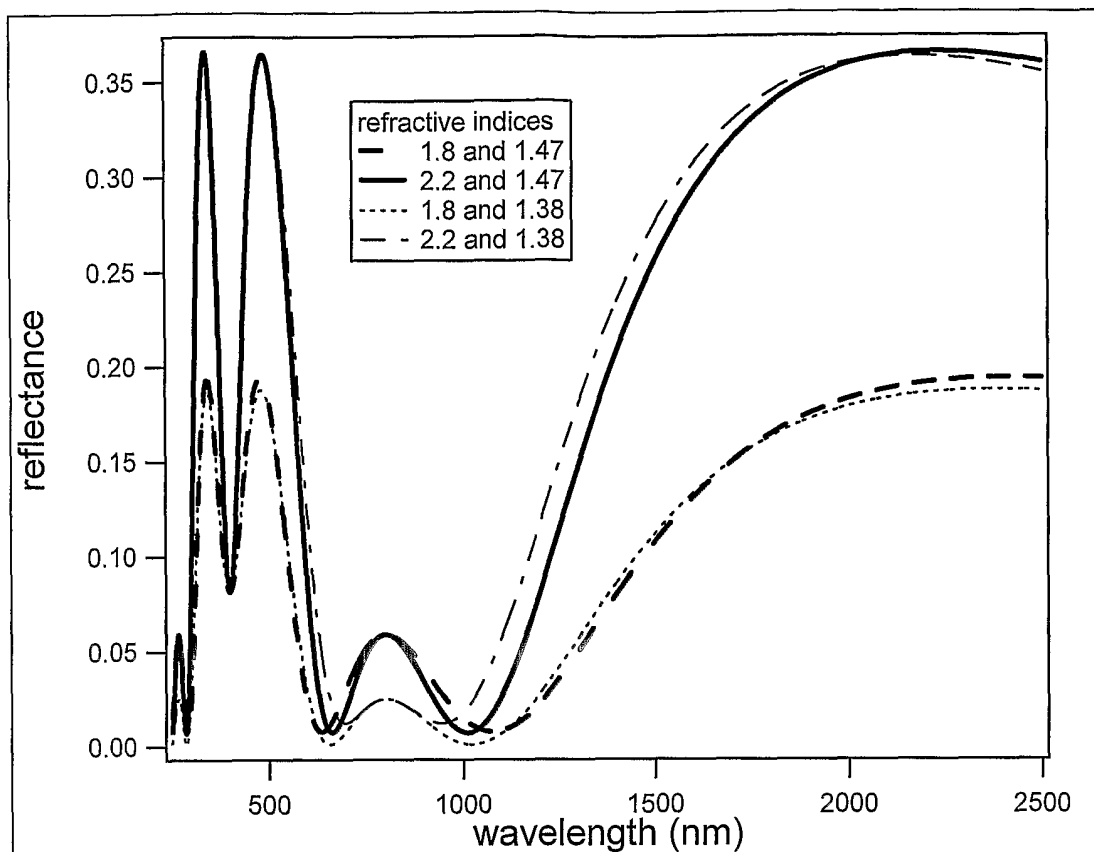
FIG. 10

	n	thickness (nm)
Air	1	
TiO_2	2.2	0 - 50
SiO_2	1.46	140
TiO_2	2.2	30
Glass	1.52	
Air	1	

TiO_2
30 nm

glass

top layer
TiO_2

inc.
rad.

SiO_2
140 nm

SUBSTITUTE SHEET (RULE 26)

FIG. 11

SUBSTITUTE SHEET (RULE 26)

