

The effects of the film manufacturing techniques, of the exposure procedures and of the development and post-treatment thermo-chemical processes on the holographic properties of HOEs in DCG

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ABSTRACT

The subject matter of this presentation is to review the results of a research program whose objective is the development of a technology for the serial manufacturing of high efficiency HOE (Holographic Optical Elements) with predetermined spectral characteristics and angular selectivity with apertures ranging from few square millimeters to square meters. The developed technology includes the machine fabrication of precision holographic films (2 to 50 micron thickness) on glass or plastic substrata and chemically and thermally adapted hologram development processes. The desired optical properties of the holographic material for a specific technical application are preset during the making of the film and are modified during the exposure and the development of the HOE.

Keywords: Optical Materials, Holography, HOE, Holographic Film Fabrication

1. INTRODUCTION

The objective of this research program was the development of the technology for the industrial manufacturing of high efficiency holographic optical elements with predetermined spectral characteristics and angular selectivity with apertures ranging from under square millimeter to square meters. This technology is used to make symmetric and asymmetric transmission and reflection gratings that are used in a various technical applications, such as: hybrid holographic concentrators for photo-voltaic and thermal energy conversion, collectors for solar photo-chemistry, holographic beam forming optics for LED applications, optical interconnects in multi-chip modules and robotic sensors for precision measurements of distance, angle and force. This diversity of products requires either a variety of materials or one or two materials whose properties could be altered to fit the diverse requirements. In the beginning of this work we looked at miscellaneous polymeric materials used in holography and photography and opted for a single material—dichromated gelatin (DCG)—and proceeded with the development of a technology to modify its properties to match the HOE manufacturing requirements. However, the photochemistry of the DCG is such that the material is sensitive only for blue-green light. This complicates the fabrication of HOE designed to operate in other parts of the spectrum. Subjecting the material to composition modification circumvents this problem.

2. SUMMARY OF THE PROPETIES OF DCG

The diffraction efficiency of a hologram is a non-linear function of the grating strength, i.e., of the layer thickness, of the wavelength and of the refractive index modulation. The phase of the transmitted or of the reflected light depends upon the spatial distribution of these parameters across the aperture of the HOE. The desired values and distributions of these parameters are achieved by precisely controlling the manufacturing processes during the coating and the drying of the holographic film and throughout the exposure and the development of the hologram. The operational characteristics of the hologram, such as the central wavelength and bandwidth may also be modified and adjusted in a subsequent thermo-chemical treatment of the HOE. The product is then a holographic film displaying large capacity for index of refraction variation that facilitates the realization of holograms with very high diffraction efficiency. In this paper we discuss the effects of the physical and chemical properties of the DCG-material and of the film fabrication techniques that contribute to the optimum performance of the films as holographic recording medium. The research efforts reported here are aimed at the development and evaluation of DCG-based holographic films and at the industrial techniques for their fabrication. The emphasis is placed on the realization of DCG films that show low scattering losses, controlled thickness profile and

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high modulation capacity. Such properties ensure the attainment of the desired diffraction efficiency, bandwidth and Bragg-shift. The basic properties of the holographic film are determined by the characteristics of the gelatin matrix. A. G. Ward and A. Courts¹ and T. H. James² discuss the role of the gelatin matrix in the photographic process extensively.

2.1. Film properties as a function of the gelatin type and gelatin concentration

The gelatin structure is characterized as a 3-dimensional network comprising cross-linked organic molecules of various sizes that possesses a high degree of thermal reversibility. The physical and chemical properties are uniquely defined by the composition and by the manufacturing procedures, e.g., mechanical strength (Bloom-strength), viscosity, pH-value (types A and B), electrical conductivity, moisture content, isoelectric point, optical transmission, glass transition, melting point, and decomposition temperature. Some parameters, e.g., the viscosity and the pH-value do not differ very much as a function of the Bloom-strength. Aqueous gelatin solutions with less than 15 % solute and at temperatures above 40 °C are considered to be Newtonian fluids. The Bloom-strength (hardness) of photographic gelatins varies between 30 and 300. Gelatins with higher Bloom-strength contain larger number of long-chain molecules that form helical structures. The hardness is a function of the temperature because the helical chains decompose at temperatures higher than 45 °C. Gehrman³ shows a 10 % reduction of the gel strength after 4 hours at 60 °C and an additional decrease of 10 % after another hour at 80 °C. The physical and chemical properties are obtained by means of thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and circular dichroism spectroscopy to measure the specific ellipticity of the DCG-film.

