# Plasma Polymerization of Optical Coatings on Organic Substrates: Equipment and Processes:

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## ABSTRACT

The use of plastic as a substrate material for optical lenses has been increasing in importance due to smaller density, simpler machining and lower price. However scratches present a major problem wherever the lens surface is exposed to the environment. Various processes have thus been developed to protect the surfaces with hard coatings. The most common technique is dipping while spinning or spraying are other methods to apply lacquer. All these techniques require post-treatments such as drying and heat or UV curing. Safety considerations as well as the long processing time and the handling required between the different steps, enforced the development of new technologies. Plasma polymerization, a technology relying on plasma enhanced chemical vapor deposition (PECVD), is used to deposit dense organic layers with reproducible, well defined surface properties. In contrast to dip coating, plasma polymerization even coats curved structures with good uniformity. This is important for bifocal or trifocal lenses, featuring sharp edges on the surface. Due to the wide range of refraction indexes available (about n=1.45-1.80), even the latest high index materials can be coated without disturbing interference fringes.

## INTRODUCTION

The principle of ophthalmic lens coating has been known for a long time and is widely practiced in Europe and Japan. Conventional mineral substrates are generally coated by PVD processes such as E-beam or resistance heated evaporation. For practical reasons, mineral substrates are being increasingly replaced by plastic lenses. In the United States, for example, most ophthalmic substrates are made of plastic such as CR39 or polycarbonate.

Aside from the many advantages such as weight, machinability, fracture resistance or material costs, plastic lenses also show some disadvantages such as lower scratch resistance and consequently a shorter life span. For this reason the antireflection coating of plastic lenses must be supplemented with a hard coating or wear protection coating. In addition to improving scratch resistance the hard coating also works as a transition and adhesion promotion layer between the organic substrate and the inorganic antireflection layer package. To protect the antireflection layer a hydrophobic top coat is frequently applied (Fig. 1) which due to its low friction coefficient also simplifies the cleaning of the lens.

Various technologies are employed for depositing hard and top coatings. The most popular method is dipping while spin coating is also widely used. In this process a drop of varnish is distributed under the influence of centrifugal force on a fast rotating substrate. Also known is the deposition of varnish by atomization (spray coating). These wet chemical processes are performed under atmospheric pressure and in a cleanroom environment. After the varnish has been deposited, it must be cured by drying, baking or UV hardening.

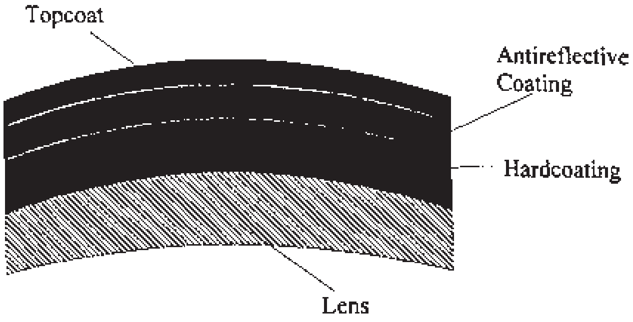

Figure 1.
State-of-the-art ophthalmic coatings for plastic lenses consist of a 2-3 µm hard coat, a multi-layer broadband antireflective coating and a hydrophobic topcoat for ease of cleaning.

The difficulties related to wet chemical processes become increasingly incompatible with the shorter in-process times and cost reduction efforts pursued by the ophthalmic industry. The overall yield of the wet coating process is modest due to the many handling steps in the clean room. It may take several hours for the substrates to pass through the coating line. In addition the partially toxic and combustible laquers and solvents required become increasingly difficult to use under current environmental protection regulations. This applies in particular to the disposal of liquid wastes.

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Plasma polymerization is a promising technique for eliminating the drawbacks of wet hardening processes. Although the working principle has been known for quite some time, it was not applied in production scale for a number of practical reasons. Since plasma polymerization exactly follows the surface contour it offers the advantage of perfectly coating separating edges and steps. In ophthalmic lens applications this advantage is particularly important for coating multifocal substrates. Another important advantage of plasma polymerization is the deposition of gradient layers which allow the coating to be matched to the mechanical, chemical, or optical properties of the substrate material. In particular the interference-free, optical adaptation of a wear protection layer to plastic lenses with a higher refraction index (such as Japanese n=1.67 material) can be easily achieved through plasma polymerization.

Since the process can be adapted to a variety of plastics, plasma polymerization offers a broad range of applications beyond ophthalmic lenses. In addition to wear protection layers, also hydrophilic to hydrophobic surfaces or diffusion barriers can be deposited.