FIG. 12

SUBSTITUTE SHEET (RULE 26)
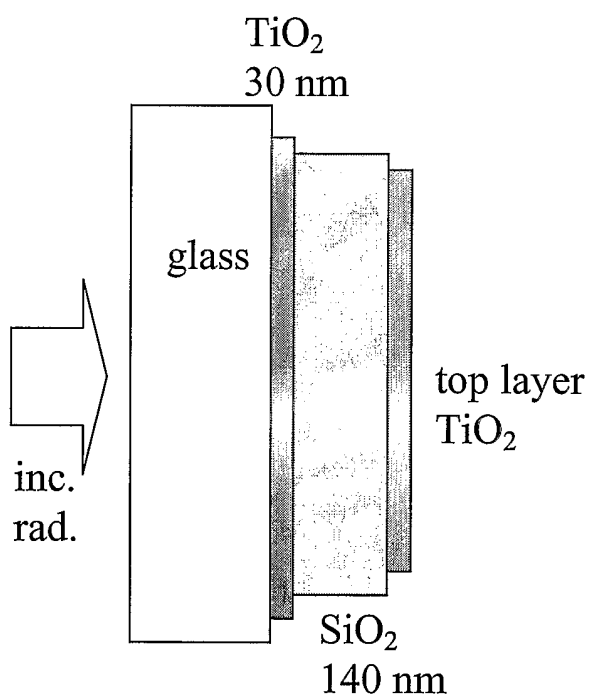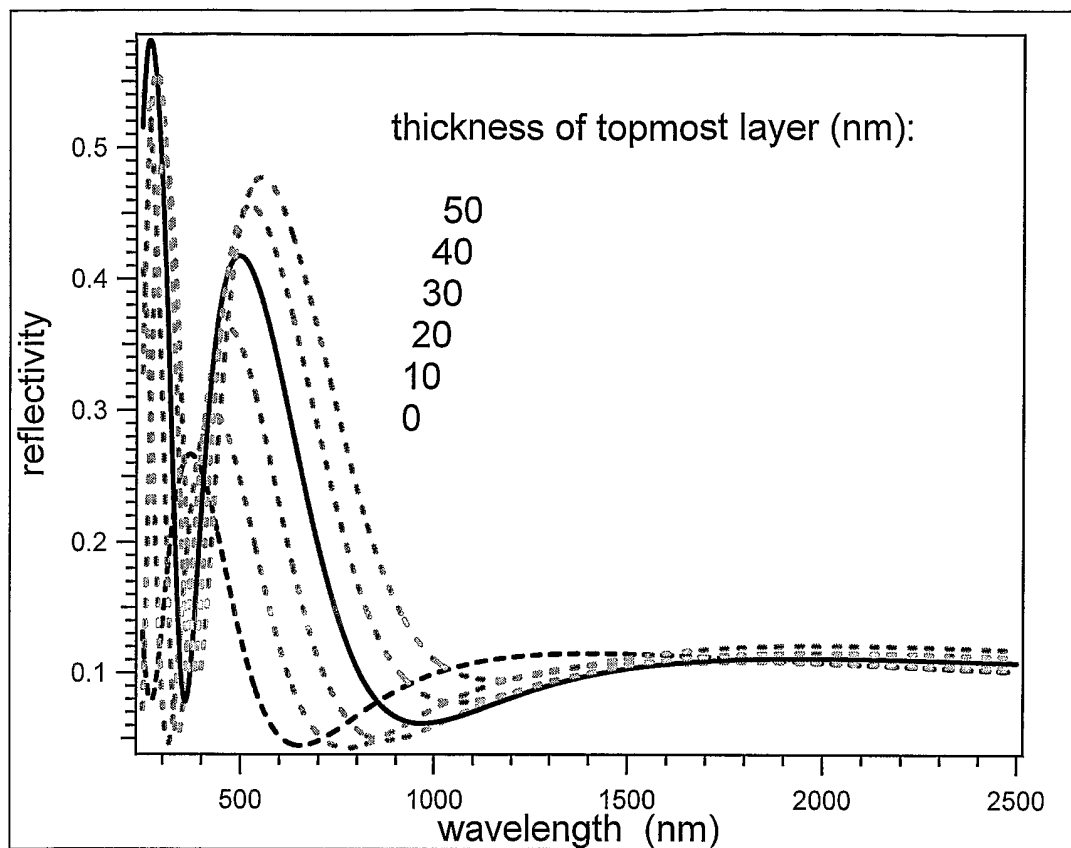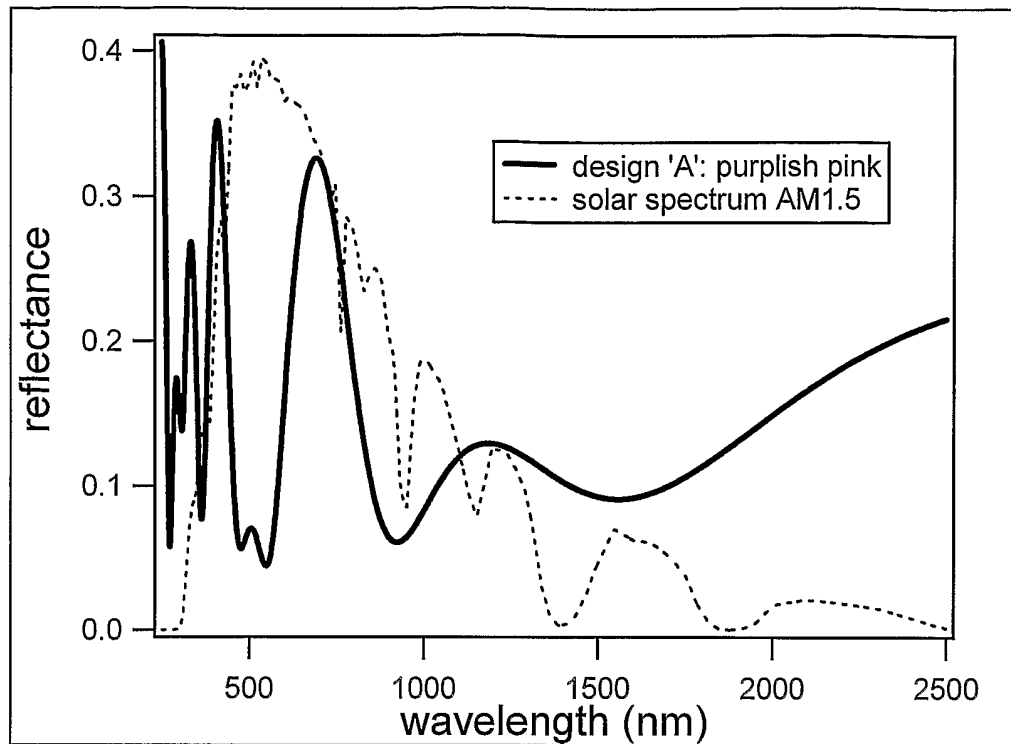
FIG. 13

glass   n = 1.52

L: n = 1.47, 93.5 nm
H: n = 1.5 , 91.7 nm

               .
               .   40 layers: $(LH)^{20}$
               .

