

**SURPHEX™: New Dry Photopolymers for Replication of Surface Relief Diffractive Optics\*****Felix P. Shvartsman****N 9 4 - 1 7 3 5 8**

DU PONT COMPANY  
Imaging Systems, R&D  
SURPHEX™ Enterprise  
Experimental Station, Box 80352  
Wilmington, DE 19880-0352, USA

**ABSTRACT**

High efficiency, deep groove, surface relief Diffractive Optical Elements (DOE) with various optical functions can be recorded in a photoresist using conventional interferometric holographic and computer generated photolithographic recording techniques. While photoresist recording media are satisfactory for recording individual surface relief DOE, a reliable and precise method is needed to replicate these diffractive microstructures to maintain the high aspect ratio in each replicated DOE. The term "high aspect ratio" means that the depth of a groove is substantially greater, i.e. 2, 3 or more times greater, than the width of the groove. A new family of dry photopolymers SURPHEX™ was developed recently at Du Pont to replicate such highly efficient, deep groove DOE's. SURPHEX™ photopolymers are being utilized in Du Pont's proprietary Dry Photopolymer Embossing (DPE) technology to replicate with very high degree of precision almost any type of surface relief DOE. Surface relief microstructures with width/depth aspect ratio of 1:20 (0.1 μm / 2.0 μm) were faithfully replicated by DPE technology. Several types of plastic and glass/quartz optical substrates can be used for economical replication of DOE.

**INTRODUCTION**

Surface relief Diffractive Optical Elements (DOE) are a specialized class of embossed optical elements which are used to replace conventional optical components in laser scanning devices<sup>1</sup> such as rotating polygon mirrors, galvanometers, and other beam-deflecting devices and their associated optics, such as, for example, integrated holographic optical pickup heads for compact disc players.<sup>2</sup> Recent progress in electron-beam lithography and ion-beam etching micro-fabrication techniques<sup>3-5</sup> demonstrated feasibility of blazed relief microstructures, which improves micro-Fresnel lens focusing efficiency. The high efficiency, deep groove, original surface relief microstructures are obtained by using a photoresist as the recording medium. While photoresist recording media are satisfactory for making individual deep groove, phase DOE, a practical method is needed to replicate faithfully such DOE to maintain the high aspect ratio needed for each replicated element. The term "high aspect ratio" means that the depth of the groove is substantially greater, i.e., 2, 3 or more times greater, than the width of the groove. Although the conventional methods of replicating of embossed holograms meet many of the needs of the graphic arts industry, they have been unsatisfactory for replicating the high efficiency, deep groove DOE required for laser scanning systems and other specific applications. In the case of thermal embossing, the deep groove, high aspect ratio relief hologram is not faithfully reproduced and in the case of molded UV-curable liquid resins, a residue of UV-cured resin remains entrapped in the deep grooves of the mold.

Numerous applications of high performance surface relief DOE has been developed for military and space applications. In the commercial equipment market a new type of surface relief diffractive scanning elements for the next generation of laser printing/scanning devices and FAX machines is being developed now by several electronic companies. Embossed holograms for security printing and graphic

\* *Proceedings of EOS/SPIE International Conference - "Holographics International '92," 26-29 July 1992, Imperial College of Science, London, United Kingdom. Volume 1732, 1992, in press.*

arts recently shifted from monochromatic rainbow holograms into full color 2D/3D images and full color 3D images are under development. Practically in every mentioned above application reliable mass replication of such opto-electronic devices and production cost are the two major factors for successful introduction of this new generation of diffractive optics into the market place.

Du Pont has a long history and experience in extensive research and development, and also in production, of dry photopolymer films for various electronic and imaging applications. First practical dry photopolymer was invented at the Experimental Station of Du Pont in 1948 by Dr. Louis Plambeck. Variety of dry photopolymer films for different applications were commercialized since then, and such Du Pont's products as Dycryl®, Lydel®, Riston®, Cromalin®, and Cyrel®, are worldwide known trade marks. Recently novel Dry Photopolymer Embossing (DPE) technology was developed at Du Pont to replicate faithfully highly efficient, deep groove surface relief DOE.<sup>6</sup> To make DPE technology practical and commercially available new type of optical grade quality proprietary dry photopolymer films SURPHEX™ were specifically developed to be used in this process.

