

# Generation of wet-chemical AR-coatings on plastic substrates by use of polymerizable nanoparticles

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## ABSTRACT

Multi-layer interference filters of surface modified SiO<sub>2</sub>- and TiO<sub>2</sub>- nanoparticles have been produced on Polycarbonat (PC) and on scratch resistant film. AR-coatings (Anti-Reflex-coatings) were prepared from a dispersion of SiO<sub>2</sub> and TiO<sub>2</sub> colloidal nanoparticles in a hybrid inorganic organic matrix. The TiO<sub>2</sub> particles have been synthesized by addition of HCl and H<sub>2</sub>O to a solution of titanium tetraisopropanolate in isopropanol. The SiO<sub>2</sub> nanoparticles were synthesized by base catalyzed hydrolyses and condensation of tetraethoxysilane (TEOS) mixed with an aqueous solvent. The surface modification of the TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles with 3-glycidoxypropyltrimethoxysilane (GPTS) avoids the agglomeration of the nanoparticles and covalent bonds between the matrix and nanoparticles are formed during a photopolymerization step. The nanoparticles were dispersed in a hydrolyzed GPTS matrix and UVI Cygacure 6974 was added as a photoinitiator. The  $\lambda/4$  ( $\lambda=550$  nm) films of TiO<sub>2</sub> and SiO<sub>2</sub> sols were prepared on PC and on scratch resistant coated PC by spin-coating techniques. The refractive index of the SiO<sub>2</sub>/TiO<sub>2</sub>-coatings can be adjusted from 1.47 up to 1.94 depending on the SiO<sub>2</sub> or TiO<sub>2</sub> concentration. By the combination of index matching and photopolymerization, a low temperature interference filter can be realized for plastic substrates with reflection of 0.5 % at 550 nm. The coatings show excellent adhesion to the substrates in the cross hatch test and promising mechanical properties.

Keywords: anti-reflection, nanoparticles, sol-gel, interference filter

## 1.INTRODUCTION

Glasses and plastics suffer from reflection losses at the substrate-air interface. AR-Coatings are applied for solar cell coatings, displays, eye glasses, computer screens and lenses in optical equipments to reduce the reflectance and increase the efficiency of the optical devices. The interference filters are produced by quarter-wavelength thin layers (wavelength at which maximum transition is desired). Such optical coatings are obtained with a stack of layers consisting of high and low refractive index materials combined with a low refractive index layer on top. Using a sol-gel process, Yoldas [1,2,3] prepared low refractive index fluoride films densified at 300-600 C. Carol [4] prepared AR-filters on plastic substrates by hydrolyzation and condensantion of silanes and metal-alkoxides by densification of the films at 50 C for 2 to 3 weeks. Floch [5,6] has produced hydrophobic AR-coatings on plastics by a sol-gel route with high scratch-resistance densifying the films at 120 C. Tsucha [7] used electron-beam curing to densify a resin consistent of a silane matrix with dispersed nanoparticles to adjust additionally the refractive index of the optical coatings.

For many polymer substrates, heat treatment is a critical processing step. Polymethylmethacrylates allow a temperature treatment of about 80°C. For conventional polycarbonate (PC), the critical temperature should not exceed 130°C in case of flat and thick (> 2 mm in thickness) substrates. For thinner and shaped articles of PC, the curing temperature has to be reduced when the form stability has to be guaranteed. In order to allow mass production, the materials performance and a cost effective process engineering, including short processing times with low investment production means, have to be tuned and optimized.

The aim of the work presented in this paper is the development of scratch resistant AR-coatings on plastics by thermal treatment of maximal 80 C using UV-polymerizable functionalized TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles. By the illumination of the thin films with UV-light, the polymerizable matrix is cured and the nanoparticles are covalently bonded to the matrix. The influence of a matrix as binding agent between the particles on the mechanical properties of the thin films will be presented. The refractive index of the coatings can be tuned with high accuracy by the variation of the concentration of nanoparticles and modulation free transmission spectra of AR-coatings on surface hardcoated PC-substrates can be realized.