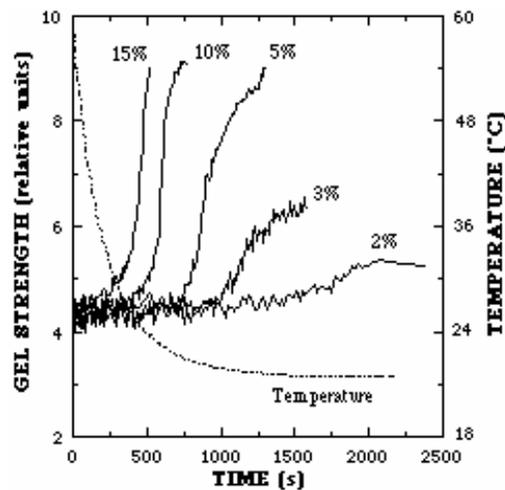
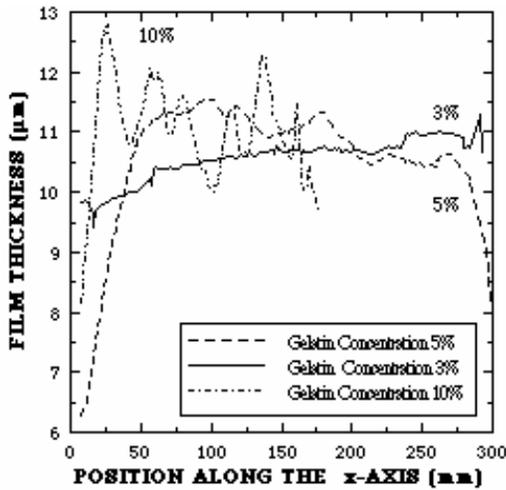


Figure 1: Film quality as function of gelatin concentration. Figure 2: Gel formation as function of concentration.

Figures 1 and 2 show the function of the gelatin concentration in the fabrication of photographic films. The latter defines the fluidity of the film during deposition and establishes the level of film thickness fluctuations. It is evident from Figure 1 that smooth film should be deposited from solutions with low gelatin concentration. However, such a film exhibits high fluidity and requires very long drying time. The gel formation time (Figure 2) and the shrinking of the freshly deposited film during drying are as well dependant on the gelatin concentration. A film with 3 % concentration shrinks by a factor of 47, whereas a 10 % film shrinks by factor of 19. The 3 % film also shows 2.5 times lower thickness fluctuations. Thin, smooth films are made from low concentration solutions, while thick films display higher film-thickness fluctuations due to the higher viscosity of the gelatin solution. The gel forming kinetics is a function of the gelatin concentration, of the temperature of the coated layer and of the temperature of the substratum. The gelatinization temperature and the rate of gelatinization are presented in Table 1 as function of gelatin concentration.

Gelatin concentration	15 %	10 %	5 %	3 %	2 %
Gelatinization temperature	33 °C	27 °C	23 °C	21 °C	18 °C
Time rate of gelatinization	0.03	0.02	0.016	0.004	0.001

Table 1: Gelatinization data for pure gelatin solutions (no wetting agent, ammonium dichromate or hardener added).

Important supplementary factors controlling the coating procedure are the temperatures of the coating solution and of the glass or plastic film substrata. These parameters are monitored and process controlled during the automated film coating. The temperature of the gelatin film during cooling is a function exponentially decaying in time for solution temperatures in the range 40 °C to 80 °C and substrata temperature range from 14 °C to 28 °C. The film changes outside these ranges substantially (rapid gelatinization, crystallization and material degradation). The melting point of gelatin films of varied Bloom-strength as function of the water content is depicted in Figure 3. The TGA analysis indicates that the rest water in the freshly deposited and dried gelatin layer is about 10 to 15 %. The viscosity of the gelatin emulsion is a function of the temperature and concentration. At low temperatures the solution turns into jellylike, non-Newtonian fluid. The melting point temperature and the dynamic viscosity are presented in Figures 3 and 4. The melting point is the temperature at which, a sample prepared of 10 % gelatin solution and held for 2 hours at 10 °C in a capillary, begins to flow.

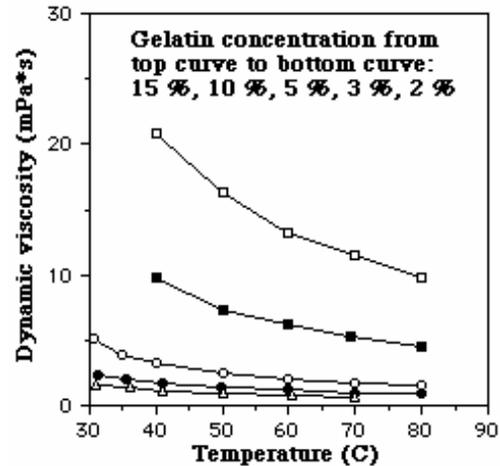
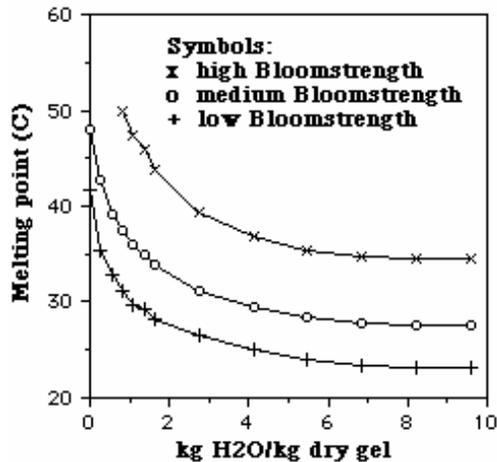


Figure 3: The melting point as function of the water content. Figure 4: Gelatin viscosity as function of the temperature.