## BASICS OF PLASMA POLYMERIZATION

Plasma polymerization, as distinct from ‘classical’ polymerization with repetition of a well-defined monomer, refers to the reactions between active radicals formed by electron impact dissociation processes in an electrical gas discharge (plasma) [1]. Plasma polymerization requires a vacuum chamber for pressures between 1 and 100 Pa, two electrodes which may be part of the vacuum chamber, an high frequency-generator with matchbox, as well as a gas supply unit (including evaporation or sublimation units for non-gaseous monomers). DC sources are usually not used in plasma polymerization because of the high insulation properties of the coatings.

The plasma is ignited under high frequency voltage and the appropriate pressure. Gas molecules are split into mostly positive ions and electrons. In contrast to the heavier ions, the low-mass electrons are able to follow the alternating field lines and are subject to much less scatter due to their small collision radius. The resulting plasma is of ‘non-equilibrium’ type and has a high electron temperature but a low gas temperature. The energies transferred by the electron impact are in the range of a few hundred kJ/Mol and can thus crack any organic compound (C-C bond 344 kJ $mol^{-1}$, C-H bond 416 kJ $mol^{-1}$). For this reason, reactions which otherwise would only be possible at much higher temperatures, can be started at room temperature (e.g. cold combustion processes).

If molecules are exposed to the plasma, excited short molecule fragments are produced, which after deposition and diffusion cross-link with other fragments. Already in the gas phase, reaction and cluster formation of these highly reactive molecular bonds take place and are continuously subject to refragmentation by electron impact or plasma beams. Experimental investigations [2] have shown that in silane plasmas radical anions are enclosed by the negative plasma boundary and tend to form high-molecular ions. In contrast, positive and neutral radicals continue to react on substrate surfaces or electrodes. If negatively charged clusters become too large, gas phase polymerization occurs and unwanted particles are produced in the vacuum chamber [3]. Through dedicated process control and appropriate selection of the basic monomers, unwanted secondary processes can be avoided, particularly in the production of high-quality surfaces for the semiconductor and optical industry.

For plasma polymerization no reactive centers on heteroatoms or multiple bonds, acting as cross-linking points, are required for reaction (as in conventional polymerization) This means that plasma polymerization is not a conventional ‘poly’-process, forming crystalline polymers from repetitive molecular units by cross-linking monomer molecules. Through the random fragmentation and relinking which continues also in the deposited polymer film for as long as it is exposed to the plasma, an amorphous polymer structure with a high degree of crosslinking is created in which the structure of the basic material is no longer maintained, except in a few special cases [4]. Another characteristic of plasma polymers is the initially high content of free radicals which can cause not only additional post-interlinking but also post-reaction on the surface with $O_2$. The polymer is thus a relatively hard and temperature-resistant duromer which already in thin films is free of macroscopic defects and cannot be attacked by most solvents.

Suitable monomers are all organic compounds that can be fed without decomposition in the gas phase into the vacuum chamber. The vapor pressure at 20°C should be at least 100 Pa. Despite the extensive fragmentation there is a considerable difference between the individual monomers with respect to the deposition rate as well as to the properties of the resulting film. According to the type of monomer, fast growing layers up to 1 µm/min can be achieved as well as negative growth rates (etching). Fluorine compounds such as $SF_6$, particularly in combination with $O_2$, can consequently also be used as a cleaning agent in the plasma. The deposition rate has always to be seen in connection with the controlability of a process, and consequently the reproducibility of the coating quality. For this reason industrial processes commonly used today show deposition rates between 10 and 100 nm/min.

The coating properties of the deposited polymer are strongly influenced by the composition of the precursor. An important role is played by the heteroatoms. Plasma polymers that contain fluorine have an extremely low friction coefficient. Silanes and organic silicone compounds in combination with $O_2$ as a reactive gas are particularly suited for wear protection coatings. Monomers that contain titanium can be used for high refractive index coatings. By adding different reactive gases or monomer/reactive gas mixtures, also coatings with a defined surface energy, from extremely hydrophobic 'antiadhesive coatings' ($E_{surf} < 10$ mN/m) to hydrophilic, wetting 'anti-fogging coatings' ($E_{surf} > 70$ mN/m) can be deposited.

Due to the large number of process-defining parameters, a variety of different surface characteristics can be achieved. It is not possible to establish a general relationship between process and film characteristics. New film properties will also, in the near future, only be determined in a time-consuming experimental approach. The principal parameters of the plasma polymerization process and the relevant film characteristics are summarized in table I.