L: n = 1.47, 93.5 nm
H: n = 1.5 , 91.7 nm

air   n = 1

FIG. 14

SUBSTITUTE SHEET (RULE 26)
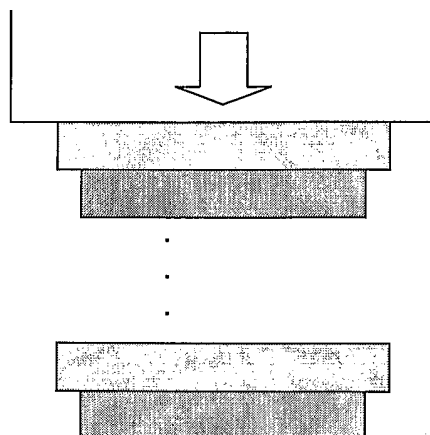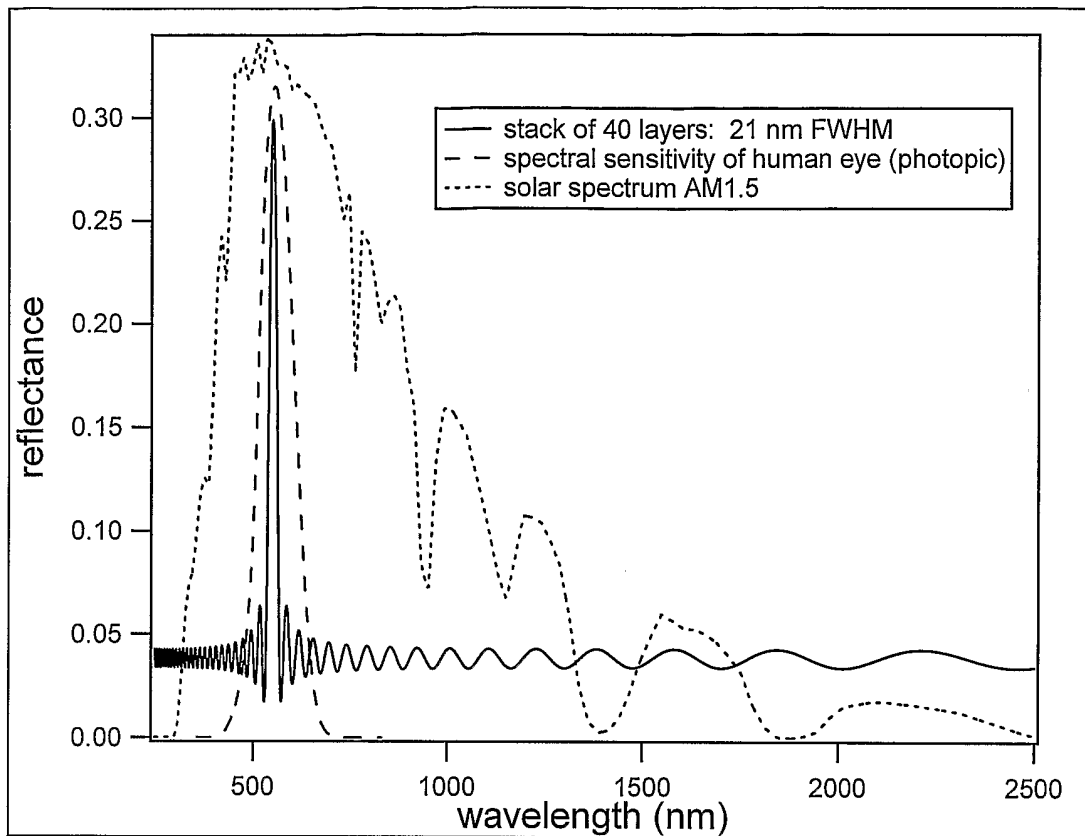
FIG. 15
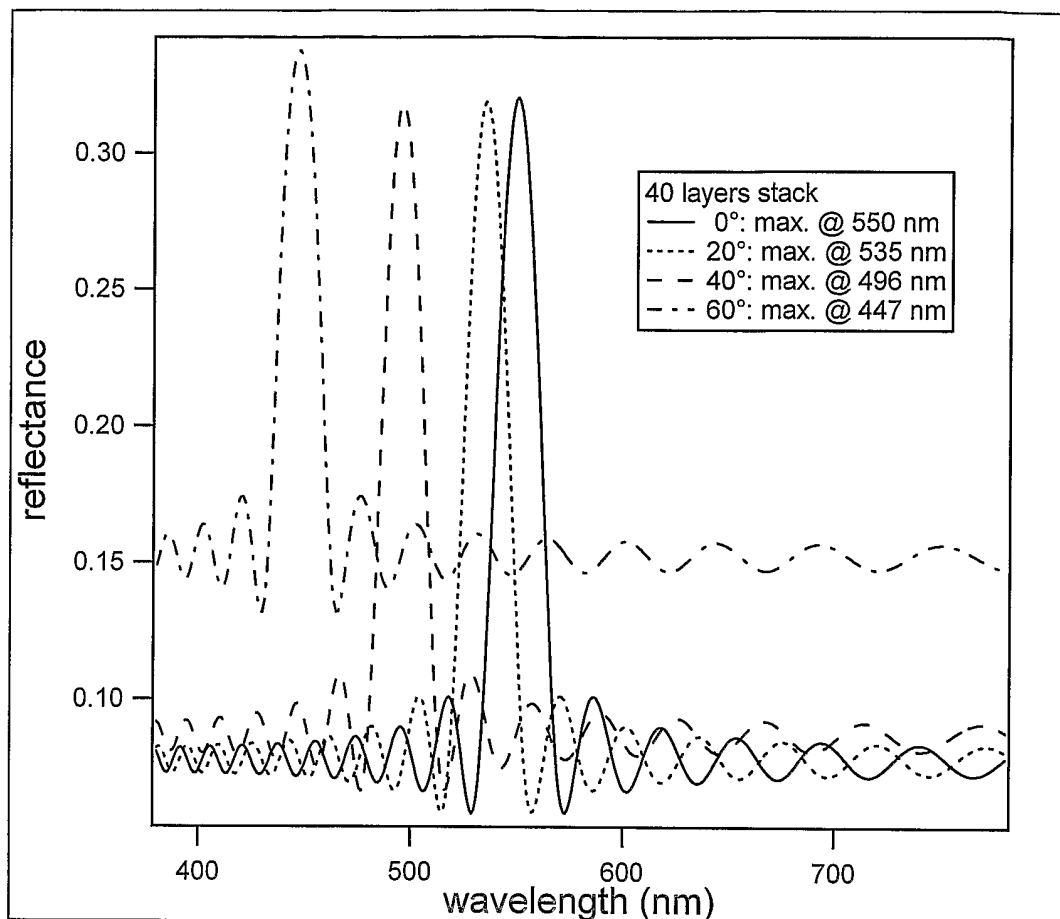
FIG. 16