### DRY PHOTOPOLYMER EMBOSSING TECHNOLOGY

Since 1948 when first practical dry photopolymer was developed, Du Pont built a powerful technological base in films, photopolymers, and also in related coating and imaging techniques. Development of the DPE technology and SURPHEX™ photopolymers started in 1987, and in 1988 it was successfully applied to replicate different types of diffractive optical elements, including binary optical elements and new generation of deep groove surface relief diffractive scanning elements. The term of "dry photopolymer" film or layer refers to a substantially solvent-free polymeric layer having a creep viscosity between 100 and 200 Megapoises, as measured with a parallel plate rheometer. Such dry photopolymer are contrasted with conventional liquid photopolymerizable layers which typically have viscosities of about several hundred Poises or less. Amounts of ingredients in the dry photopolymerizable compositions will generally be within the following percentage ranges based on total weight of the photopolymer layer:

- polymeric binders 35 - 50%
- monomeric system 15 - 25%
- plasticizers 5 - 15%
- initiating system 1 - 5%
- other ingredients 1 - 5%

In general dry photopolymeric compositions contain an unsaturated monomeric system, a free radical-generating initiating system, and polymeric binders. Other components, which provide new dry photopolymer films SURPHEX™ with specific and unique functional capabilities needed in the DPE technology, can be present in the photopolymerizable compositions in varying amounts. Such components include: plasticizers, antioxidants, optical brighteners, ultraviolet radiation absorbing materials, thermal stabilizers, hydrogen donors and release agents.

The photosensitivity of the photopolymerizable composition is enhanced by a photoinitiating system which may contain a component which sensitizes the composition to practical radiation sources, e.g., visible light. Conventionally a binder is the most significant component of a substantially dry photopolymerizable film or layer in terms of what physical properties the film or laminate will have while being used in the DPE process. The binder serves as a containing medium for the monomer and photoinitiator prior to exposure, and after exposure contributes to the optical and other physical characteristics needed for the optical element. Cohesion, adhesion, flexibility, miscibility, tensile strength, and index of refraction are some of the many properties which determine if a binder is suitable for use in a diffractive optical element.

Several types of optical grade quality dry photopolymer films SURPHEX™ having uniform thickness across the film are being produced in the brand new state-of-the-art commercial clean room facility recently built at one of the Du Pont plants. Descriptions of SURPHEX™ photopolymers and some of potential applications are given in **Table 1**:

**Table 1.** SURPHEX™ products and potential applications

<b>PRODUCT</b>	<b>DESCRIPTION</b>	<b>APPLICATION</b>
SURPHEX™ - P	Family of UV curable photopolymer films for DPE on <b>Plastic</b> and <b>Glass</b> substrates	Diffraction optical components, diffraction scanning elements, diffusion screens for projection and active matrix TV displays
SURPHEX™ - G		
SURPHEX™ - H	Family of UV curable photopolymer films for continuous DPE of embossed <b>Holograms</b>	Security printing applications: credit cards, driver licenses, bonds and currency; sales advertisements, gift packaging

Productional thickness of the SURPHEX™ films can be adjusted and optimized in the range of **2-50 μm** to achieve the best replication quality of the high width/depth aspect ratio recorded in the original DOE. Refractive index of the cured, free standing SURPHEX™ films is **1.50±0.01**. Uncured photopolymer layer is a self-adhesive film which bonds firmly to the substrate surface by a simple lamination process without additional adhesive layer or primer. SURPHEX™ films have optical characteristics comparable to those of the substrates and match sufficiently the refractive index of the substrate materials. The photopolymer layer is a thermoplastic composition which upon exposure to actinic radiation, forms a blend of compatible and miscible polymers of higher molecular weight by crosslinking and/or by polymerization. This changes the rheological character of the composition and decreases its solubility in common solvents. Shelf life of the unprocessed SURPHEX™ films is **>2 years**. Precisely controlled physical and chemical properties of the developed photopolymeric formulations allow to produce high quality DOE, which in most cases can not be achieved by utilizing conventional replication technologies and materials.

In the dry photopolymer film manufacturing process specially pre-filtered (0.2 μm filtration station) solution of the SURPHEX™ photopolymer, is being machine web-coated onto the temporary support polyethylene terephthalate film. The primary criteria for the support film is that it possess dimensional stability and the surface smoothness and release characteristics needed to laminate a uniform dry photopolymer layer to the substrate surface without distortion of the layer when the support film is removed. To meet this criteria the cohesive force of the photopolymer layer and its adhesive force to the substrate must be greater than its adhesive force to the temporary support film. A second temporary cover sheet or interleaf may be placed on the second surface of the photopolymerizable layer to protect it from contaminants during storage in roll or stacked cut sheet form and to prevent blocking of the stored element. If used, the protective cover sheet or interleaf is removed from the surface of the photopolymerizable layer before the layer is laminated to the substrate. Different polymer films can be used as the cover film provided the film has a suitable surface smoothness and has less adhesion to the photopolymerizable layer than the layer has to the support film. Suitable protective cover sheets or interleafs include polyethylene, polypropylene, etc.