Due to the demanding optical specifications of ophthalmic substrates and the required short in-process times, ophthalmic optics is an excellent field of application for plasma polymerization processes. For this purpose a coating geometry was developed and patented, adapted to ophthalmic lenses of widely differing shapes and sizes. The geometry can be easily scaled. PPV coating systems of three different sizes have been developed. Due to the geometric similarity of the systems, the processes can be transferred from one system size to another.

## EQUIPMENT

PPV is a p̲lasma p̲olymerization system with a v̲ertically arranged main axis. The system consists of a cylindrical RF electrode in a cylindrical vacuum chamber. A carousel type substrate holder rotates inside the ring gap formed by the two cylinders (Fig. 2). The substrates are completely immersed in the plasma and are coated on all sides, regardless of their shape: lenses are simultaneously coated on the front and back. To minimize any contamination by flitters and particles, the substrates are positioned upright in the substrate holder. Depending on the size, the system is loaded and unloaded either through lateral door or a swiveling cover flange. These openings allow quick handling of substrates and protective liners.

The basic equipment includes the following components: An annular process chamber with a rotating substrate holder and a set of protective liners, a water-cooled RF electrode, coils for creating a magnetic field in vertical direction (parallel to the main axis of the system), a feeding and replenishing system to supply the process chamber with monomers and reactive gases, a speed-controlled multistage vacuum pumping system, and a computer-controlled electrical system for fully automatic process control. The entire process sequence including pumpdown, coating and venting of the system is performed automatically. Production processes are started by pressing a button. The control software comprises modules for process and maintenance statistics.

For producing the vacuum conditions required for coating, a three-stage speed-controlled pumping system is used. This system comprises additional equipment to make it suited for plasma processes in continuous operation. The pumpdown time to 0.2 Pa is typically 5 to 10 minutes. The system is supplied with monomers and gases via a special gas cabinet because the utilized precursors are liquid under normal conditions. This cabinet, designed for industrial use, is equipped with all necessary purging, cleaning and replenishing facilities. All monomers used have a low toxicity and produce harmless products. Whereas large PPV systems consist of a welded stainless steel structure, medium and smaller systems are machined from aluminum for thermal reasons. All protective liners are made of stainless steel because they require periodic cleaning.

The large scale PPV 1000 for the ophthalmic market was launched in 1991 (Fig. 3). The system can coat up to 250 lenses per batch. The typical in-process time for ophthalmic wear protection coatings is 80 to 120 minutes, depending on the index and hardness of the coated substrate. With a coating surface of 1.2 $m^2$, this system can also be used for coating larger parts. For practical reasons it is limited to thin parts approximately in the size DIN A4 or US letter.

The medium size PPV 500 (Fig. 4) incorporates the latest process know-how and the practical experience gathered from the larger PPV systems. With a capacity of 72-96 lenses, this system achieves the typical throughput of widely used medium-size box coaters for AR coating. Through the two-handler principle for substrates, low coating costs are achieved (as in large systems) combined with high flexibility (as in medium systems). In addition to the processes available in the PPV 1000, the PPV 500 is also suited for interference-free coating of substrates up to $n_D=1.7$. The variable plasma volume of the PPV 500 also allows the processing of shaped parts with a greater depth.

The small PPV 100 system features the same geometric arrangement as the two larger systems. For this reason the processes developed on the small system can be transfered to the larger PPV systems without the usual scale-up difficulties. With a capacity of 12 lenses or 8 substrates (10x10 cm), this system is designed for R&D work and small series production (for example sensitive substrates). Due to the modest infrastructure requirements, the PPV 100 can also be operated in a laboratory environment.

## WEAR PROTECTION COATINGS ON OPHTHALMIC LENSES

Typically wear protection coatings for plastics are deposited by plasma polymerizing one or several monomers in an low-

Table I
Parameters and Controlled Variables of a Plasma Polymerization Process

| Physical variable | Controlled variable | Other variables |
|---|---|---|
| Power density | RF power, magnetic field | Chamber geometry |
| Process pressure | Gas flows, pump speed | Conductance |
| Gas composition | Gas flows | Reaction products |
| Gas velocity | Flow, pressure | Reaction pattern |
| Excitation frequency | Generator frequency | |

pressure plasma. The plasma polymers are free of defects and characterized by excellent resistance against mechanical and chemical attacks, as well as high transparency and temperature stability. These coatings offer invisible and durable protection against mechanical and chemical damage.