The aqueous gelatin solution exhibits amphoteric properties due to the simultaneous presence of carboxylic and amino groups. This influences strongly the viscosity, the swelling and the strength and the melting point of the material.^{4,5} The pH-value influence on the swelling of the gelatin is shown in Figure 5. The adsorption isotherm for gelatin is depicted in Figure 6. The gelatin is hygroscopic by nature and forms water and OH complexes, thus retaining water as function of temperature. When subjected to higher temperatures, the gelatin releases first the bulk water retained by the matrix. The brake-up of the water complexes takes place at higher temperatures. The DSC measurements show the loss of volume water at 93.81 °C and the aqueous complex decomposition at 223.48 °C. The experimental data shows further a dependence on the type and brand of gelatin used for the fabrication of the layer and on the selected drying conditions.⁶

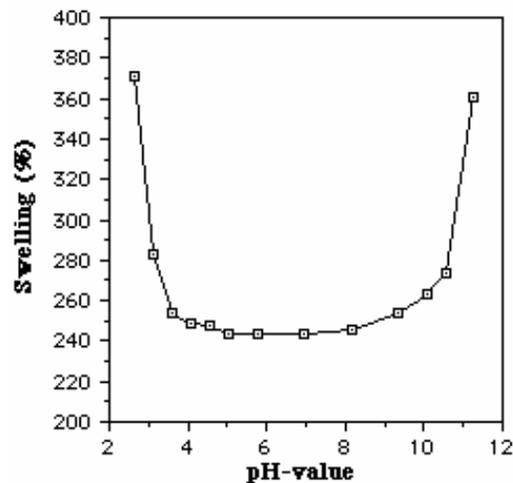


Figure 5: The swelling of gelatin as function of the pH-value.

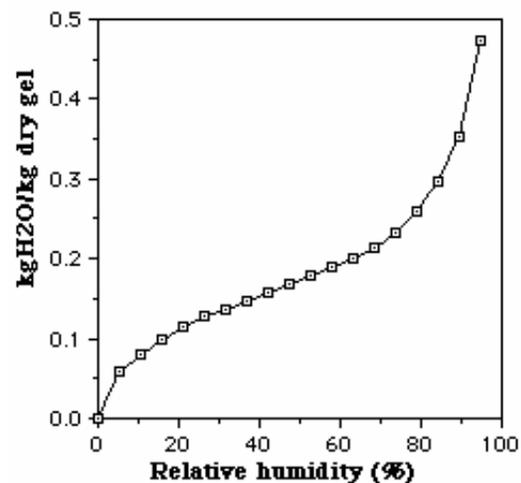


Figure 6: The adsorption isotherm of gelatin.

The DSC measurements are presented in Figure 7. The TGA curve of Figure 8 indicates that the loss of substance for temperatures up to 150 °C is due to water loss. The protein molecules begin to break up at temperatures above 250 °C.

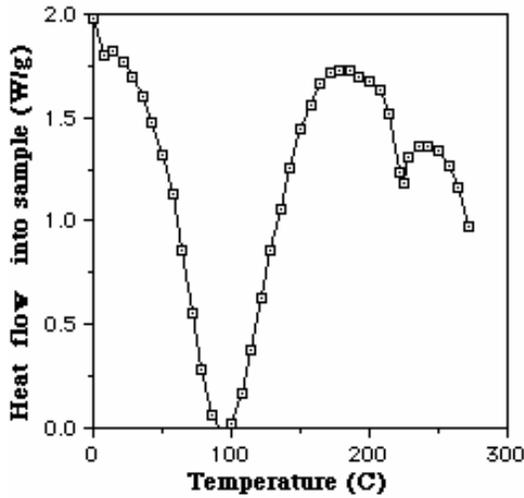


Figure 7: DSC showing water loss at 93.81 and 223.48 °C.

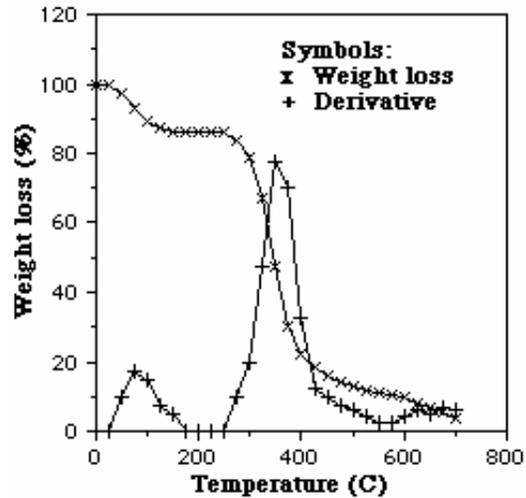


Figure 8: Temperature dependent weight loss of gelatin.

The mechanical properties of the gelatin depend strongly on the moisture content of the gelatin matrix absorbed from the environment. The Figures 9 and 10 illustrate the rupture stress and the creep elongation of gelatin film samples that were dried from the gel state at 20 °C and from the sol state at 60 °C as function of the environmental relative humidity. The rupture stress curves for both drying temperatures converge to a low value at high relative humidity. The elongation shows increases for both types for relative humidity in excess of 60 %. This is due to the weakening of the bonds that bind the macromolecules together. The creep elongation is larger for the gelatin sample dried from the sol state at 60 °C.

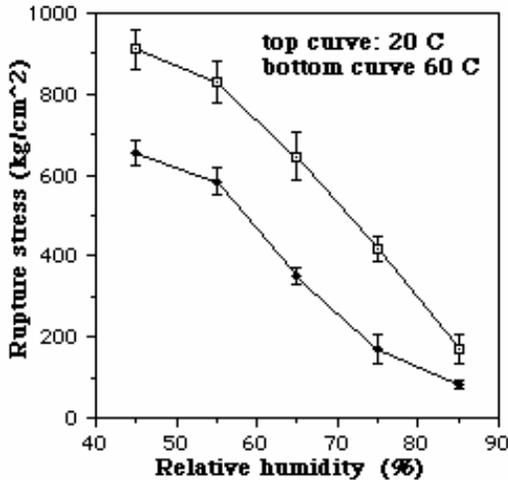


Figure 9: Rupture stress as function of T and the R.H.

