PE-CVD Hardening and Matching Coating for Ophthalmic Plastic Lenses

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Keywords: PECVD; SiO_2; Ophthalmic coatings

ABSTRACT

In the field of ophthalmics the use of CR39 plastic lenses is more and more spreading out, both for lightness and safety reasons. Concurrently, usage of wide-band anti-reflection coatings is increasing, either in Europe (where it is already widespread), and US (where it is rapidly growing), since those coatings greatly enhance the clearness of vision and remove anti-aesthetic reflections.

However, two fundamental issues are to be solved in order to achieve the best performances:
- hardening of lens surface to avoid scratching;
- optical and mechanical matching between the organic substrate (with a high thermal expansion coefficient) and the subsequent anti-reflection coating made by means of several inorganic layers.

This paper describes a process called H.O.P. (Hardening Organic Process), set up at Ce.Te.V. to accomplish the two issues in one coating, deposited by PE-CVD. Results here reported are taken from thermal, optical and mechanical tests of these films, together with repeatability and reliability data.

It is finally described the application of this process to an equipment able to perform in the same run also the anti-reflection coating by means of reactive magnetron sputtering.

INTRODUCTION

Plastic lenses, though being safe and light-weight, need to be coated in order to enhance their otherwise very poor scratch resistance, which is instead a glass best performance. The widespread solution for surface hardening is the dipping process, which nevertheless worsens the optical characteristics of CR39 lenses.

On the other hand, customers used to an antireflection coating on glass, have begun to require it on plastic lenses too, bringing up the issue of bad compatibility between an organic material (the CR39 substrate) and inorganic layers which typically constitute the AR coating. The traditional coatings set up for glass, though being intrinsically hard, are not intended for following the thermal expansion shown by the plastic material, huge if compared with the glass one (about three orders of magnitude larger). Every trial of depositing an AR coating on raw CR39 has resulted either in a non-adherent layer showing cracking problems in thermal shock tests, or in a “soft” surface easily scratched.

Neither is the problem easily solved when the lens surface is hardened by dipping, thus new compromises have been made up by lens and coating producers to face this issue, acting on compositions of lacquers and anti-reflecting layers and relevant process parameters, in order to achieve good compatibility while keeping an acceptable scratch-resistant behavior. The different whole coatings currently available on the market do require a double-step process.

The Hardening Organic Process achieved through Plasma Enhanced Chemical Vapor Deposition has shown best performances in improving the scratch resistance of CR39 lenses, while offering a good substrate to the subsequent AR coating realized “in house” through Reactive Magnetron Sputtering. Moreover, both coatings can be deposited in the same run in the unique production plant designed by Ce.Te.V., patent pending, currently being tested in our facilities.

THE PE-CVD HARDENING ORGANIC PROCESS

PE-CVD is a well known technique in semiconductor industry, where good quality silicon oxide is deposited from silane gas or liquid sources (mainly TEOS - tetraethoxysilane), at temperatures higher than 250°C. Such values are not suitable for plastic lenses, which are damaged over 80°C. In processes run around room temperature, the mechanism involved in precursor fragmentation and film growth is the hydrolysis versus the thermolysis typical of the high temperature processes [1]. When feeding the plasma with a TEOS/Oxygen mixture, the resulting silicon oxide is rich in silanol (Si-OH) components, coming from a chemical reaction at the substrate surface as follows:

$$Si(OH)_n + Si(OH)_n \Rightarrow (OH)_{n-1}Si\text{-}O\text{-}Si(OH)_{n-1} + H_2O$$

This hypothesis is easily verified through an infrared spectrum (Figure 1) of the deposited film which shows absorption bands due to O-H bond stretching at 3300-3400 cm^{-1} and Si-OH bond stretching around 900 cm^{-1}.

Society of Vacuum Coaters 505/856-7188
37th Annual Technical Conference Proceedings (1994) 1-878068-13-X

Such a coating cannot be suitable for lens protection, being hydrophilic and anyhow inorganic. Results are bad adherence on the CR39 and intrinsic stress, which causes cracking and delamination during quality and environmental tests (thermal shocks are performed by salt boiling water test, which highly damages water-absorbing films).

In a former paper [2], Ce.Te.V. had already presented a solution involving a coating with graded chemical composition versus its thickness, starting from a SiO_xC_y plasma polymer and moving toward a silica-like surface layer, changing the oxygen flux in the gas feed. While well performing as mechanical matching between the lens and the anti-reflection coating, and being scratch-resistant, yet it showed a refractive index typical for plasma deposited SiO_2 (n_i=1.44-1.45), which on a CR39 substrate with index 1.5, could partially modify the optical characteristics of the subsequent AR coating.

QUALITY TESTS AND CHARACTERIZATION

Evaluation of the hardened lenses is made by means of several quality as well as environmental tests, while film characterization is performed on glass and silicon monitors for optical and structural characteristics.

Abrasion
Scratch resistance is evaluated with a standard eraser (rubber test - MIL C-675-C) and with a four zero steel cheesecloth, loaded at 0.5 Kg/cm^2.

