4.1.6 INTERFERENCE COATINGS

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1. INTRODUCTION

Electromagnetic (EM) radiation impinging on a substrate is redistributed according to the radiation distribution equation T + R + A = 1, where T, R and A are the transmittance, reflectance, and absorbance of the matter respectively. Reflectance is a fundamental phenomenon which occurs when the EM waves propagates across a boundary between two media that have different refractive indices. If sometimes it is a disturbing effect which must be avoided, its control over defined ranges of the electromagnetic spectrum permits to obtain a vast variety of optical filtering properties. One of the most effective ways to control the reflectance of a substrate is to deposit very thin low-loss dielectric films having typical thickness of $\lambda/4$ and $\lambda/2$, known as interference coatings. By suitable variations in the design and the choice of the materials, properties such as antireflection, high reflection, neutral beam splitting, short and long wave pass, dichroic, monochromatic and notch filtering can be achieved.

The basic physics of interference phenomena is described in many text books [1-3] and it will not be recalled. Advanced texts [4,5] treat the problem in terms of the optical admittance Y of a surface, a parameter which tells how easy or hard it is for the light to pass through it. Today, computer programs allow to easily calculate the reflectance (and consequently the transmittance) of single and complex assembly of thin films in any configuration.

The reflectance is determined by the Fresnel relation [1] and its value depends on the angle of incidence, the state of polarization of the EM wave and the absorption of the media. For isotropic homogeneous transparent substrates under normal incidence the reflectance at one interface takes a very simple form:

$$R = \left(\frac{n_o - n_s}{n_o + n_s} \right)^2 \qquad (1)$$

where n_o and n_s are the refraction indices of the medium (usually air $n_o = 1.0$) and the substrate (usually glass $n_s = 1.52$) respectively. For such a configuration the total reflectance is approximately 4% per interface.

The results of such reflection can be a glare and a low contrast when objects or displays are seen through a normal glass pane. Such effects can be considerably reduced by antireflecting the glass pane surface. The requirements to achieve that depend on whether the surface is active (e.g. luminescent) such as a monitor screen or passive such as a liquid display, a shop window, etc., which can bee seen only when illuminated.

Antireflecting glass surfaces constitute therefore the overwhelming majority of all optical coatings produced. The reduction of the spectral reflectance R(λ) in a given wavelength range finds many applications ranging from the attenuation of radar echoes to the improvement of glazing properties in the visible near infrared range, in particular when glare effects are disturbing, e.g. in picture-frames, display-cases for room and ambients, shop windows, cars, attachment glasses to preserve church windows, monitors, displays, front panes for transparent switches, cover panes to improve the efficiency of solar collectors, photovoltaic modules, multilens objectives, etc.

It can be achieved either by destructive interference or by roughening the surface very finely. In the first case, the reflected light can be almost extinguished by depositing on the glass surface one but usually a multilayer system consisting of high and low refractive index materials. This will enhance the spectral transmittance. In the second case, the directed incident light is to a large extent converted by the rough surface into a diffuse light through scattering. The phenomenon has no effect on the spectral transmittance.

2.1 Antireflex interference coating

For normal incidence in air ($n_o \approx 1$) the reflectance of a single dielectric homogeneous layer of index of refraction n_l having a thickness of $\lambda_o/4n_l$ (quarter wave coating) deposited on a glass of index n_s (usually 1.52 at $\lambda = 600$ nm) is given by

$$R = \left(\frac{n_0 - Y}{n_0 + Y}\right)^2 = \left(\frac{n_0 n_s - n_1^2}{n_0 n_s + n_1^2}\right)^2 \qquad (2)$$

so that R = 0 if $n_l = (n_o\, n_s)^{½}$. A zero reflectance can therefore be obtained at only one particularly wavelength with a single layer of a material of index of refraction $n_l = 1.23$ and a thickness $d = \lambda_0/4n_s = 122$ nm, such as a porous silica coating.

Larger band widths are only obtained by depositing multilayer quarter wave coatings made with high (H) and low (L) index of refraction, e.g. (y_0/HL HL...)Y_{sub}. For a 2 quarter wave coatings of index n_l and n_2, the so-called V-coat system glass/HL/air, zero reflection is obtained if $n_2/n_l = (n_s/n_0)^{1/2}$. Such a configuration may include a pure 95 mm thick silica coating of index $n_l = 1.45$ and a 77 nm thick mixed SiO_2-TiO_2 coating of index $n_2 = 1.79$. A slightly more complex configuration may involve the insertion of a half wave flattening layer between the two quarter waves layers but more complex configurations have been proposed, also including other functional properties such as antistatic ones [4,5].