## 2. EXPERIMENTAL

To generate the high refractive index component  $\text{TiO}_2$ , 2.1 g of tetraisopropylorthotitanat was slowly dropped in to a mixture of isopropanol with 0.981 g con. HCl (37 wt%/H<sub>2</sub>O) and 0.205 g water under stirring at 25 °C for 24 hours. To silanise the surface of the formed  $\text{TiO}_2$ -nanoparticles 2g GPTS was mixed with 200 g of the  $\text{TiO}_2$ -sol under reflux and vigorous stirring at 50 °C for 5 hours. Because the photoinitiator UVI 6974 (Union Carbide) is not soluble in isopropanol, a part of isopropanol (10g) was removed from the sol by vacuum distillation at 14 mbar and 25 C and 14 g of 2-isopropoxyethanol were added. To produce films with different refractive index, GPTS (prehydrolyzed with 0.1 N HCl) and 2 wt% of UVI 6974 (in relation to the GPTS species) were added to the particulate sol.

The  $\text{SiO}_2$  nanoparticles [8] were synthesized by base catalyzed hydrolyses and condensation of tetraethoxysilane (TEOS). 670 ml TEOS were mixed with 1058 ml deionized water and 1980 ml ethanol to give a homogeneous solution. 4,043 ml NH<sub>3</sub> (25% in water), were added under vigorous stirring at 25°C. The mixture was heated up to 50°C under reflux and stirring for two days until no more residual TEOS could be detected (by IR-spectroscopy). This silica sol was concentrated by vacuum distillation to 30 wt% of  $\text{SiO}_2$  in water. After adding 2-propanol and 0.5% glucose as stabilizer, the sol was concentrated by vacuum distillation to 30 wt% of  $\text{SiO}_2$  and the water was removed to 0.3 wt%. (Karl Fischer titration). The silanisation of the  $\text{SiO}_2$ -nanoparticles was carried out with a mixture of 3.94 g of  $\text{SiO}_2$ -nanoparticles with 1 g of GPTS. The GPTS was slowly dropped into the  $\text{SiO}_2$ -sol at reflux and the mixture was stirred at 50°C for 5 hours. The size distribution of the  $\text{TiO}_2$  and  $\text{SiO}_2$  nanoparticles was measured by PCS technique (ALV-5000 Multiple Tau Digital correlator-ALV Laser mbH). The photopolymerizable matrix was prepared by hydrolyzation of a mixture of (5:3 mol%) 23.634 g of GPTS and 12.45g of TEOS with 2.10 g H<sub>2</sub>O (0.1 n HCl). To complete the hydrolyzation process the sol was stirred 24 h at 25 C. Finally 3 wt% of UVI 6974 was added. The refractive index change of the GPTS/TEOS/ $\text{SiO}_2$  films was achieved by the variation of the concentration of the  $\text{SiO}_2$  nanoparticles in the photopolymerizable GPTS/TEOS matrix. To simplify the nomenclature of the GPTS/TEOS/ $\text{SiO}_2$  sol, the system will be called in the following text system GPTS- $\text{SiO}_2$ .

In order to investigate the influence of an additional hard coating on index matched coatings on PC, a scratch resistant coating which was developed from the INM [9,10,11] and commercialized by Rupp+Hubrach was slightly modified by the variation of the aluminum hydroxide content in combination with  $\text{SiO}_2$ -nanoparticles.

The adhesion of the low index  $\text{SiO}_2$ -film was improved by the application of a primer system. A photopolymerizable sol of MPTS/GPTS (1:1-mol%) was hydrolyzed with 3 mol H<sub>2</sub>O (0.1n HCl) and the two initiators, Irgacure 184 (Ciba) as a radical initiator for MPTS and UVI Cygacure (Union Carbide) as a cationic initiator for GPTS, were added to the prehydrolysed sol.. All films were applied on PC-substrates of a size of 10X10 cm<sup>2</sup>. Before the coatings were applied, the substrates were cleaned with in a 20 mol% KOH-H<sub>2</sub>O solution for 10 min. After cleaning the substrates, the films were prepared by spin-coating in controlled atmosphere (30% relative humidity) in a clean room. The photopolymerization was performed in a Beltron UV- conveyer equipment by simultaneous UV and IR treatment (0.4 W/cm<sup>2</sup> and 80°C). For the high and low refractive index films, an intensity of 21 J/cm<sup>2</sup> was adjusted, the primer was photocured with 4 J/cm<sup>2</sup>. After the photocuring process, the film stacks were additionally stored at 80 °C for 10 min. The film thickness and refractive index was measured by ellipsometry. The particle size was measured by photon correlation spectroscopy (PCS) and high resolution transmission electron microscopy (HTEM).