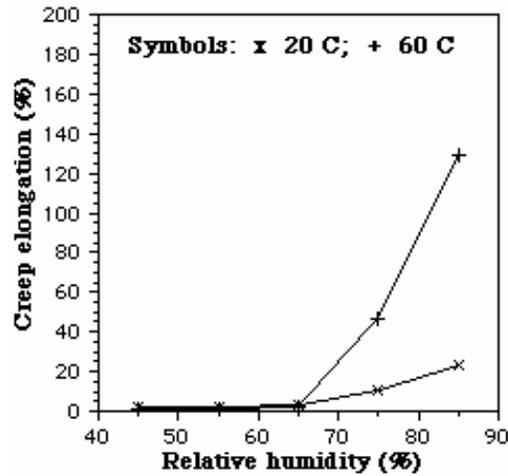


Figure 10: Creep elongation as function of T and the R.H.

The internal structure of the gelatin layer determines the holographic properties of the film. The molecular composition and the transition from one structure into another determine the sensitivity and the range of refractive index modulation. The latter is a function of the cross-linking capacity of DCG-layers. Two distinct molecular structures are present in the gelatin film—the triple helix structure and the amorphous pattern of the proteins. Our experience with DCG-films shows that this order or disorder type transition is responsible for the variation of the holographic properties. The investigation of the molecular structure was performed via CD (Circular Dichroism) spectroscopy that provides information on the spatial configuration of the macromolecules. The measurement gives information on the fraction of triple helix structures in the film and the change of these structures into amorphous polypeptides that constitute the background gelatin matrix.

The results from these measurements are presented in Figures 11 and 12. The CD spectra in Figure 11 are obtained from gelatin layers dried at four different temperatures. They exhibit a characteristic maximum at 224.5 nm that is a measure for the amount of triple helix structures. The diminution of the maximum as function of the drying temperature indicates a decrease in the amount of triple helix structures in the gelatin layer. The quantity of triple helix structures diminishes with increasing temperature, i.e., the disordered state is the preferred state at higher temperature. The fraction of triple helix structures falls off linearly with increasing temperature. Figure 12 shows the quantity of triple helix structures as a function of the thermal treatment temperature. The sample was first dried at 20 °C and subsequently heated for 3 hours in the spectrometer between measurements. The simultaneous diminishing of the maximum at 224.5 nm and the growth of the minimum at 238 nm indicates strong configurational (cis-configuration) change. The results show that the preferred orientation of the triple helix structures is in the plane of the film, i.e., the quantity of triple helix structures oriented in the film plane increases with increasing drying temperature.⁷

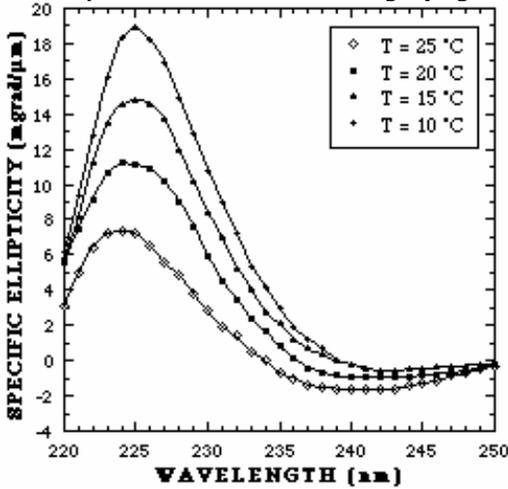


Figure 11: Spectra as a function of the drying temperature.

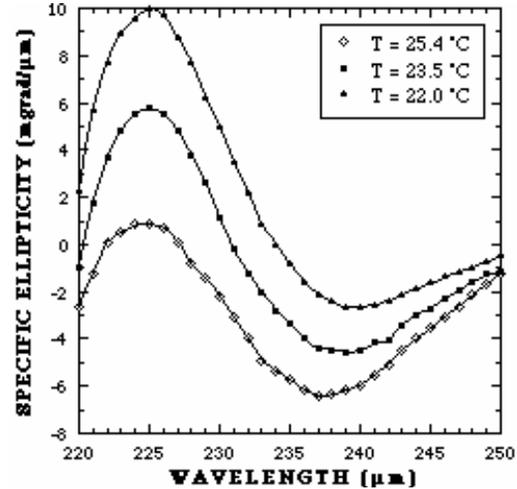


Figure 12: Spectra as a function of treatment temperature.

The forgoing discussion of the structural dependence of the film properties on the drying and heat treatment temperatures may be summarized as follows:

1. High drying temperature: the number of triple helix structures in the gelatin layer is small; an interconnected network of these structures is almost non-existent. The amorphous state is dominant. The film exhibits high sensitivity and high modulation
 2. Low drying temperature: the triple helix fraction is large (30 %) but consists mainly of small structures; the number of crystalline molecules is large. The film sensitivity is high (small helices) and the modulation capacity is low (large number of crystal-like molecules).
 3. Intermediate drying temperature: the number of the triple helix structure is intermediary but they are well developed; the sensitivity is low (the large structures are abundant) and the modulation capacity is intermediate.
- Additional information on the subject of the triple helix structures and their distribution is given in References 7 and 8.