Sol-gel production. Most of the AR coatings using interference effects are today produced by vacuum-based technologies, especially magnetron sputtering. However sol-gel processed coatings have already been commercialized since the early 60s [6].

Schott Glass [7] produces large panes (up to 380 × 177 cm^2) of several AR products using the dip costing process. AMIRAN® is a one or two sides coated glass with 1 to 3% rest reflection used for free view from inside to outside (e.g. for restaurant with a view) or from outside to inside (e.g. for shop windows) or for a clear view in interior situations (e.g. teller's desk). The product CONTURAN® (two side coating with the configuration SiO_2-TiO_2/TiO_2/SiO_2 with reduced reflection down to 0.3 to 0.9% is particularly used for instruments and indicator boards, cover panels, lamps, antiglare filter for monitors while MIROGARD® (two side coated glass with reflectance < 1% and low UV transmittance) is especially designed for picture framing in museums.

Denglas Technologies LLC [8] also produces AR multilayer coatings, some with added functional properties, through the dip coating process on various glass substrates. Under the brand name Denglas® BRAND the surface reflectance and glare are reduced by 97% ($R < 1\%$) with a 3-layer broad band AR coating coated on both sides (application in picture framing for ultimate clarity and true color rendition). The Clearview® Denglas combines reflection-free viewing with superior scratch, wear and fingerprint resistance (40" × 70"), and is especially designed for show cars, museum display cases, supermarket, food, LCD and plasma displays. The AR Tempro® presents similar properties after a tempering process. 3-layer process to reduce one-side reflection to less than 0.5% are also offered on beam-splitter products (SpectraFILM™ Beamsplitters for TV broadcast applications in conjunction with Teleprompters).

Prinz Optics [9] offers also dip coated AR coatings ($R < 0.5\%$) on borofloat substrates especially designed for UV, VIS and the NIR region up to a size of 110 × 80 cm^2 for broadband and specific chosen wavelength (e.g. for protective glasses for Nd:YAG laser welding equipment).

Recent technological developments. Most of the developments have been pursued in order to lower the production cost by avoiding the heat treatment steps or by developing very low index of refraction material or to add some interesting additional properties, e.g. an antistatic function.

The use of surface modified SiO_2 and TiO_2 nanoparticles (4 to 10 nm in size) dispersed in a hybrid inorganic-organic matrix to produce nanocomposite quarter wave layers with low and high index of refraction was pioneered at INM [10,11]. The advantage of the process is the production of scratch resistant transparent coatings with tunable index of refraction (between 1.47 and 1.94) by varying the concentration of crystalline particles either by thermal treatment at temperature as low as 80°C or by UV irradiation. This has opened the way to obtain interference coatings not only on glasses but also on heat-sensible substrates. The surface modification of the inorganic particles with 3-glycidoxypropyltrimethoxysilane (GPTS) avoids the agglomeration of the nanoparticles and covalent bonds between the matrix and the nanoparticles are formed during the polymerization step. Figure 1 shows the reflection of a two λ/4 layer system deposited on a polycarbonate (PC) substrate (PC/GPTS-TiO_2 (71 nm, n = 1.93)/Primer (n = 1.49, 20 nm)/GPTS-SiO_2 (n= 1.483, 92 nm). The optically non-active primer layer is necessary to achieve good adhesion between the two nanocomposite layers.

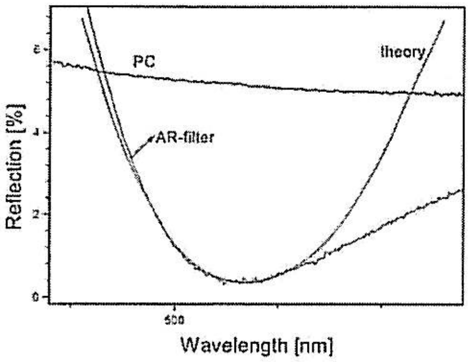


Figure 1. Reflectivity of a 2 layer λ/4 stack TiO_2-SiO_2 nanocomposite layer on a polycarbonate substrate (measured and calculated) and of the uncoated substrate.