The adhesion test was made by scratching the surface of the AR-filter in a transversal pattern with a grating knife and the tape test using a „Tesa“-tape was performed. In the eraser test, a rubber was pressed on the coating with a load of 5 Newton and was moved 10 times over the coated substrate. In the ultrasonic test, a coated substrate was stored in a solution of H<sub>2</sub>O and 10 wt% of tartaric acid and sonicating for 3 min. In the humidity test, the coated substrates were stored at 96% relative humidity and 25 °C for several hours. In the boiling test, the coated substrates were stored in boiling water for 1 h. In the saline-test, the coated substrates were stored in water containing 0.7% NaCl at 25°C for 8 hours. The coated substrates were cleaned with ethanol and a quantitative analyses of the films was performed with a microscope to detect film delamination or grazing after all these tests.

The Taber abramer test was carried out with a TABER Industries 5150 Abraser (load 500 g/wheel, rubber CS10F) and the damage of the coating and substrate material was measured with a HAZEGUARD PLUS (BYK Gardner GmbH).

## 3. RESULTS AND DISCUSSION

In order to tune the index of refraction for both the high and low index layers, films with different compositions were prepared and the index of refraction was measured. In figure 1a and b, the index of refraction of GPTS- $\text{SiO}_2$  and GPTS- $\text{TiO}_2$  films on planar PC-sheets for different  $\text{SiO}_2$  and  $\text{TiO}_2$  concentrations are shown. As expected, a linear relation is obtained. Starting from the index of the GPTS-matrix material ( $n_d=1.505$ ), indices from  $n_d=1.47$  up to  $n_d=1.9$  can be adjusted by the variation of the composition.

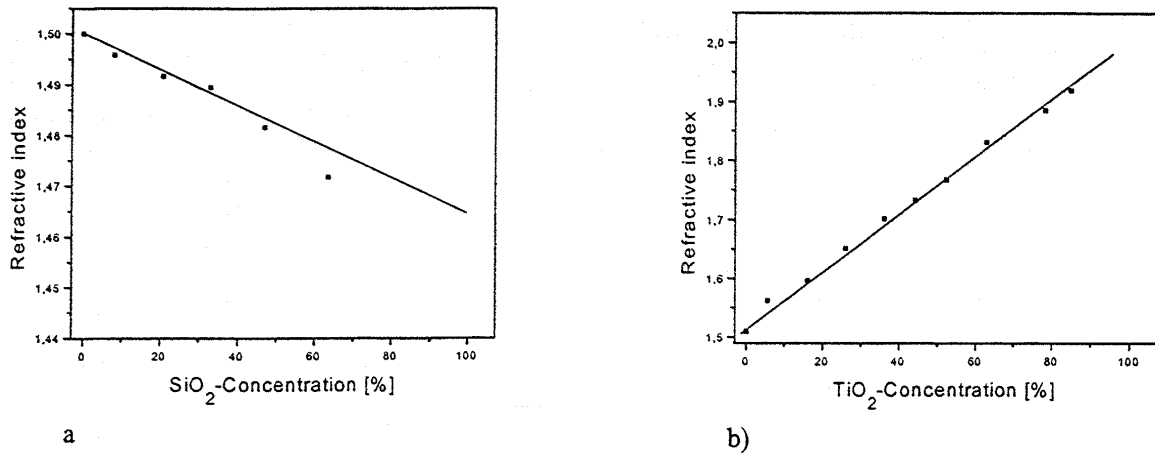


Figure 1: Refractive index variation of the GPTS-SiO<sub>2</sub>-System in dependence of SiO<sub>2</sub>- nanoparticles concentration, b) Refractive index variation of the GPTS-TiO<sub>2</sub>-System in dependence of TiO<sub>2</sub>-nanoparticles concentration. The substrate material is PC.

In figure 2a and 2b, HTEM micrographs of GPTS-SiO<sub>2</sub> film (10 wt% of SiO<sub>2</sub>) and GPTS-TiO<sub>2</sub> film (70 wt% of TiO<sub>2</sub>) are shown. The TiO<sub>2</sub>-nanoparticles in Figure 2a are clearly visible due to the high scattering contrast of the particles. Due to the smaller scattering contrast of the SiO<sub>2</sub>-particles in the GPTS-matrix, the contrast is slightly reduced in comparison to the TiO<sub>2</sub> nanoparticles. The TiO<sub>2</sub> particles have an average diameter of 4 nm and the SiO<sub>2</sub>-particles have an average diameter of 10 nm.