2.2. Dependence of the film parameters on the composition of the coating solution and on the exposure energy

The gelatin type and the concentrations of the gelatin, of the ammonium dichromate and of the hardener, determine the composition of the coating solution uniquely. The solution composition defines subsequently the rate of gelatinization, the swelling and shrinking of the DCG film and its modulation capacity and photographic sensitivity.^{7,9,10} The optimum dichromate concentration is determined from a large number of tests that yield information on the maximum attainable modulation of the refractive index Δn_{max} , on the coefficient of linear expansion α (swelling coefficient) and on the photographic sensitivity κ as functions of the exposure energy and of the ammonium dichromate concentration. These coefficients are defined according to equations 1 and 2, where E is the exposure flux density ($J \cdot cm^{-2}$).

$$\Delta n(E) = \Delta n_{max} \cdot [1 - \exp(-\kappa \cdot E)] \quad (1)$$

$$d' = d \cdot (1 + \alpha) \quad (2)$$

The functional dependence of these parameters on the ammonium dichromate concentration χ is presented in the Figures 13 to 16. It is evident from these figures and the discussion in subsection 2.1 that the maximum useful concentration is in the range of 15 % to 20 %. Higher concentrations lead to tanning and hardening of the holographic film. The parameters presented in the figures below are obtained from DCG films dried under standard conditions: 20 °C drying temperature and 45 % relative humidity. These parameters could be generally changed if the film is dried under different conditions, i.e., at higher temperatures (hot films: 23 °C to 27 °C) or at lower temperatures (cold films: 10 °C to 15 °C) and/or at different relative humidity exhibit varying properties.⁷ Warm dried films exhibit higher modulation capacity and lower sensitivity, while cold dried films display high sensitivity and low modulation capacity.

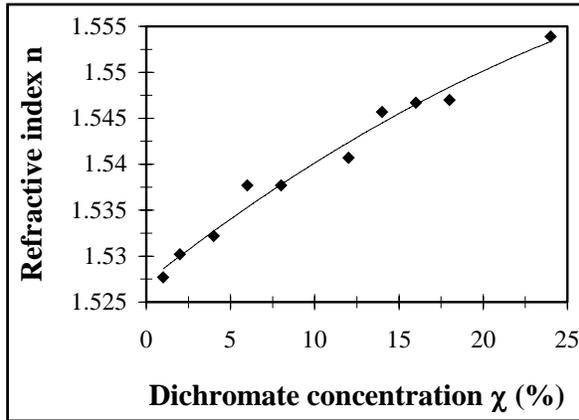


Fig. 13: The attainable refractive index in DCG films.

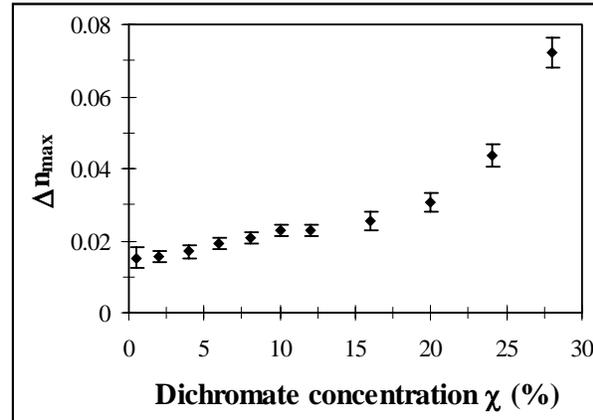


Fig. 14: Attainable refractive index variation in DCG film.

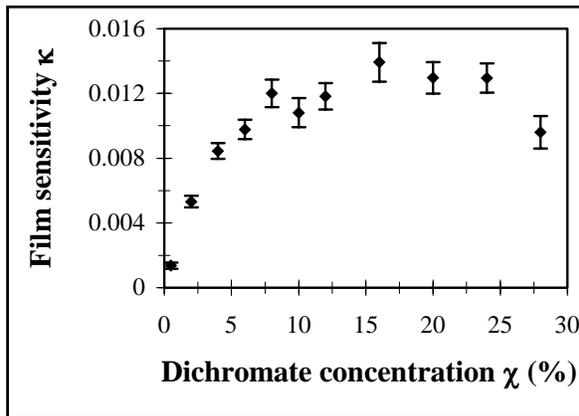


Fig. 15: Sensitivity of DCG films as f'n of concentration.

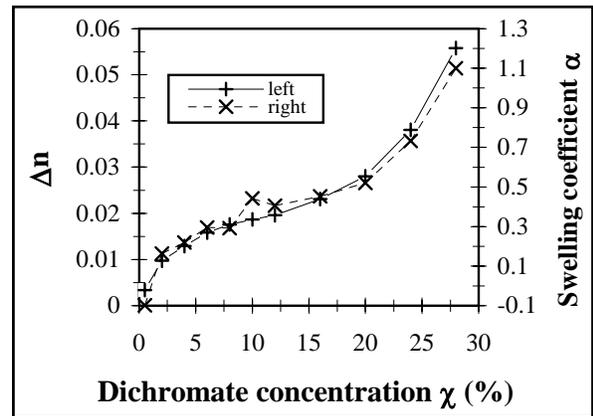


Fig. 16: Refractive index variation & swelling coefficient.