Hard coatings on ophthalmic lenses must not only be scratch-resistant and free of defects but several optical requirements must be satisfied too. The refractive index of the coating must be matched to the index of the substrate as closely as possible to prevent modulations in the transmission. The transmission must be sufficiently high across the entire visible spectrum. A number of tests for mechanical and chemical testing of ophthalmic substrates is listed below (table II). A single test is not sufficient to determine the coating quality. For example high hardness may produce excellent results in the steel wool test, but shows very poor results in a mechanical test with higher surface pressure.

Basically two different groups of lens material are used in ophthalmic applications: the chemically well-defined CR39, for lenses with a standard refractive index of $n_D$=1.5, and the chemically very heterogeneous group of high-refractive glasses. CR 39, a cast plastic made of diallyl glycol carbonate, is used worldwide as base material for most organic ophthalmic lenses. In a dedicated plasma polymerization process a layer package is deposited, comprising an adhesive film and three consecutive hard coatings with increasing $SiO_x$ content. A continuous transition of the film properties from a zone matched to the substrate to a glass-like film on the top-surface is achieved. The optical quality of a (n=1.5) coating on CR39 is illustrated in figure 5. The coating increases the transmission by approximately 2%, the modulation of the transmitted light is negligible. A comparison of the abrasion resistance of a plasma polymerized coating with different hard varnishes including a nanocomposite type is shown in figure 6. Each test lens was subject to four different mechanical tests (erasing rubber according to MIL-C-675; abrasive pad 400g, 50 strokes; polishing test 740 g, 100 strokes; steel wool, manual). In recent time also plastic lenses with a higher refractive index up to n=1.67 have been introduced.

Since high-refraction lenses are less scratch resistant than CR39, hard coating is essential. The task is more difficult because high-refraction materials are more sensitive to optical differences between the substrate and the thin film coating. Even small deviations result in modulations of transmission. By mixing two monomers continuous adaptation of the hard coat to various base materials is feasible. Figure 7 schematically shows the process sequence of a Diaplas hard coating for high-refractive plastic lenses, Figure 8 shows the resulting changes in hardness and refractive index. Organic substances are added as high-refraction monomers to the Silicon-monomer in order to achieve the desired refractive index. The refractive index can be continuously adjusted between $n_D$=1.45 and 1.80.

In the European market a large share of hard-coated lenses (70%) is subsequently given an antireflection coating. For this reason, optimized mechanical and chemical adaptation of the hard coating to the subsequent AR layer package is important. Due to the modular design of the process, plasma processes can be adapted to different interference layers, optimizing the overall performance of the ophthalmic coating.

## OUTLOOK

In addition to the hard coating of ophthalmic lenses there are other interesting applications for organic substrates that can be implemented with plasma polymerization. Mechanical and optical properties similar to those of the layer systems described above are required for plastics parts used in a rough environment. Polycarbonate helmet visors for example feature excellent scratch and impact resistance when coated with a plasma polymerized protective layer.

The surface energy can be considerably influenced with different monomers or incorporating polar -C=O or -OH bonds by adding oxygen. In contrast to the widely used corona treatment, the plasma polymerized hydrophilic or hydrophobic effect remains rather stable over time. Weathering tests have