Remarkable improvement of the scratch resistance (about 2% haze after 100 cycles Taber test) and of the reflectance (R_{min} < 0.5%) have been obtained by first coating the substrate with a thick hard coating whose index of refraction has been matched to that of the substrate (n = 1.586).

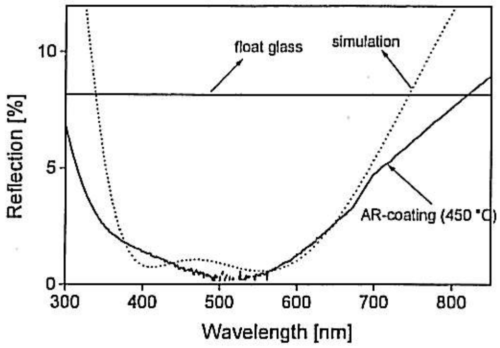


Figure 2. Reflectance of a 3-layer nanocomposite AR coating deposited on both sides of a glass substrate fired at 450°C/15 min. Simulation using optical thicknesses of appropriate single composite layers fired at the same temperature.

Excellent scratch resistance can however only be obtained (haze value as low as 2.5% after 1000 Taber test cycles, only twice of that of a float glass) if the coatings are sintered at high temperature. The result of a 3-layer UV-system deposited on glass where each layer has been cured after deposition by UV light (2.5 J/cm^2) and the final sintering was realized with the whole stack at 450°C/15 min is shown in figure 2.

Broad band low reflectance (< 0.1%) in the wavelength range 400 to 700 nm was also reported in [12] for a four-layer stack deposited on PMMA substrates using sol prepared with Si and Ti alkoxides and non-disclosed additives. The technology was commercialized for dashboard instrument panel in Prius Toyota hybrid car.

It is also worth to mention the developments made at the French Commission for Atomic Energy for the Mega-Joule class laser. Coatings made with a sol consisting of nanosized (10 nm) spherical amorphous silica suspended in ethanol [13] have, after solvent incorporation, only a ~ 57% porosity and the refraction index is as low as 1.22. Therefore single layer AR coatings reach a transmission value of 100% at a single wavelength which can be adjusted by varying the layer thickness (equation 2). The coating is not scratch resistant but a strengthening was achieved by a post-treatment in ammonia vapor.

The same coatings have been used to lower the reflection of KDP crystals, previously coated with a hybrid protective layer [13], used as harmonic converters for the Phebus laser. This two layer system gives a broad transmission increase which was adjusted to cover both SHG (526.5, 1.053 nm) and THG (351 nm) harmonics.

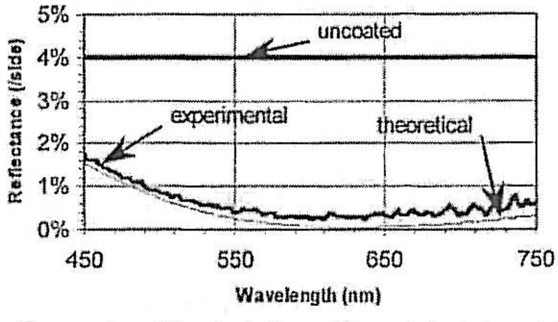


Figure 3. Reflection spectra of the single-layer AR-coated window side with blue residual reflection color.

Moreover large scale (up to 1 × 1.7 m^2) single layer broad band, scratch resistant coatings have been obtained using a low speed spin coating technique (2 m chuck diameter) by incorporating a siloxane binder to the sol. The coatings have been oven-cured at 120°C only for 30 minutes [14]. The refraction index could be adjusted continuously between 1.22 and 1.44 by varying the colloid/binder ratio. A 30 wt% polymer ratio was enough to confer adhesion resistance in compliance with the moderate test US-MIL-C-0675C. The optical performance were: $n = 1.28$ @ 550 nm, $R_{min} = 0.4\%$ @ 590 nm, $R < 1\%$ in the 470 to 750 nm range (figure 3).

The process is particularly interesting as it lowers considerably the safety hazard due to the coating solution handling and storage, is a low sol-consumption and allows to AR coat any large heat sensible substrate.

Two layer broadband AR coatings using sol-gel polymeric TaO_2 and SiO_2 materials have been dip coated on very large blast shield components (glass/H(half wave)L(quarter wave)) with baking temperature not exceeding 150°C. The laser amplification was increased by 6.3% [13].