Thermal shock
Evaluation is made through alternate 2 minute-dipping in a boiling solution of water and 5% NaCl, and room temperature water. A minimum of ten baths with zero defects is required, but on sample lenses even more than twenty baths have been performed without detecting any problems.

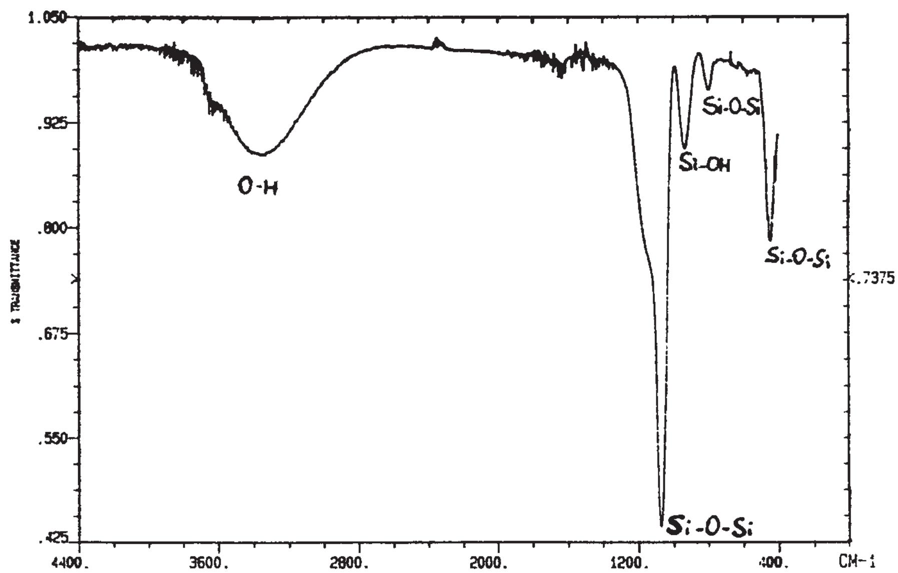

Figure 1. Infrared spectrum of low temperature SiO_x

Successive studies and experiments have led to the new Hardening Organic Process, which offers a higher compatibility with the same thickness, but shows a repeatable higher refractive index. The coating is deposited in a radio-frequency plasma in capacitive configuration, at pressures ranging from tens to hundreds of millitorr, from a proper gas mixture containing vapor of a liquid precursor which retains in the film structure some of the groups $C-H_n$ of its formula.

Acting on process parameters, a hard coating has been obtained with a higher number of degrees of freedom in the cross-linked structure, that allows to withstand thermal shocks without cracks and delaminations of the AR layers deposited on top of it.

Same test with a minimum of five baths is required for the total coating (H.O.P. + AR).

One-hour dipping in plain boiling water also do not damage the hardening coating.

Adhesion
The tape and cross hatch tests are performed on the sample lens respectively after the salt boiling water and the one-hour dipping tests. No detachments are to be detected.

Optical characteristics
The refractive index is 1.47, high enough to avoid interferential colors on the hardened lens. No optical absorption is revealed in 400-700 nm range (Fig. 2).

Chemical and structural analysis
Infrared spectra taken on a H.O.P. coated silicon sample show typical absorption bands for Si-O-Si network vibrations at 1050 (with a shoulder at 1150 cm^{-1}), 800 and 400 cm^{-1}. A significant presence of $C\text{-}H_n$ groups is detected at 2900 cm^{-1}. As deposited film spectrum compared with the one taken after nine months on the same sample do not show a significant water uptake (Figure 3).

Figure 4 reports quality control data over a period of time to test repeatability of the final process, compared with results in the previous working month. CR39 lenses of different quality levels are included, while highest quality substrates always give better results.

PRODUCTION EQUIPMENT

An innovative system is being tested in Ce.Te.V. able to deposit in the same run, with a single vacuum cycle, more than 150 lenses (depending on the diameter) on both sides, with the plasma H.O.P. coating and thereafter the AR coating by Reactive Magnetron Sputtering. Moreover, due to the plasma technique used for hardening, this plant can be thought for ophthalmic lenses or optical components with geometries causing problems in the dipping process.

CONCLUSIONS

The new Hardening Organic Process set up by Ce.Te.V offers a higher compatibility with the AR coating, with a repeatable refractive index of 1.47, which prevents interferential colors on the hardened lens. Quality tests confirm a good scratch resistance and environmental tests assure durability. The plasma polymerized layer, deposited in the production equipment currently being tested, is suitable for all ophthalmic lenses (even with difficult geometries) and plastic optical components, whose characteristics could be modified by the dipping process.