The principal conclusion from the experimental results given above is that the refractive index (Figure 13), the maximum attainable refractive index modulation (Figure 14) and swelling coefficient (Figure 16) increase with growing dichromate concentration. This may be due to the higher concentration of Cr^{6+} available for cross-linking in the gelatin matrix. The swelling increases with increasing refractive index modulation until the saturation of the refractive index modulation is reached, as this is shown in Figure 17. Subsequently, the swelling decreases monotonically, which may be explained by the additional hardening of the film.¹⁰ The intensity distribution of an interference pattern of two plane waves of equal intensity generates a refractive index variation that exhibits a cosine-profile. The latter displays marked flattening at high exposure energies that indicates high level of cross-linking causing hardening of the layer, thus causing a diminution of the swelling and large stresses in the gelatin matrix.⁹ It should be pointed out that the film parameters are also strong functions of the exposure energy that is seen from the following figures, where c denotes the dichromate concentration in Figures 18 and 19. However, high exposure energies also cause the film to rupture as this is described in Reference 11.

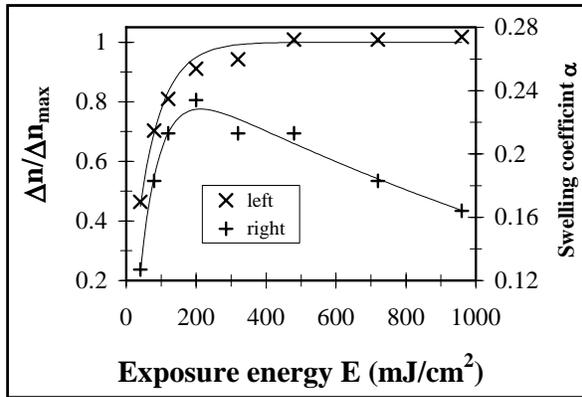


Fig. 17: $\Delta n/\Delta n_{\max}$ and α as functions of the exposure energy.

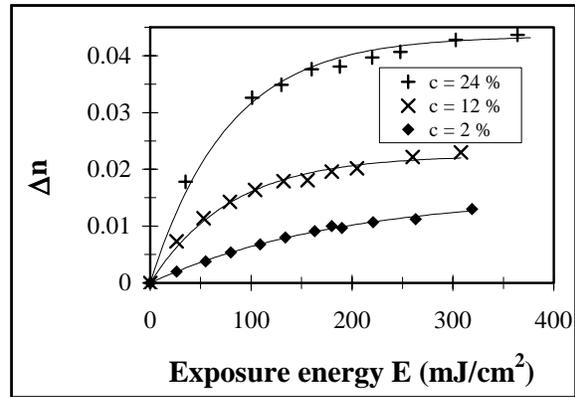


Fig. 18: Δn as f'n of the exposure energy and the concentr.

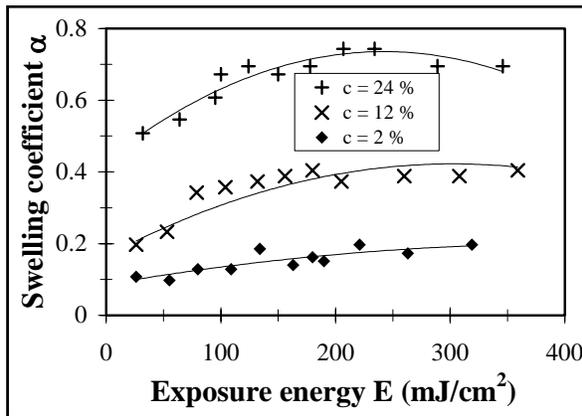


Fig. 19: Swelling as f'n of exposure energy and concentr.

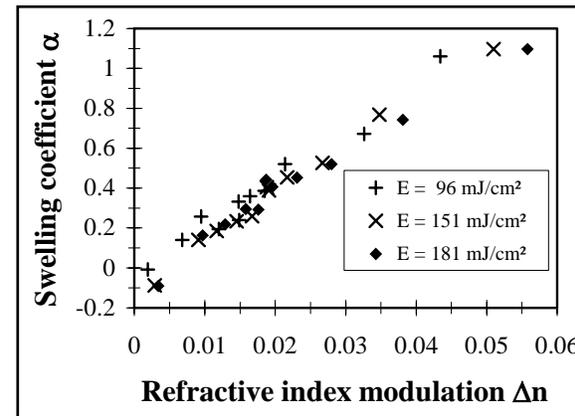


Fig. 20: Swelling as f'n of the exposure energy and of Δn .

The rupturing of the film and the emergence of voids increase the swelling of the film and the absorption of additional water in the development process. Curran and Shankoff¹² and Sharlandjiev and Markova¹³ have discussed the appearance of voids in holographic films. The air-filled voids modify the refractive index modulation and change the transmittance of the hologram. Holograms with large swelling coefficient exhibit large refractive index modulation, but display large absorption and scattering. The inner structure of the holograms is obtained from electron microscope photographs. The photographs in Figure 21 illustrate the destructive effects that take place during the fabrication of the hologram. The left photograph shows a “soft” process while the photograph on the right shows complete destruction in a “harsh” process.