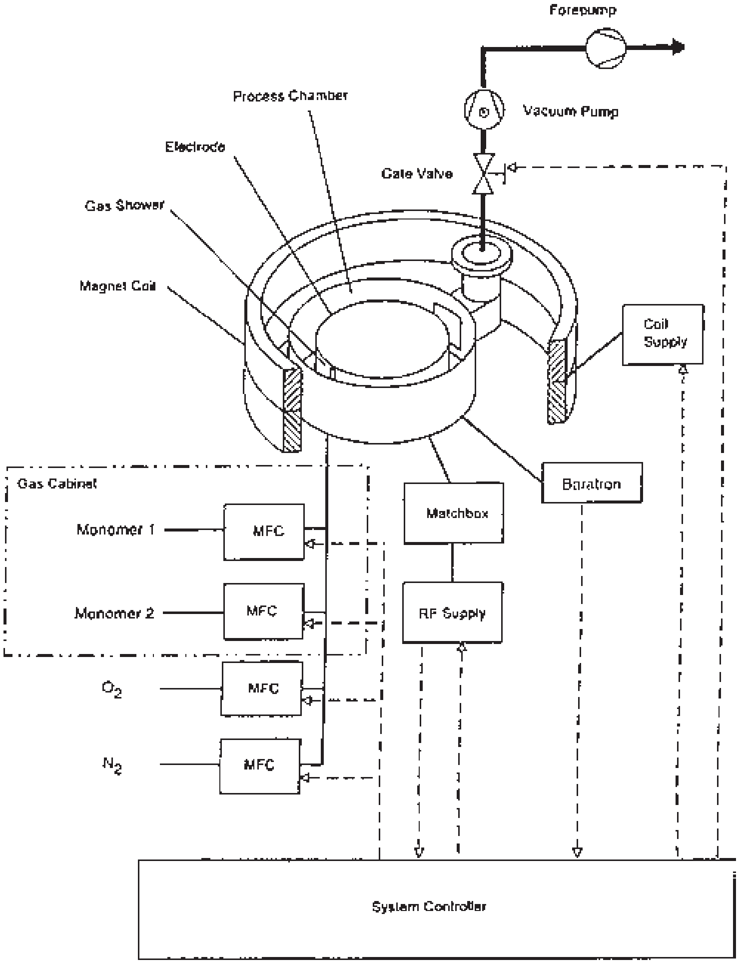

Figure 2.
Conceptual setup and main components of the PPV plasma polymerization system for hard coating of ophthalmic lenses.

Table II
Test Methods for Ophthalmic Lenses

| | |
|---|---|
| Coating/substrate adhesion: | Tape test according to MIL-C-675 B/C<br>Salt water boiling test according to DIN 58 196 |
| Scratch resistance: | Abrasion test according to MIL C-675, DIN 196-4, ISO 9211 |
| | Various testing methods developed with customers are also used. These are similar to the erasing rubber test, but use different abrasive agents (grinding, polishing pads, dry or wet)<br>As non-standardized methods drum and steel wool tests are conducted. |
| Chemical resistance: | 4% NaOH, 10 min, 50° |

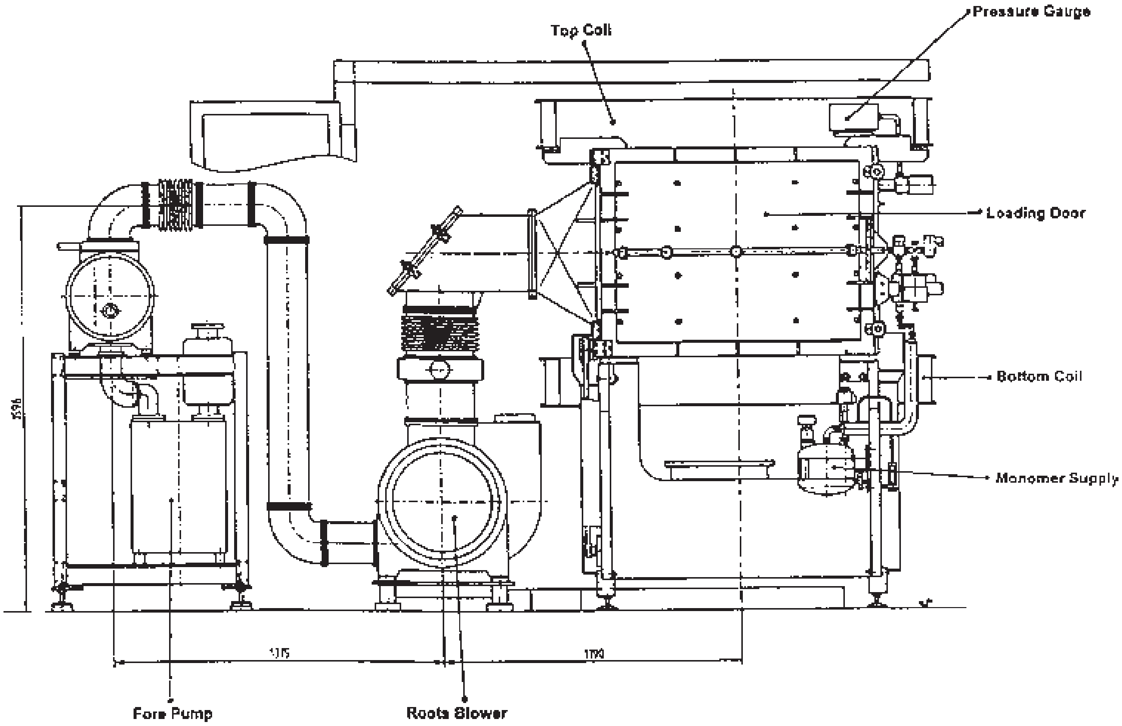

Figure 3.
Front view of the large scale PPV 1000 production system for up to 250 plastic lenses per batch.