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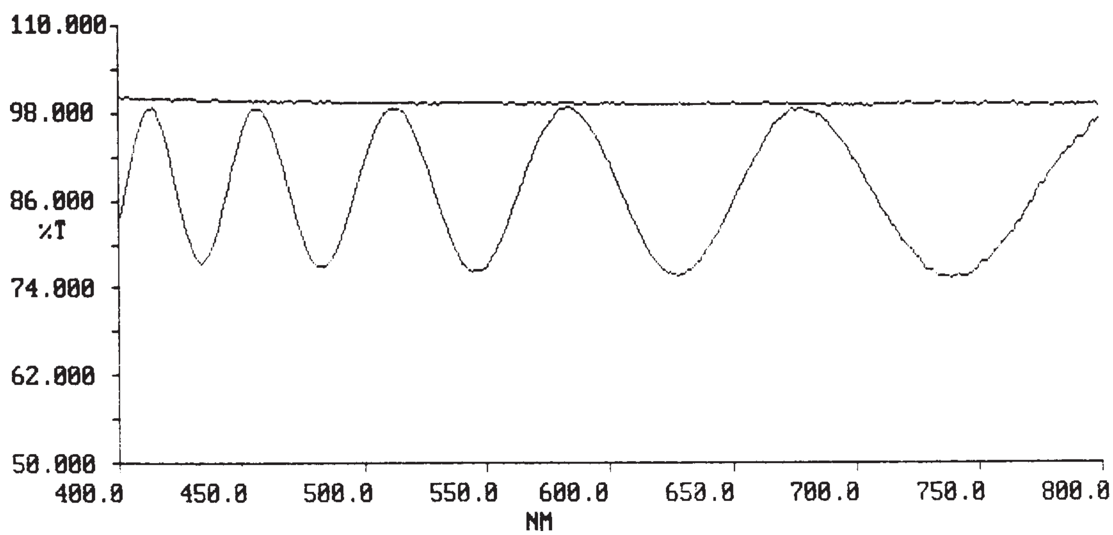

Figure 2. Spectrophotometric profile of a H.O.P. coated glass (measured in reflection).

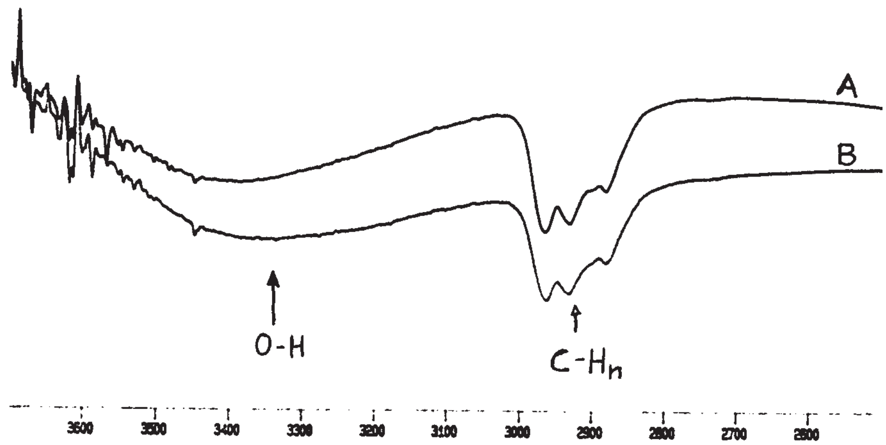

Figure 3. Infrared water absorption bands compared on the same sample after nine months.

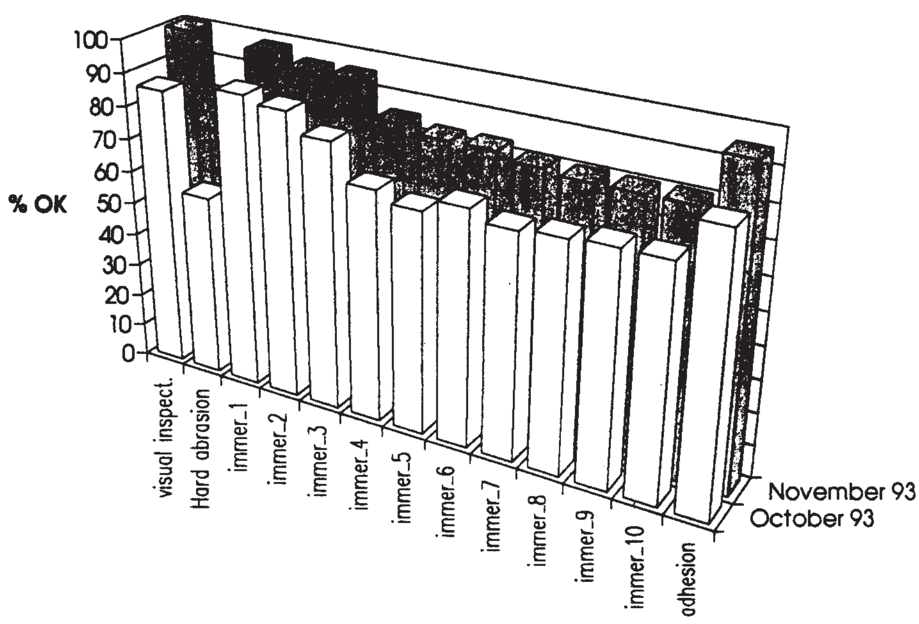

Figure 4. H.O.P. data from Q.C. tests