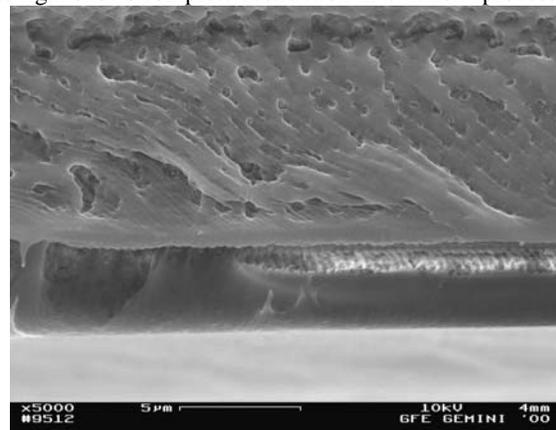
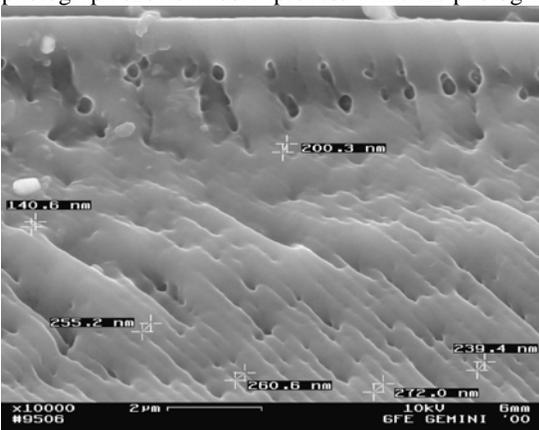


Figure 21: Electron microscope photographs of developed DCG holograms that exhibit ruptures and voids in the film.

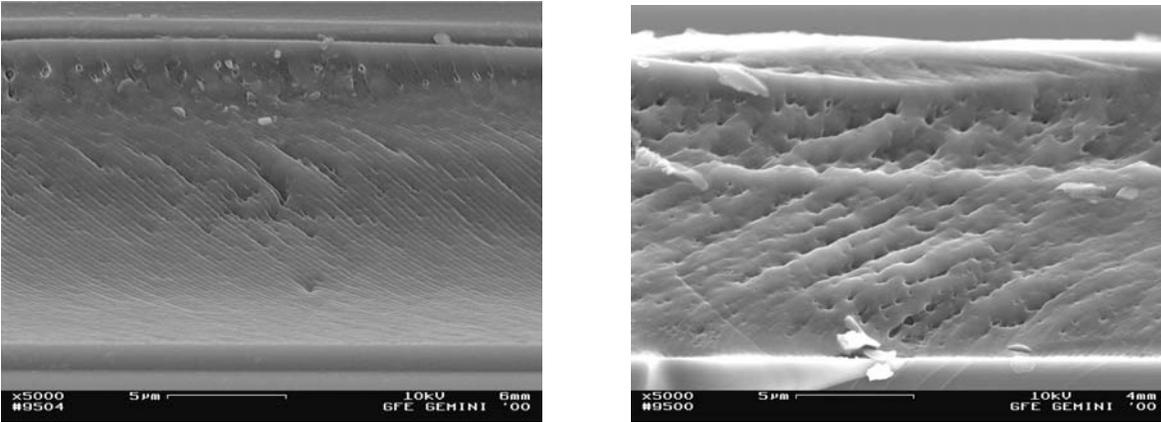


Figure 22: Electron microscope photographs illustrating the diverse structures that are obtained with different processes.

Figure 22 illustrates several effects that take place in the fabrication of the hologram. First of all, the segment of the gelatin layer adjacent to the substratum exhibits weak modulation that is due to the limited penetration of light during the exposure. Second, the lamellae are bent considerably in the proximity of the substratum and of the free-space interface, which suggests a variation of the coefficient of expansion across the DCG layer. The lamellar structure vanishes near the free-space interface and is replaced by series of nano-sized voids. Finally, one observes the appearance of grooves and pits in the lamellar structure that may be caused by the washing out of gelatin material not sufficiently cross-linked. Cracks and voids are created during the development of the hologram when the water is expelled in the isopropyl alcohol baths. The form and size of the structures depend strongly upon the temperatures of the baths. The process becomes quite violent at high temperatures and rapid dehydration rates that are needed for large red shifts and bandwidth enhancement. This leads at times to partial detachment of the gelatin layer from the substratum. However, we believe that the process could be controlled, thus permitting a made to order creation of the voids. The latter play a unique role in the shaping of the bandwidth, as Sharlandjiev and Markova showed this in a recent paper.¹³ In their paper, the simulation of the diffraction efficiency of reflection DCG holograms is based on a model that considers monodispersed ellipsoidal voids whose concentration in the gelatin matrix determines the bandwidth. The evaluation of the diffraction efficiency of the reflection holograms is then performed on the basis of light scattering from periodic ensembles of nano-voids. However, Figure 21 shows that the interspersed void phase is not periodic and comprises structures of varying forms and sizes. The erosion of some of the lamellae produces decreasing spatial frequency and causes red shift. The resulting aperiodic lamellar structure acts like a spatial frequency chirp and leads to bandwidth enlargement.