glass   n = 1.52

H: n = 1.65, 83 nm
L: n = 1.47, 93 nm

.
.   2m + 1 layers: (HL)^m H   :
.

H: n = 1.65, 83 nm
L: n = 1.47, 93 nm
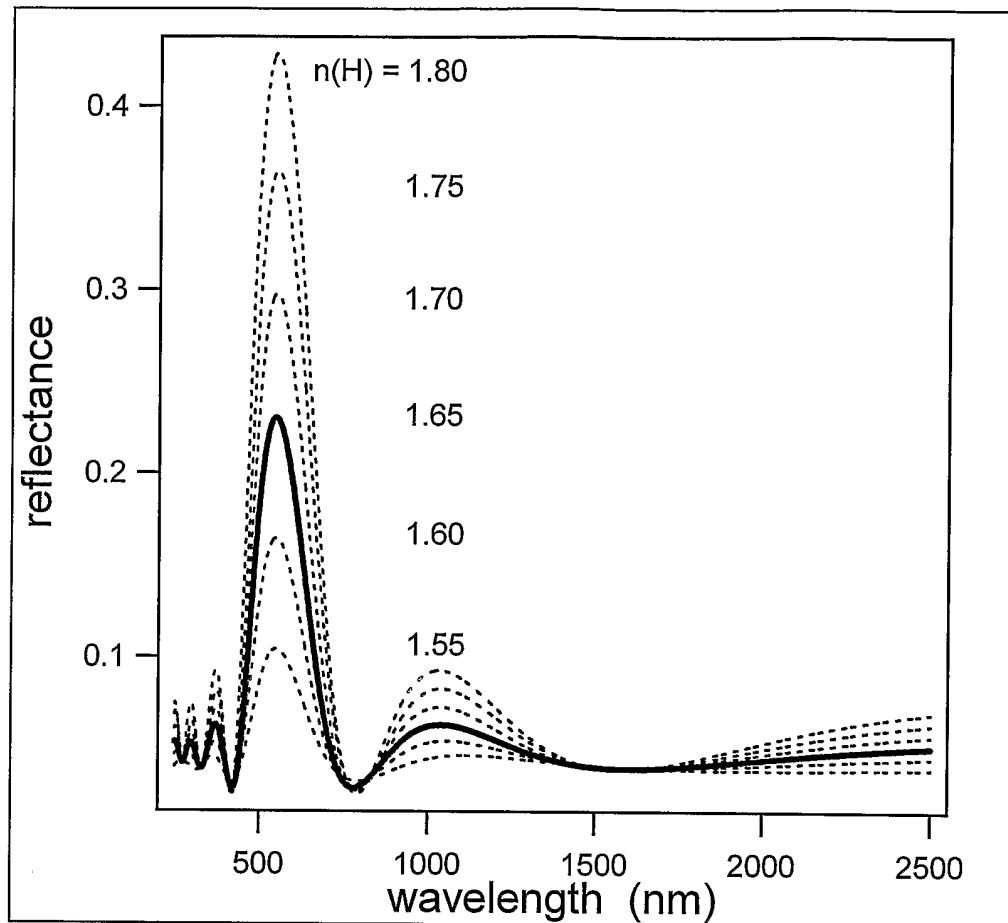H: n = 1.65, 83 nm