In the laminating step the protective cover sheet or interleaf, if present, is first removed from the photopolymer layer and the layer is applied to the surface of the substrate under pressure and typically with heat so that interfacial air is removed and void free adhesion between the substrate and the layer is

achieved. Preferably a hot roll laminator is used to achieve such void free adhesion. The embossable photopolymer layer can be laminated to the surface of the substrate in a form of a dry film using any conventional laminating system. Particularly useful are commercial hot roll laminators, e.g., Du Pont Cromalin® Laminator and Du Pont Riston® Hot Roll Laminator. To support the substrate during lamination, it is placed on a temporary carrier sheet of commercial color proofing receptor, e.g., Cromalin® MasterProof Commercial Receptor. The SURPHEX™ film is laminated to the substrate using hot roll laminator operating at a roll surface temperature of 115-124°C. Lamination covers the substrate surface uniformly and seals it around the edges to the carrier sheet. Subsequently laminated substrate is cut out from the temporary carrier sheet with a razor blade.

Typical example of the DPE process is shown schematically in Figure 1. All processing steps are being performed in ambient conditions under yellow light. Surface relief microstructure is transferred to the laminated substrate by embossing the dry photopolymer layer with a stamper carrying a surface relief corresponding to the diffractive optical element.

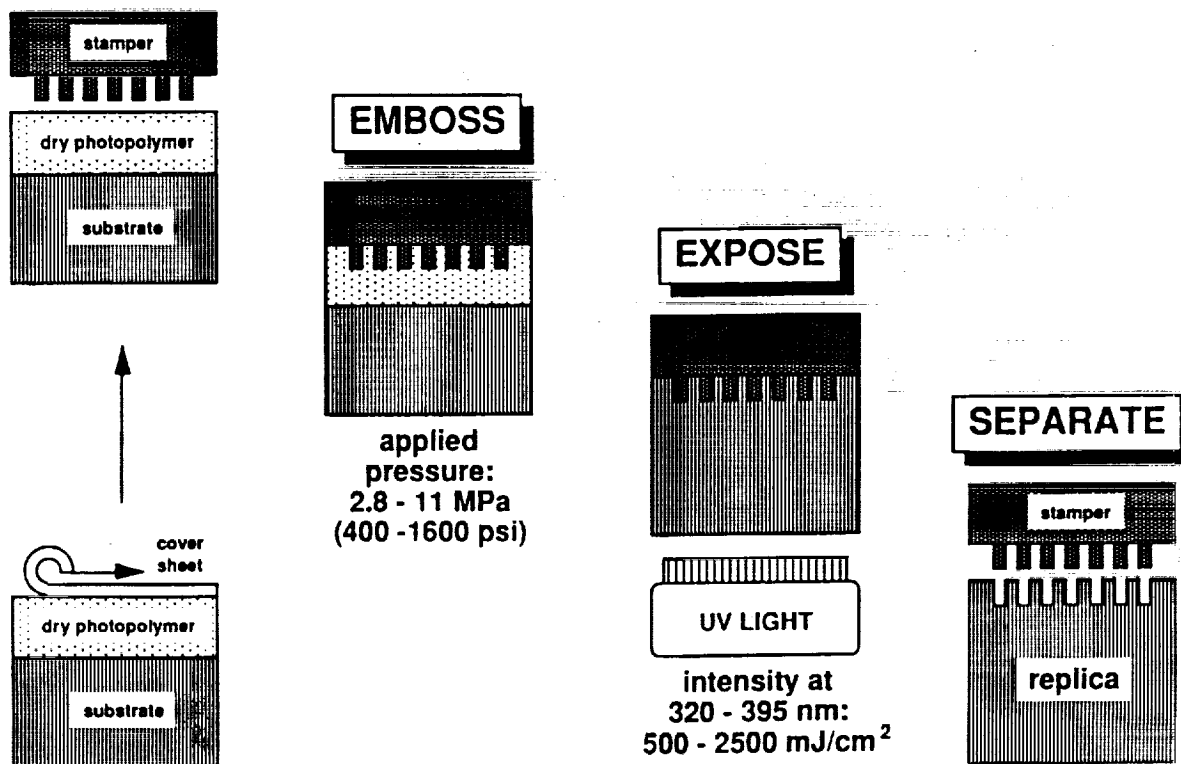


Figure 1. Dry Photopolymer Embossing concept

In the first step of the DPE process the cover sheet is removed from the laminated substrate. The stamper is then laminated to the substrate using a photographic roller or other pressure rolls laminating equipment. The tackiness of the photopolymer layer holds the stamper in place and such sandwich is then placed between two flat plastic (polycarbonate or polymethyl methacrylate) shims to protect the sandwich from the press platens. The sandwich is loaded at room temperature into a 30 ton capacity hydraulic platen press equipped with a manual lever action. The load is quickly