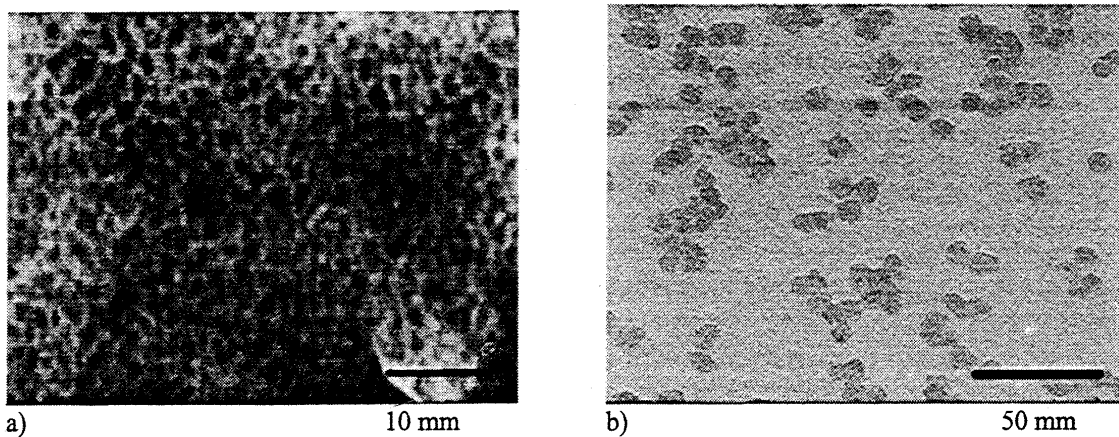


Figure 2: a) HTEM-micrograph of functionalized TiO<sub>2</sub> 70 wt% (referring to GPTS content) nanoparticles dispersed in GPTS matrix, b) HTEM-micrograph of functionalized SiO<sub>2</sub> (10 wt% calculated from the GPTS content) nanoparticles dispersed in a GPTS matrix

These values obtained by HTEM-micrographs correlate very well with the results obtained by photon-correlation spectroscopy (PCS) measurements of the coating sol. In figure 3, the particle size distributions obtained by PCS for both material systems are shown. The particles have a narrow size distribution and no agglomeration was detected.

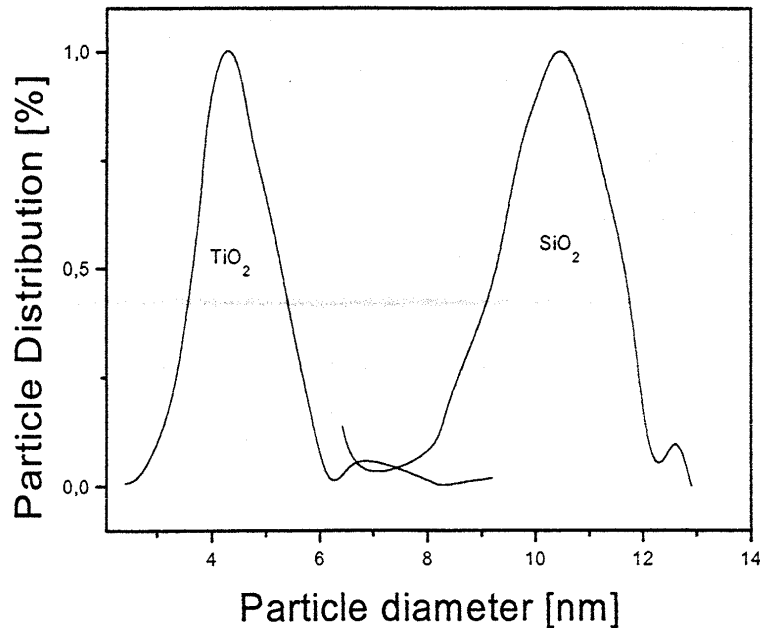


Figure 3: Particle size distribution of  $\text{TiO}_2$  and  $\text{SiO}_2$  nanoparticles measured by PCS-technique.

In order to realize an AR-filter with V-shape on PC-sheets, the following stack of different layers was selected, (figure 4).

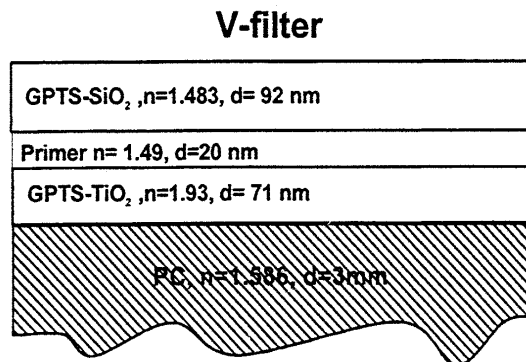


Figure 4: Stack of layers with anti-reflexion properties on PC,  $\lambda/4$  film of GPTS-TiO<sub>2</sub>, primer (MPTS/GPTS) and  $\lambda/4$  film of GPTS-SiO<sub>2</sub>.