AR optical fibers used to guide light between high power lasers have been also developed withstanding high damage threshold (220 kW cm^{-2} in the visible range @ 25 kHz repetition ratio) [13].

Scratch resistant and easy-to-clean AR coating for Thomson Multimedia CRTs have been obtained with a 3-layer stack (medium/high/low refractive index). The medium index material consisted of a mixture of TaO_2 and SiO_2. The easy-to-clean property has been obtained by overcoating the system with a hydrophobic layer. Broadband antireflection below 1% over the 450 to 750 nm visible range have been achieved [14] using both thermal and UV-curing processes.

Antireflection (AR)-antistatic (AS) coatings. AR coatings are often used on glass devices which are charged electrostatically, like CRT tubes. An antistatic property is achieved by adding or substituting the high index refraction layer by a transparent thin layer made of a conducting oxide such as SnO_2.This has been obtained for instance for a two-layer system [15] in which the coating facing the glass substrate was made from a mixture of $TiO_2 + SiO_2 + SnO_2$ (thickness 82 nm, $n_2 = 1.80$) while the outside coating was pure silica (thickness 95 nm, $n_1 = 1.45$) assuring sufficient hardness and abrasion resistance. The sheet resistance was $1.10^8\ \Omega_\square$ and the minimum reflectance was 0.8% at 555 nm with a luminous reflectance of about 1%. Two-layers sol-gel system (glass/SnO_2/SiO_2) with surface resistance of $4 \times 10^6\ \Omega_\square$ have also been proposed as AR/AS [16].

The interesting feature is that the coatings (applied on CRT) have been deposited by spin coating and processed between 90 and 100°C by photoirradiation with a low pressure Hg lamp (15 to 40 mW/cm^2, 10 min.).

V-shaped AR/AS double layer coating using thin semiconducting nanoparticles oxide (SnO_2:Sn , In_2O_3:Sn) or Ag-Pd nanoparticles as inner layer and SiO_2 as outer layer with sheet resistance of 10^7, 10^4, $10^3\ \Omega_\square$ and a minimum reflectance of 1, 1.5 and 0.3% respectively have been recently reported [17]. Compared to a sputtered system, wider spectral low reflectance is obtained using sol-gel coatings due to a gradient index variation in the first layer. The reflectance was further significantly reduced by incorporating porous silica nanoparticles (50 nm size) in the 2nd layer. Double-layer AR-AS coatings where the first layer was a mixture of TiO_xN_y and ATO nanoparticles and SiO_2 with sheet resistance in the $3 \cdot 10^{10} - 2 \cdot 10^9\ \Omega_\square$ are reported in [19].

Antireflective-electromagnetic wave shielding coatings. Two-layers interference sol-gel systems formed with an outer 80 nm SiO_2 layer and a very thin (30 nm) inner layer composed of colloidal silver, titanium oxynitride (TiO_xN_y) and ATO nanoparticles have been recently reported [18] with sheet resistance $R_{\square} \leq 100\ \Omega_{\square}$ and broad low reflectance values of $< 0.4\%$ in the spectral range from 450 to 600 nm. Such coating shields both the very low and extremely low frequencies (VLF 2-400 kHz and ELF 5 Hz-2kHz) but their transmittance is low ($\leq 70\%$). The use of TiO_xN_y and ATO particles turns the coating insensitive to UV light.

2.2 Sub-wavelength structured surfaces

Traditional AR coatings are usually designed to operate over a narrow targeted wavelength range and perform poorly outside the designated range and their performance degrades at incident angles beyond 20°. Moreover, the cost of multilayer thin film AR coatings addressed to solve these issues is high. Conventional multilayers are also too expensive for cheap application like small-scale displays, dash boards, solar receivers, etc.

A promising approach is the development of sub-wavelength structures, also called motheye surfaces [19,20].

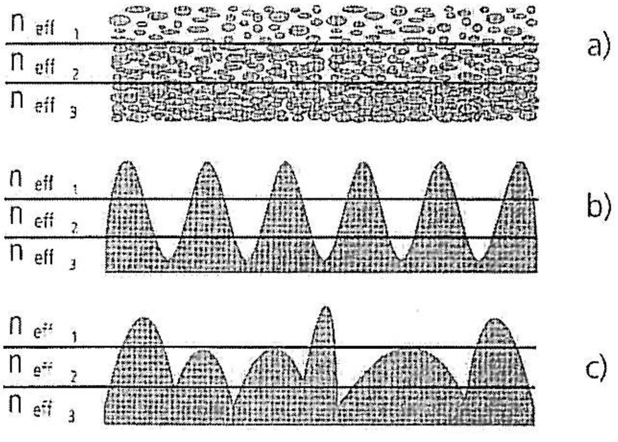


Figure 4. Approaches for subwavelength-structured AR surfaces (from [20]).