air   n = 1

FIG. 17

FIG. 18

SUBSTITUTE SHEET (RULE 26)
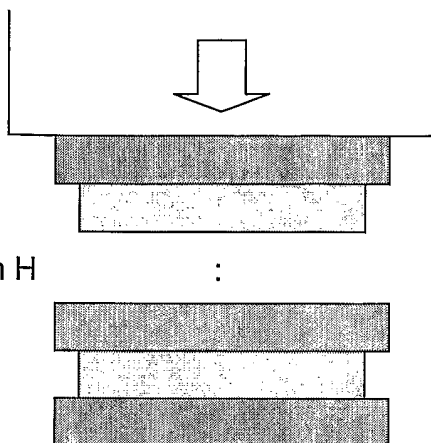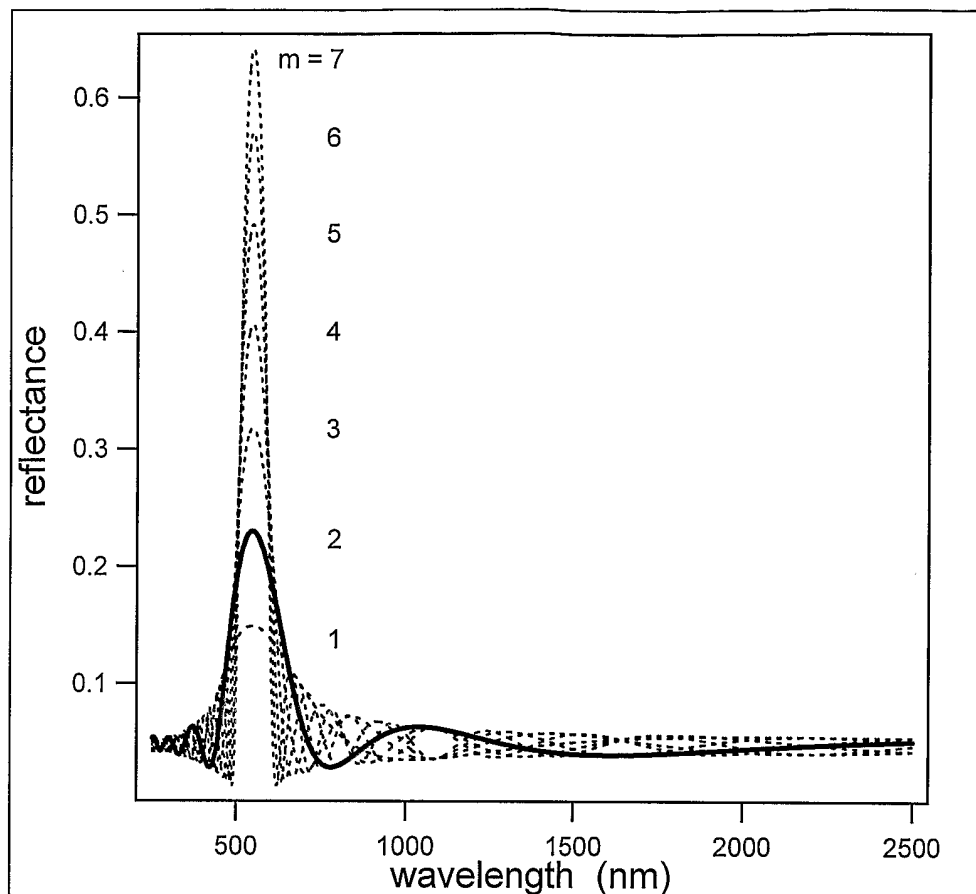
FIG. 19

glass n = 1.52

L: n(L), t(L)
H: n(H), t(H)