3. AUTOMATED FABRICATION OF LARGE FORMAT HOLOGRAPHIC FILMS

In this section we will discuss the film manufacturing technology that was developed at the RWTH Aachen University of Technology and further advanced at Holotec GmbH Aachen. The film manufacturing technology comprises the coating of photosensitive films on glass and flexible plastic substrata. In the hologram fabrication technology the following steps are necessary for the production of various types of HOE:

Coating: The developed technology permits the fabrication of holographic layers on glass substrata of up to 2 m², where the layer thickness can be controlled between 2 and 30 μm with a maximum deviation of ± 0.5 to ± 1 μm. The gelatin matrix is sensitized during the coating process; consequently a sensitizing step is not necessary.

Drying: The drying conditions are defined by the desired properties of the holographic layer. As discussed above, a low drying temperature (10 °C) results in films with moderate modulation capability and high sensitivity. High drying temperature (25 °C) produces films with especially high modulation capability. The standard drying temperature is 20 °C at 45% relative humidity. The layers exhibit medium modulation capacity and medium sensitivity, so that the desired modulation can easily be reached by the selection of an appropriate exposure energy density.¹⁴

Exposure: DCG layers are typically sensitive for wavelengths below 540 nm. At present an Argon-ion laser is used at the 488 nm line for the exposure. Other operating ranges are achieved by chemical and thermal after-treatment of the HOE.

Copying: Optical contact copying procedure is used for the manufacturing of large aperture holograms or when a large number of copies are desired.^{15,16}

Development: The developing process has large impact on the optical properties of holograms in DCG. Refractive index modulation and the shift of the Bragg angle have to be controlled correspondingly to the design specifications of the HOE. Scattering and absorption have to be maintained at a low level throughout the entire wavelength range of interest.^{17,18}

After-treatment: The spectral sensitivity of dichromated gelatin imposes limitations on the use of HOE in wide spectral range. This restraint may be overcome using a chemical or a thermal, or even a combination of both, processes to change the film material or the hologram to achieve the desired operating wavelength and bandwidth.



Figure 23: The programmable coating machine comprising the coating table, the control tower and the associated process equipment.

The coating machine shown in Figure 23 is designed for the serial manufacturing of holographic films on glass substrata up to a size of 0.5 m by 0.5 m. On the left is shown the control tower. The containers with the hot gelatin mixture and the hot purging water are shown on the front side of the lower shelf. The peristaltic pump is in the back of the gelatin bath (not in view). The upper shelf contains the processor, the data acquisition system and the spectrometer used to measure the film thickness. The coating table is depicted on the right side. In front is the bath circulator that is used to control the temperature of the granite slab. The disposal container for the collection of the effluent and the purging water waste is placed under the coating table. The film thickness variation at the edges extends 5 to 10 mm into the coated surface. Two 10 cm stripes, cut from the same material as the substratum that is being coated, are attached to the substratum at both ends. The onset of the nozzle flow at the beginning and at the interruption at the end of the layer deposition procedure takes place over these disposable stripes. The film profiles depicted in Figures 24 and 25 are given as examples for films manufactured with coating machines for glass substrata (Figure 24) and with endless flexible plastic film (Figure 25). The standard holographic films have a thickness from 5 μm to 20 μm .

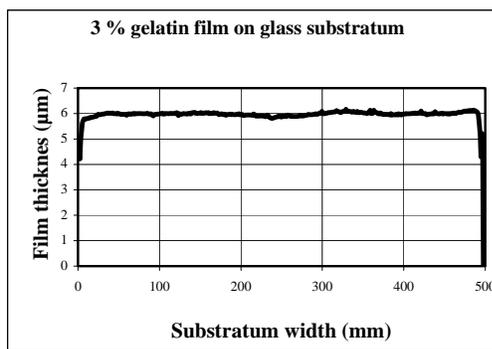


Figure 24: Film thickness profile on glass substratum.

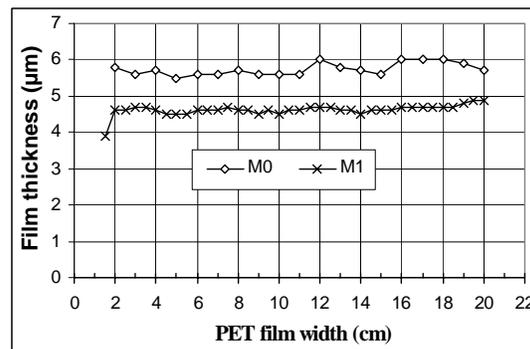


Figure 25: Film thickness profile on PET substratum.

The film in Figure 24 was fabricated on glass substratum using the following parameters:

Emulsion: $g = 3\%$ (g -concentration of gelatin in relation to weight of water), $Ag = 1\%$ (Ag -concentration of Agepon in relation to weight of water).

Emulsion temperature: $70\text{ }^{\circ}\text{C}$

Coating nozzle temperature: $65\text{ }^{\circ}\text{C}$

Granite bench temperature: $18\text{ }^{\circ}\text{C}$

The film in Figure 25 was fabricated on PET substratum using the following parameters:

Emulsion: $g = 10\%$ (g -concentration of gelatin in relation to weight of water), $DC = 20\%$ (DC -concentration of dichromat in relation to weight of gelatin, $Ag = 0.5\%$ (Ag -concentration of Agepon in relation to weight of water).

Emulsion temperature: $50\text{ }^{\circ}\text{C}$

Profile position on PET film: M0 at the start of the coating process; M1 at the end of the coating process.

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