Such structures with dimensions in the range of 250 nm are potentially inexpensive because they can be replicated by embossing or other replication techniques, either directly on polymeric substrates or on recently developed sol-gel nanocomposite materials deposited on glass substrates. Periodic surface-relief profiles behave as a graded index AR thin film system. The depth is related to the longest wavelength for which an AR effect is wished and the period to the shortest wavelength of interest. For coating materials of index of refraction of 1.5, a sinusoidal pattern with a spatial wavelength of 200 nm and a peak-to-valley amplitude of 175 nm should lead to a visible reflectance as low as 0.2%. Figure 5 and 6 show typical results of the Fraunhofer institute [21]. The Ormocer coating was hardened by additional UV irradiation. Wider band width can be achieved using stochastic structure.

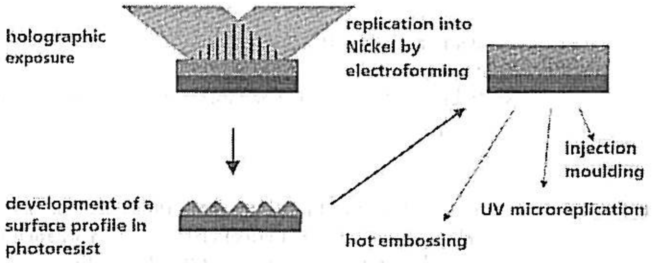


Figure 5. Principal steps of generation and replication of microstructured surfaces by means of interference lithography (holographic exposure) (from [21]).

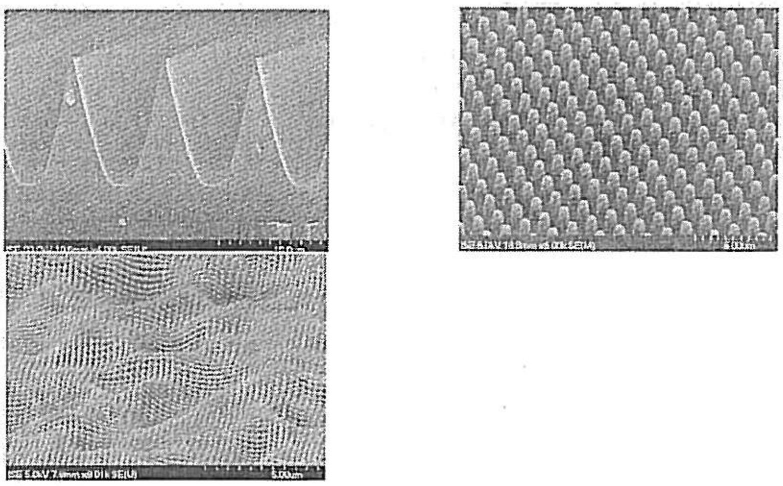
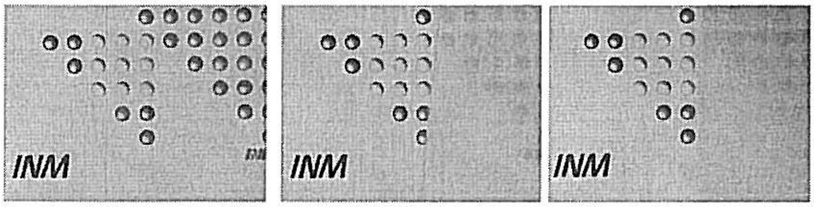


Figure 6. (a) Linear structure, (b) moth-eye anti-reflective structure and (c) a combined anti-reflective/anti-glare surface structure generated by interference lithography (from [21]).

The fabrication of large (60 × 80 cm) structured stampers (nickel shim) for replication by interference lithography is reported in [21].

The undesirable reflection of substrates can also be reduced by antiglare effect based on microscopic surface roughening. An analysis of the relationship between the phase shift of the reflected light and roughness [22] $\sigma_p = 2\,\pi\,\sigma_h \cos\theta/\lambda$ where σ_0 and σ_h are the variance of the phase shift and the surface height and θ is the angle of incidence shows that for normal incidence a complete loss of the reflected information can be obtained in the visible range for $\sigma_h = 0.4$ to 0.8 µm. For this purpose, etching glass surfaces in HF solution or leading in alkaline solution are well-known but not ecologically friendly processes.