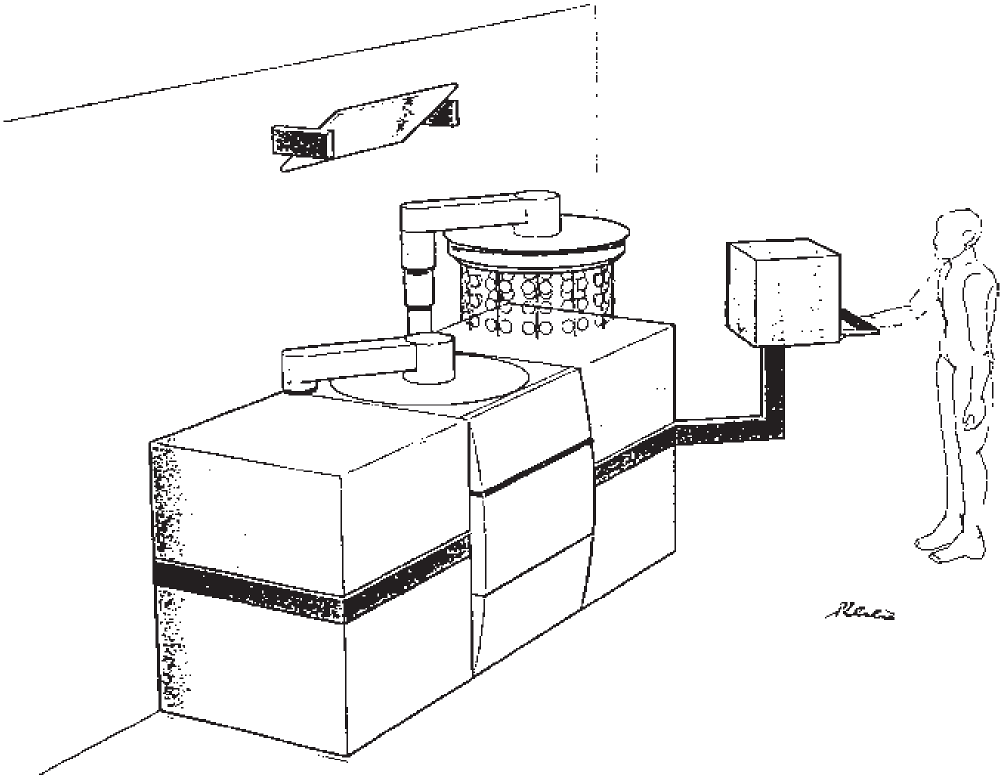

Figure 4.
The second-generation PPV 500 plasma polymerization system enables interference-free plasma hard coating of high index material up to $n_D$ 1.7.

shown excellent wetability of hydophylized substrates even after several months [4]. The adjustable diffusion characteristics also allow the process to be used for coating of contact lenses where excellent $O_2$ diffusion and wetability are required. Plasma polymerization is also suited for barrier layers against $O_2$ and corrosive compounds or ions (protection of inorganic coatings, metal mirrors, etc.). In the thioacetamide test, an excellent corrosion resistance on different metals was achieved.

A particular challenge is the deposition of interference layers. Different refractive indices must be deposited in a nanometer thickness range and a distribution accuracy of less than 1%. Despite the demanding requirements, the first functional coatings have recently been produced in our lab as well as in several other places (e.g. [5,6]). As a conclusion, the plasma polymerization process can be used for depositing a variety of coatings on plastic substrates. This is achieved through adaptation of the deposit to the basic material and subsequent continuous film modification.

## REFERENCES

[1] Yasuda, H.;
Plasmapolymerization, 1985, Academic Press Inc, ISBN-12-768760-2

[2] Howling, A. A., Sansonnens, L., Dorier, J-L., Hollenstein, Ch.;
J. Phys. D: Appl. Phys. 26 (1993), 1003-1006]

[3] Selwyn G.S., Heidenreich, J.E., Haller, K.L.; J. Vac. Sci. Technol. A9, 2817 (1991)

[4] Telgenbüscher, K., Leiber, J.;
Schlussbericht BMFT-Forschungsvorhaben Plasmapolymerisation, Förderkennzeichen 13 N 5616, 19.April 1993

[5] Segner, J.; VDI Handbuch Plasmapolymerisation, VDI Seminar Bad Soden 12.-13.Nov.1993