This stack of high and low refractive index layers was calculated theoretically by a multilayer simulation program (TF Calc-HS 3.1) and realized experimentally by spin-coating the adequate material compositions derived from Figure 1a and b on a PC-substrate. The primer, which is optically not active, had to be used to achieve good adhesion of the GPTS/SiO<sub>2</sub>-film on the TiO<sub>2</sub> doped GPTS matrix film.

The reflection losses obtained at a single side of uncoated PC and AR-coated PC in dependence of the wavelength of the incident light are shown in figure 5. The theoretical reflectivity obtained by the simulating program is also included.

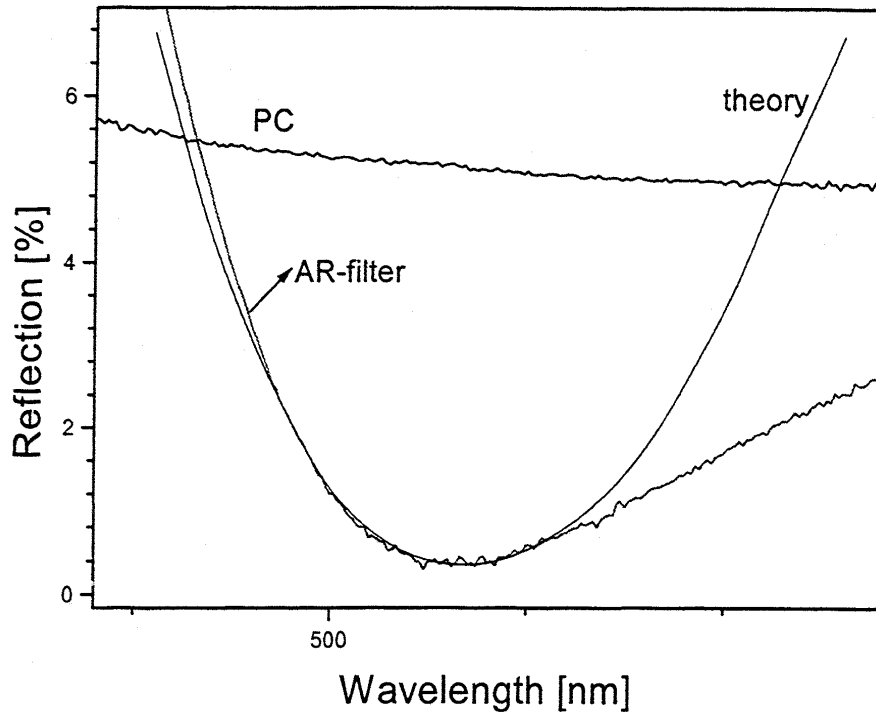


Figure 5: Reflectivity of a stack of  $\lambda/4$ -TiO<sub>2</sub> and  $\lambda/4$ -SiO<sub>2</sub> -layers on PC and of uncoated PC. The theoretical reflectivity obtained from a commercially available multi-layer calculation program is also included.

From figure 5 it is evident, that for uncoated PC reflection losses of about 5.2 % at 550 nm are reduced to 0.5% by the two layer AR-coating. The asymmetric shape of the V-filter is contributed to the high dispersion of the refractive index of the GPTS-TiO<sub>2</sub> film .

First experiments to evaluate the mechanical properties of the AR-coating were performed using the Eraser and Taber Abraser test. In the Eraser test, a damage of the PC-substrate was obtained after 10 rubber cycles. The GPTS/TiO<sub>2</sub>/SiO<sub>2</sub>-coated PC-sheet showed a damage in the microscope after 14 rubber cycles. Although this is not a dramatic improvement of the scratch resistance in the Eraser test, it is very astonishing that an over all thickness of 200 nm of low temperature cured films results in 25% higher scratch resistance in the Eraser-test.

Similar results were obtained in the Taber-Abraser test, figure 6.