air   n = 1
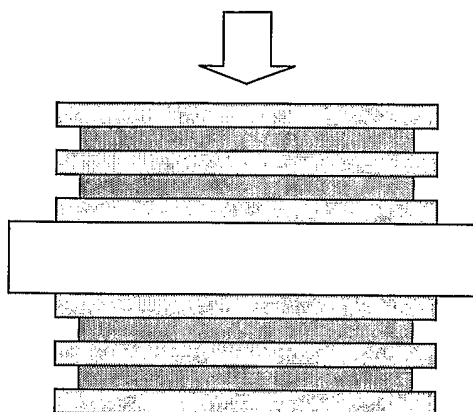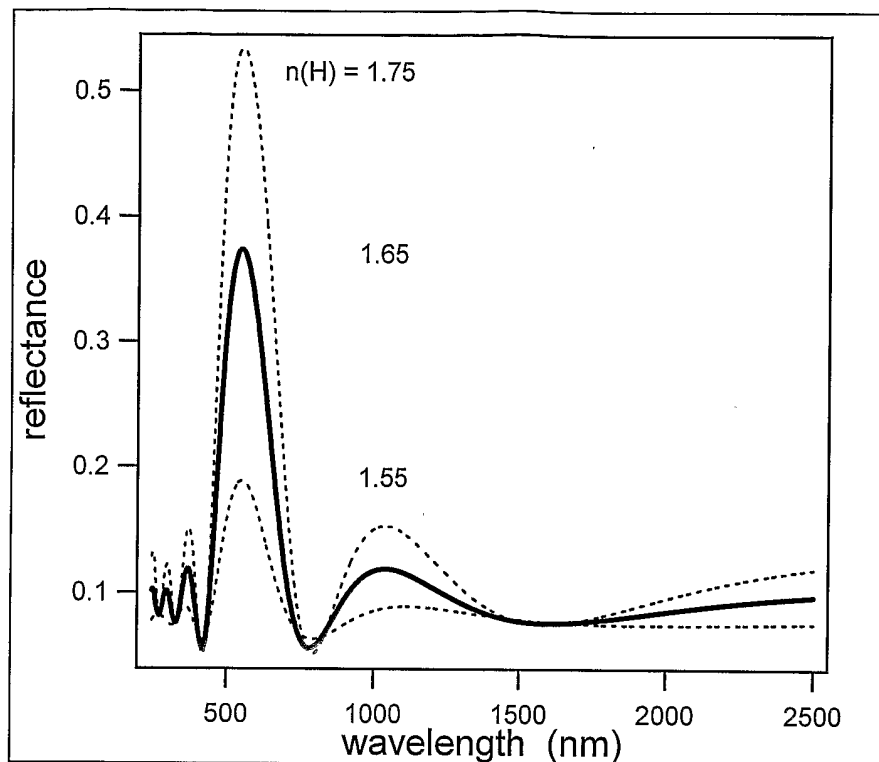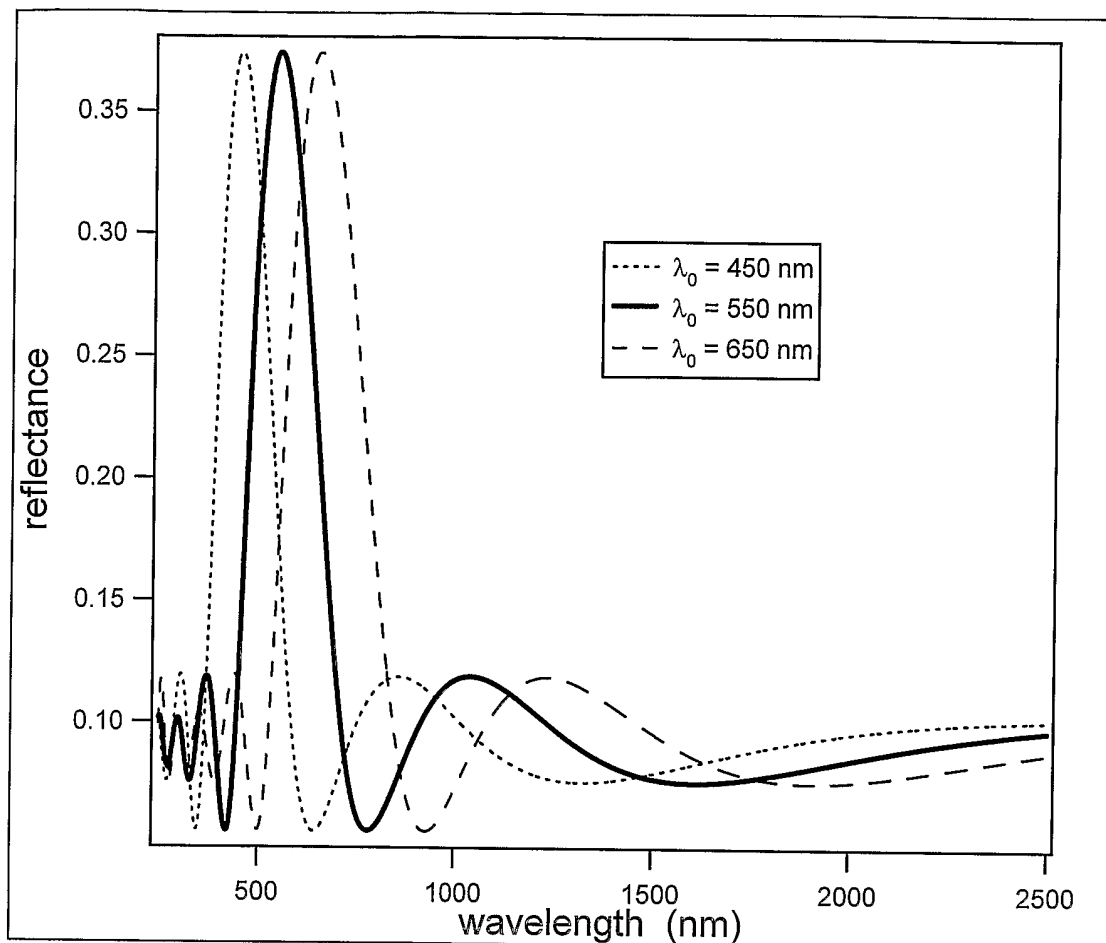