A cheap and easy up-scaled process was demonstrated at INM by dip-coating 2 µm thick sol-gel coatings containing micrometer size agglomerates of transparent SnO_2 colloidal particles after sintering at 500°C during 1 h. The normal reflectance was reduced from 8-9% (glass substrate) down to 3% for $\sigma_h = 1.6$ µm. The coating has a transmittance of 94%, a haze of 16% and a clarity of 65% but is only adequate as picture framing (object to be seen placed behind and close to the coated glass) (figure 7).



Antiglare glass
on the picture

Antiglare glass
20 cm away from
the picture

Antiglare glass
50 cm away from
the picture

Figure 7. Appearance of an object placed behind a rough coated glass. Left: on the picture, middle: 20 cm away, right: 50 cm away.

Similar results can be obtained by spraying. Antistatic-antiglare properties have been obtained using ITO conducting nanoparticles [23].

3. OTHER OPTICAL PROPERTIES

The deposition of $\lambda/4$ and $\lambda/2$ layers of different materials (e.g. SiO_2, TiO_2) can be configured to achieve many other properties such as heat reflection filters, achromatic beam splitters, conversion filters, cold light mirrors, color effect and graded filters, etc.

All these products require the deposition of many layers. The conventional sol-gel process is not well adapted to obtain highly sophisticated properties as many deposition/heating/cooling steps sequences are necessary. It is nevertheless interesting especially for large scale products, especially because stacks of layers can be deposited simultaneously by the dip coating process on both sides of the substrates reducing the number of steps by a factor two or even more. For this purpose, the "angle-dependent dip coating" process is used since it allows to deposit the same layer with different thickness on both sides [24].

In this way, either the quality of the interference filters or the productivity of filters requiring many process steps can be enhanced. This technique is used industrially by Prinz Optics [9], which offers a broad range of specialty sol-gel made interference coatings on flat and tube glass substrates.

Near infrared reflecting filters with reflectance of 90% in the spectral range 1.1 to 1.4 µm have been developed at INM using the nanocomposite SiO_2 and TiO_2 sols described in [11]. Stacks of 5 layers have been deposited by dip coating. The configuration was glass/HLHLH where H is a 125 nm thick TiO_2 nanocomposite, L is a 180 nm thick SiO_2 nanocomposite, each layer being UV cured after deposition and the final stack sintered at 450°C, 15 min [11] (figure 8).

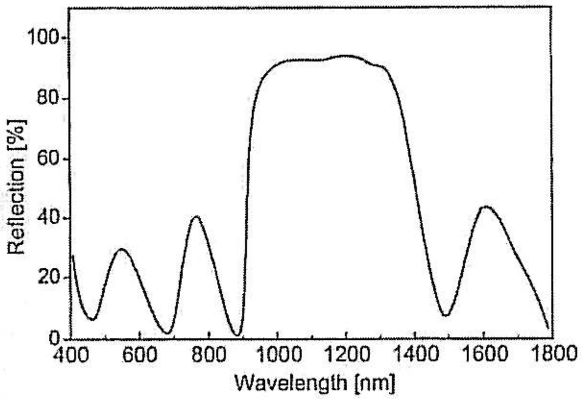


Figure 8. Reflectance of a 5 layer coating deposited on each side of a glass substrate. Final sintering at 450°C, 15 min (from [11]).

An increase of the width of the reflectance curve by 200 nm on each side was achieved by using the angle dip coating technique [25]. The ratio of the thicknesses for a 4° angle is about 0.8 so that the reflectance maximum of each stack can be slightly shifted.

A similar approach (nanocomposite sols, ADDC process) was used to coat plastic substrates where the coatings have been only polymerized by UV light (2.1 J/cm^2) with a further post treatment at 80°C for 15 min [26].

4. CONCLUSION

The sol-gel process is presently used industrially for the production of interference coatings offering a wide range of optical properties. The most recent advances have been realized in the development of large scale low cost AR and antiglare systems (most of them made of a single layer) with the advent of nanocomposite and porous materials for which the chemical nanotechnology is undoubtedly an asset compared to physical deposition processes.

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