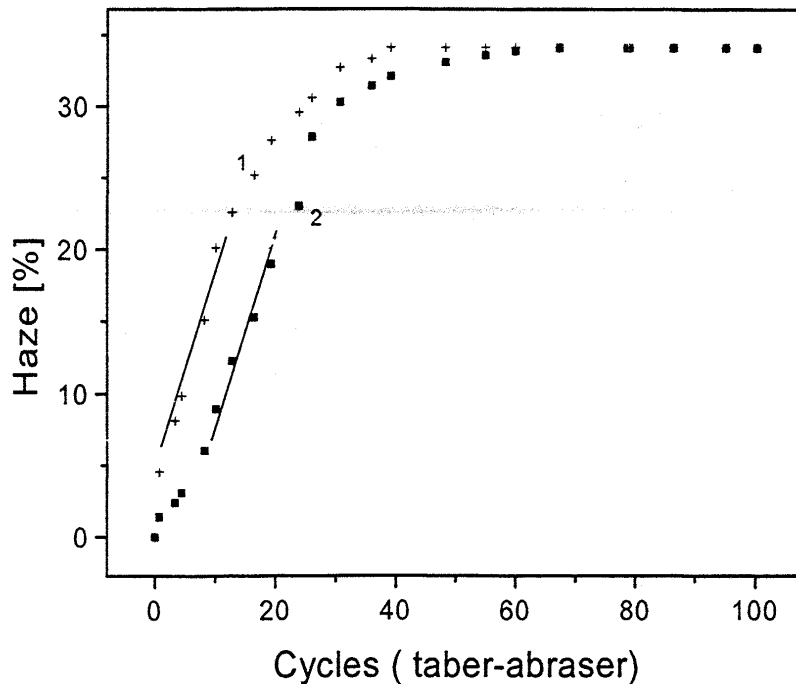


Figure 6: Haze in dependence of the cycles by Taber Abraser test, 1) PC and 2) GPTS/TiO<sub>2</sub>/SiO<sub>2</sub> (AR-coating) on PC.

Both for coated and uncoated PC, the haze reaches a maximum of 35% after about 60 cycles of the Taber-wheels. After 60 cycles, the surface of the sheets is destroyed completely resulting in a haze independent of additional cycles. The AR-coated PC shows slightly better scratch resistance for small number of cycles in comparison to the uncoated substrate. A quantitative comparison of the mechanical surface behavior in the Taber test can be obtained by the calculation of the slope of the haze curve in the area of highest haze gradient. Slopes for the haze curve of coated and uncoated PC-sheets are almost identical in the region of the highest haze gradient. Only for cycle numbers up to 6 cycles of the Taber-wheels a difference in the slopes of both curves are evident. A comparison of the slopes for uncoated and AR-coated PC-sheets results in about 18% enhancement of the scratch resistance up to 6 cycles, of the Taber-wheels. After about 6 cycles the GPTS/TiO<sub>2</sub>/SiO<sub>2</sub> film stack is destroyed and the following increase in haze is only given by the PC substrate material. Although damage mechanisms in the Eraser-test and Taber-Abraser-test are completely different, the obtained results indicate that AR-films of two hundred nm in thickness will only slightly enhance the scratch-resistance of a soft material. To obtain AR-characteristics in combination with high scratch resistance, the additional coating of the soft substrate with a hard coating is therefore indispensable.

Films of a thickness greater than the wavelength of the incident light applied onto substrates with large differences in the index of refraction ( $\Delta n$ ) result in a modulation of the reflected light intensity by interference effects. The modulation amplitude depends on the film thickness. Figure 7 shows a typical reflection spectrum of the described commercialized hard coating on PC.

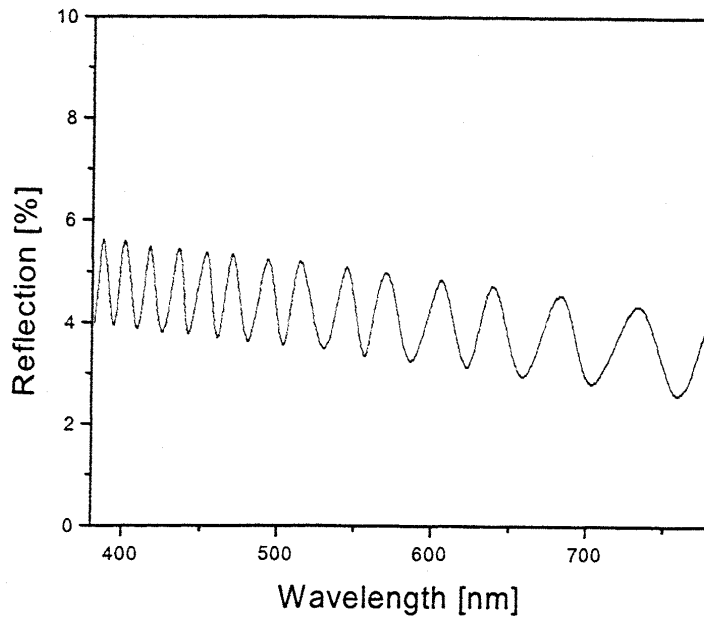


Figure 7: Reflection measurement of an AR-coating on PC.