increased to a pressure of 2.8 - 11 MPa (400 - 1600 psi). Pressure applied to the sandwich should be optimized depending on the width/depth aspect ratio of the grooves recorded in the stamper. The load is released after 5 - 15 seconds dwell time and the shimmed sandwich is removed from the press. The shims are then removed from the

sandwich. The embossed information layer is then firmly bonded to the substrate and the embossing made permanent by ultraviolet radiation exposure. The stamper/substrate sandwich is placed, with the transparent substrate facing the light source, into a high intensity ultraviolet exposure unit, and after a 5 - 15 second exposure with a UV light intensity at 320 - 395 nm of 500 - 2500 mJ/cm<sup>2</sup>, the stamper is removed by flexing the sandwich assembly slightly.

### PROPERTIES OF THE DRY PHOTOPOLYMER FILM SURPHEX™

The term of "dry photopolymer" film or layer refers to a substantially solvent-free polymeric layer having a creep viscosity between 100 and 200 Megapoises, as measured with a parallel plate rheometer. Such dry photopolymer are contrasted with conventional liquid photopolymer layers which typically have viscosities of about several hundred Poises or less. Viscosity is measured as creep viscosity with a parallel plate rheometer using a Du Pont Model 1090 Thermal Mechanical Analyzer. In this procedure, a 0.915 mm thick sample is placed in contact between two flat discs (about 6 mm in diameter). A quartz probe which is capable of accepting additional weights is positioned atop the upper disc and the same/disc assembly is maintained at constant temperature of 40°C and RH of 44% throughout the measurement. Creep viscosity is calculated from the rate of decrease of sample thickness under equilibrated conditions. The 0.915 mm sample is prepared by laminating together sufficient layers of the test film to obtain the desired thickness. The laminate is then cut to provide a circular sample slightly larger in diameter than that of the rheometer plates.

As shown in Figure 2, a free standing, 25 µm thick cured SURPHEX™ film has 98 - 99% of transmittance in the long UV, Visible, and up to 2000 nm in the near IR region of the spectrum.