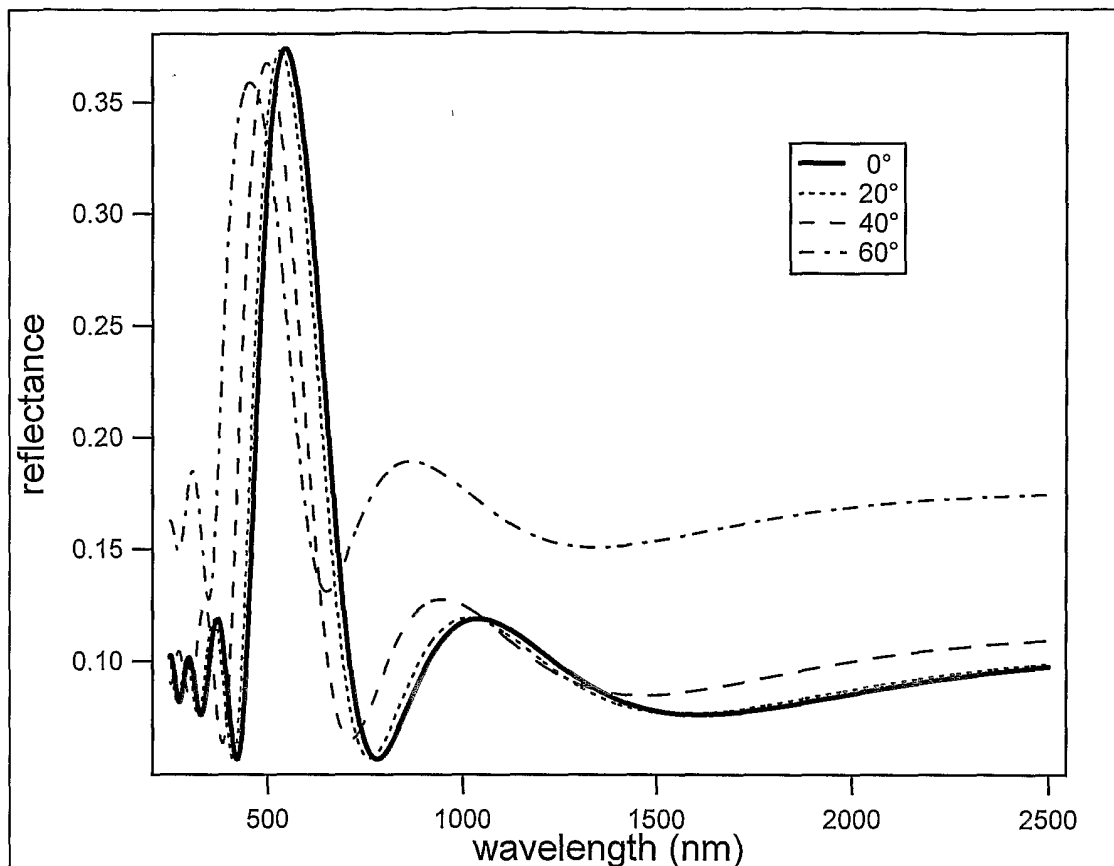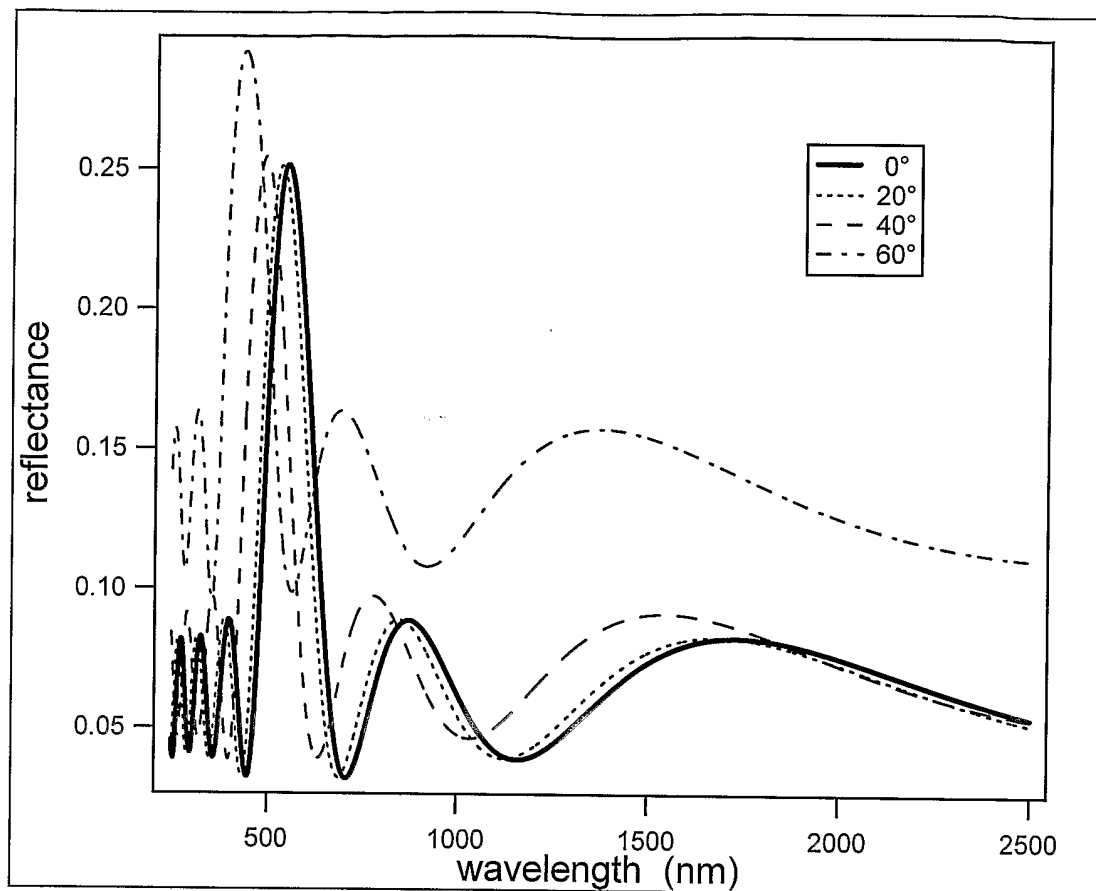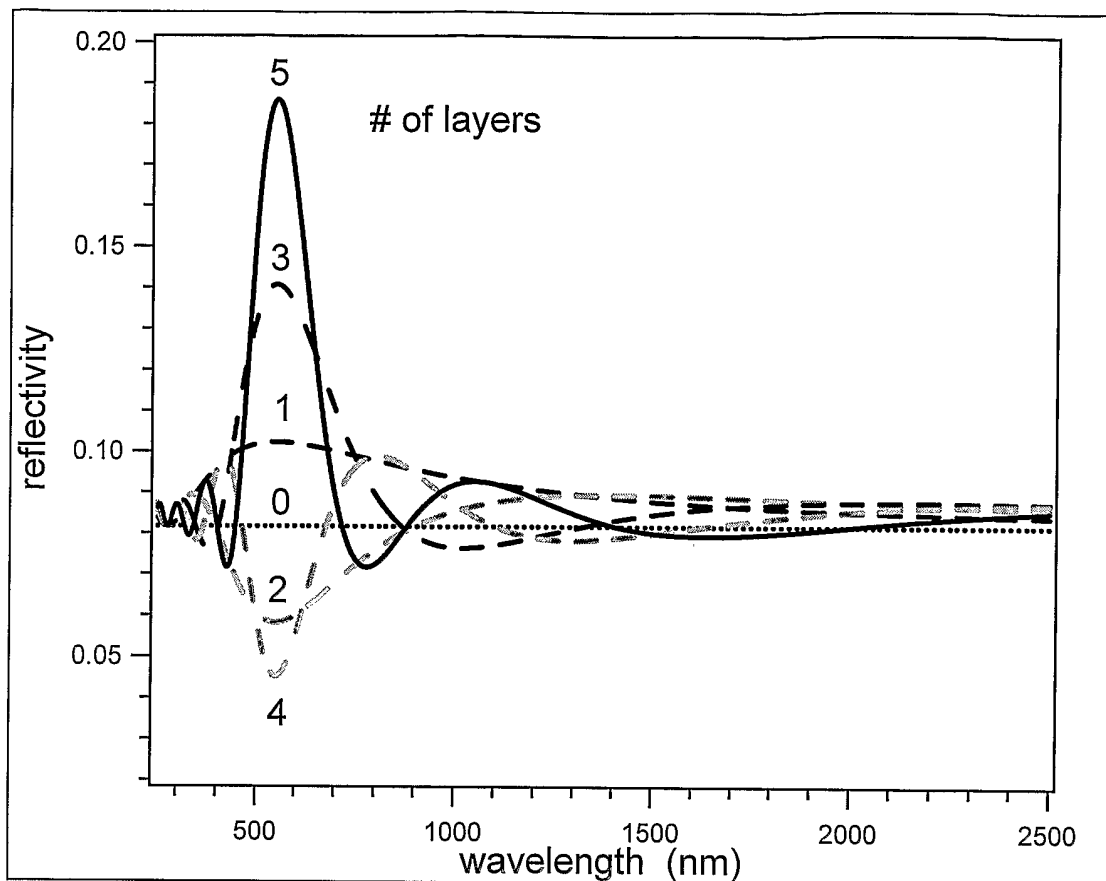
SUBSTITUTE SHEET (RULE 26)