Analyzing this spectrum with the multilayer simulation program gives values of  $3 \mu\text{m}$  for film thickness and an index of refraction of  $n_d=1.515$  which is in excellent agreement to published results on CR-39 [12]. This frequency modulation can be eliminated by matching the index of refraction of the substrate and the film. The drastically change of reflection losses by index matching in combination with a 2 layer AR-coating is shown in figure 8. The unmatched hard coating with  $n_d=1.494$  results in reflection peaks in the blue and red wavelength regions leading to coloration effects in reflection. The index matched hard coating with the 2 layer AR-coating shows modulation free reflection spectra similar to the results from figure 5, where no hard coating was applied.

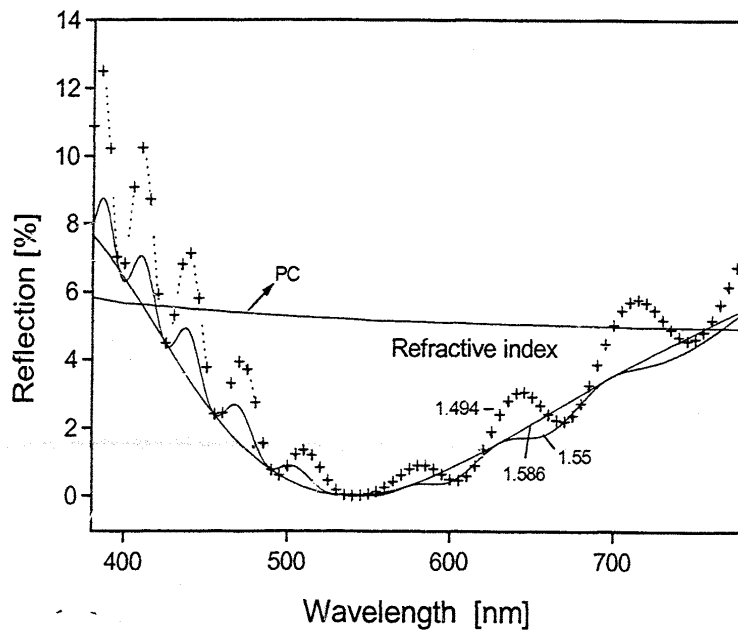


Figure 8: Reflection measurement of  $\lambda/4$ - $\text{TiO}_2$  and  $\lambda/4$ - $\text{SiO}_2$ -coatings on PC with an index matched scratch resistant coating.

The tremendous improvement of the scratch resistance of a PC-sheet by application of a index matched commercial hard-coating is shown in figure 9.

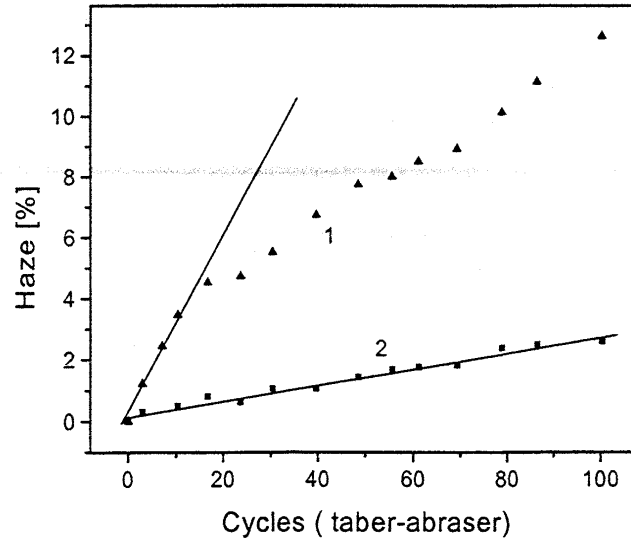


Figure 9: Haze in dependence of the cycles by Taber Abraser test, 1) scratch resistant hard coating (3  $\mu\text{m}$  thickness) and 2) scratch resistant hard coating plus GPTS/TiO<sub>2</sub>/SiO<sub>2</sub> (AR-coating stack about 200 nm in thickness).