[6] Rostaing, J.C., Coeuret, F. et al.; Th.Solid Films, 236 (1993) 58-62

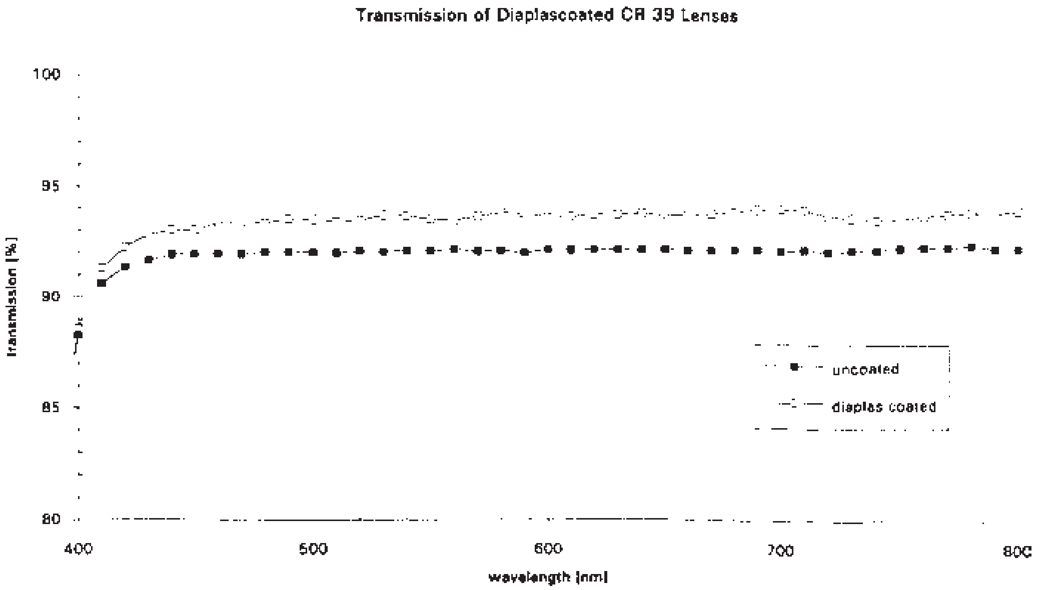

Figure 5.
Transmission of a CR39 lens, before (——) and after (- - - -) applying a plasma $n_D$ 1.5 hard coating The excellent optical quality of the film is shown. The transmission of the coated lens is about 2% higher than the uncoated lens. The modulation of transmitted light is negligible.

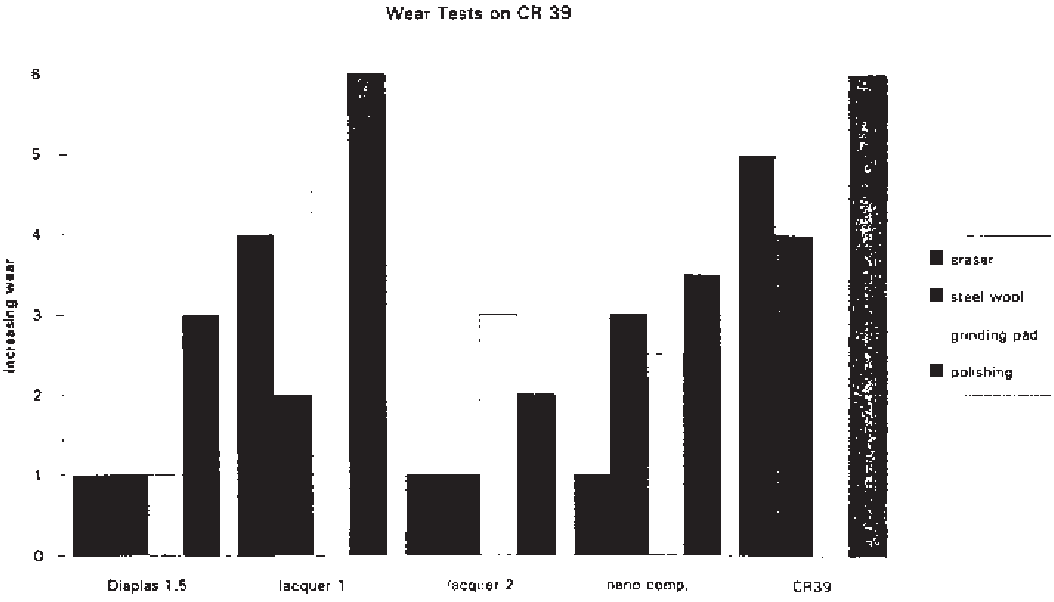

Figure 6.
Comparison of the abrasive resistance of uncoated, wet coated and plasma coated lenses. The laquered samples include a sol gel coated lens, representing the recent state-of-the-art dipping process. Each lens was tested with 4 different abrasion procedures. Rubber eraser testing was executed according to DIN 58196-4, ISO 9211-4 and MIL 657. Grind and polish tests were done on the same equipment with a grinding and polishing pad, applying a liquid abrasive for the latter. Steel wool testing was done manually.