FIG. 20

SUBSTITUTE SHEET (RULE 26)

FIG. 21

SUBSTITUTE SHEET (RULE 26)

FIG. 22

FIG. 23

FIG. 24

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   F24J2/50

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   F24J   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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/103453 A (OYA TARO ; SHINGU TADASHI (JP); TEIJIN LTD (JP)) 27 December 2002 (2002-12-27) abstract; figures	1-3
E	-& EP 1 398 660 A (TEIJIN LTD) 17 March 2004 (2004-03-17) paragraph '0014! - paragraph '0019!; figures	1-3
A	US 4 896 928 A (PERILLOUX BRUCE E ET AL) 30 January 1990 (1990-01-30) abstract; figures	1
A	US 4 546 050 A (AMBERGER CHARLES J ET AL) 8 October 1985 (1985-10-08) abstract; figures	1

-/--

[X] Further documents are listed in the continuation of box C.   [X] 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
13 July 2004	22/07/2004

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	Van Dooren, M

Form PCT/ISA/210 (second sheet) (January 2004)

International Application No

PCT/CH2004/000130

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 053 980 A (NIPPON SHEET GLASS CO LTD) 22 November 2000 (2000-11-22) abstract; figures	1
A	EP 0 786 676 A (FLEX PRODUCTS INC) 30 July 1997 (1997-07-30) the whole document	1
A	US 4 273 098 A (SILVERSTEIN SETH D) 16 June 1981 (1981-06-16) the whole document	9
A	US 4 822 120 A (BACHNER FRANK J ET AL) 18 April 1989 (1989-04-18) the whole document	9

INTERNATIONAL SEARCH REPORT

*Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 02103453	A	27-12-2002	JP	2003075920 A	12-03-2003
			EP	1398660 A1	17-03-2004
			WO	02103453 A1	27-12-2002
			TW	567389 B	21-12-2003
			US	2004004760 A1	08-01-2004
EP 1398660	A	17-03-2004	JP	2003075920 A	12-03-2003
			EP	1398660 A1	17-03-2004
			US	2004004760 A1	08-01-2004
			WO	02103453 A1	27-12-2002
			TW	567389 B	21-12-2003
US 4896928	A	30-01-1990	NONE		
US 4546050	A	08-10-1985	CA	1279535 C	29-01-1991
			MX	166886 B	11-02-1993
EP 1053980	A	22-11-2000	JP	2001002449 A	09-01-2001
			EP	1053980 A1	22-11-2000
EP 0786676	A	30-07-1997	EP	0786676 A2	30-07-1997
			AT	172545 T	15-11-1998
			CA	2048564 A1	17-02-1992
			DE	69130383 D1	26-11-1998
			DE	69130383 T2	11-03-1999
			EP	0472371 A1	26-02-1992
			HK	1012719 A1	31-03-2000
			JP	3041094 B2	15-05-2000
			JP	6118229 A	28-04-1994
			US	5214530 A	25-05-1993
US 4273098	A	16-06-1981	NONE		
US 4822120	A	18-04-1989	US	4721349 A	26-01-1988
			JP	51066841 A	09-06-1976
			JP	60185903 A	21-09-1985
			US	4337990 A	06-07-1982