PC-substrates with a 3  $\mu\text{m}$  hard coating have shown no damage in the Eraser test after 50 rubber cycles. The GPTS/TiO<sub>2</sub>/SiO<sub>2</sub> applied on the hard-coat has shown a damage after about 30 cycles resulting in an improvement of a factor  $> 2$  compared to the GPTS/TiO<sub>2</sub>/SiO<sub>2</sub> on PC without hard coating. These AR-coatings on PC and PC plus hard coating show no delamination or defects after the boiling, ultrasonic and NaCl tests and excellent adhesion (GT0/0) was proved in the cross hatch and tape test.

A summary of the different production steps to realize the presented AR-coatings on PC-substrates is schematically shown in figure 10.



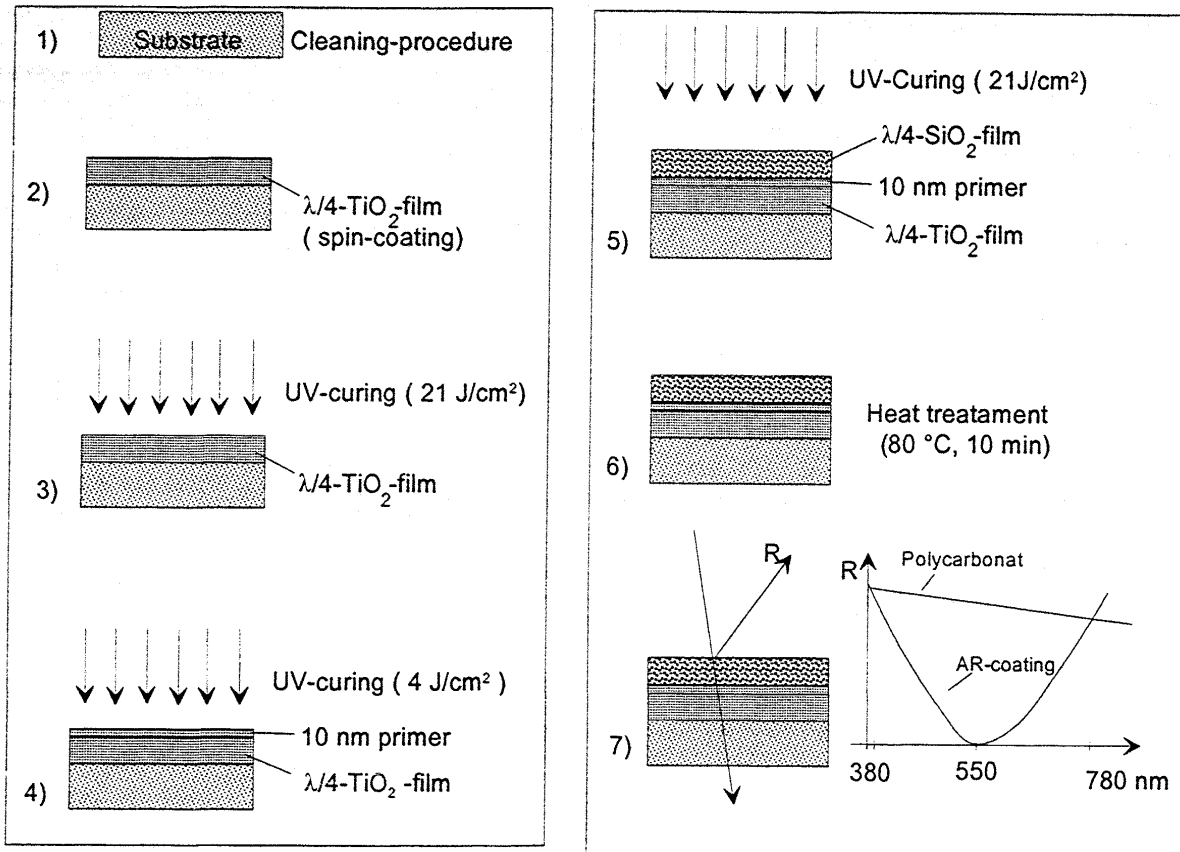


Figure 10: Scheme of the different steps to obtain wet-chemical AR-coatings on plastic substrates by the use of polymerizable nanoparticles

#### 4. CONCLUSION

The results show that the use of functionalized nanoparticles produced by sol-gel processes is a good strategy to change the refractive index of photopolymerizable organic-inorganic thin films. This principle has been used to produce polymerizable AR-coatings by applying multiple stacks of quarter wavelength layers consisting of low and high refractive index films on a substrate. Short processing times at low temperatures allow the application of this technique for other polymer substrates with lower thermal stabilities compared to PC. Investigations on AR-coatings on polymethylmethacrylate are in progress.

#### 5. ACKNOWLEDGEMENTS

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