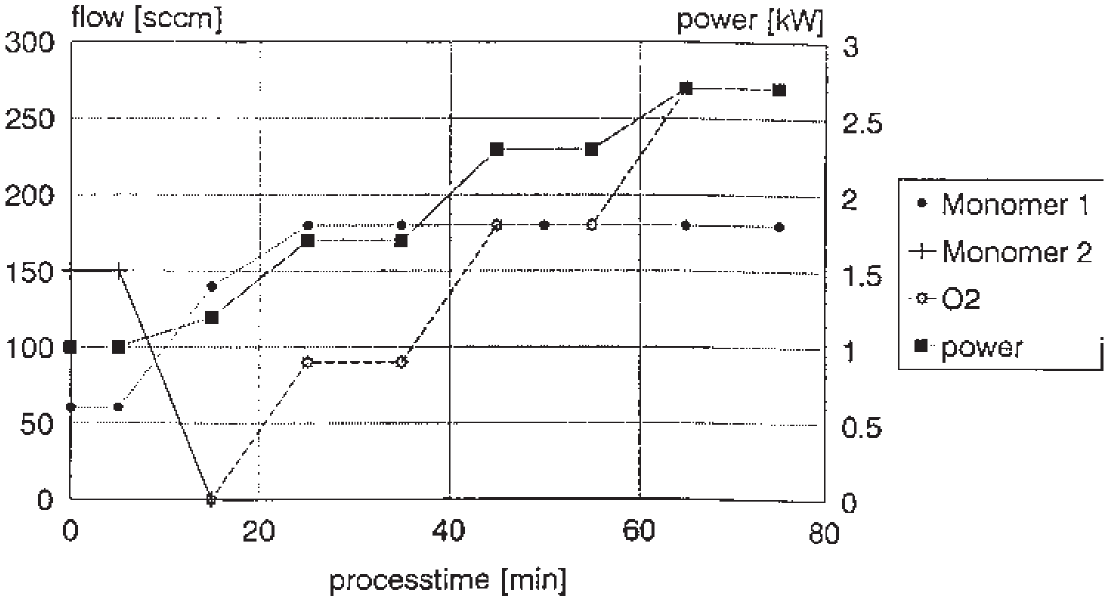

Figure 7.
Time dependence of some important process parameters during a plasma polymerization process.

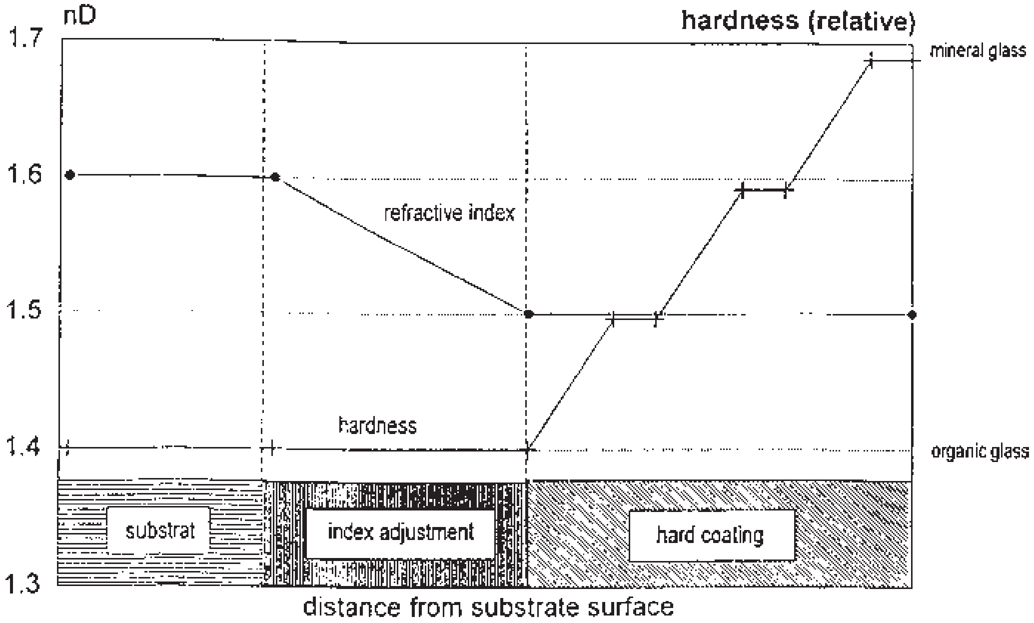

Figure 8.
Diagram illustrating the progression of layer hardness and refractive index
for a plasma polymerized coating deposited according to figure 7.