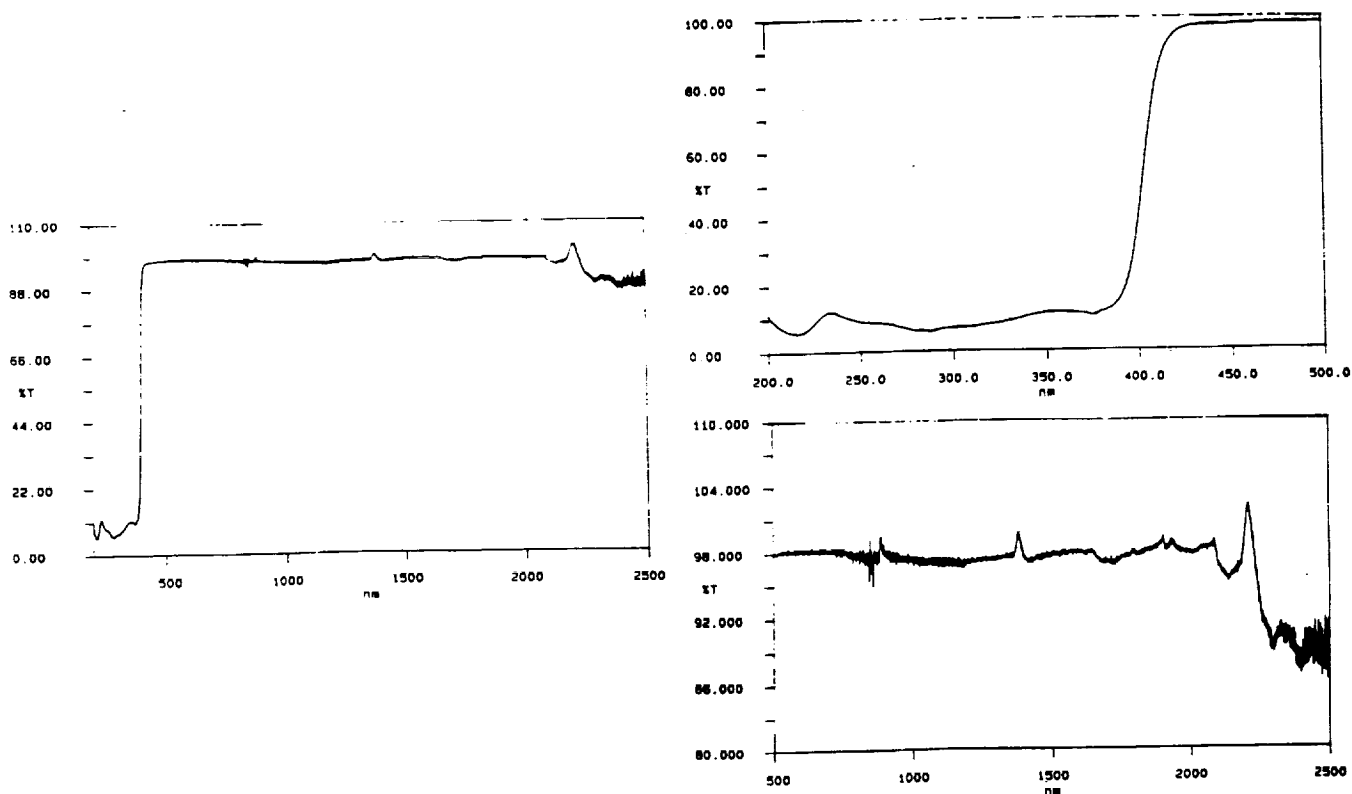


Figure 2. SURPHEX™, 25 µm cured film: UV, Visible and near IR transmittance spectra

In the IR region of the spectrum, shown in Figure 3, between 2500 - 5000 nm transmittance of the SURPHEX™ films decreases to ~80%, comparing to the previously reported<sup>7</sup> results of ~ 50%, when a prototype of a dry photopolymer film OPTIMER\*-89 was tested in DPE technology. At the longer wavelengths transmittance of the SURPHEX™ films drops to 40 - 60%, reaching only ~30% at 10.6 μm wavelength used for CO<sub>2</sub> laser applications.

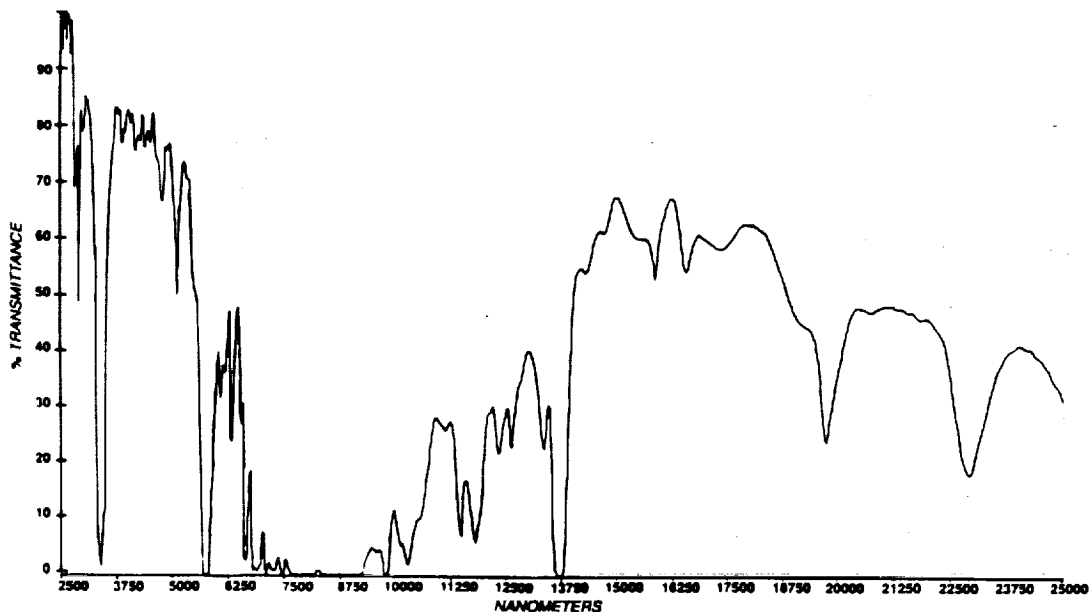


Figure 3. SURPHEX™, 25 μm cured film: IR transmittance spectrum

Differential scanning calorimetry revealed good thermal stability of the SURPHEX™ films. As one can see in Figure 4, SURPHEX™ film has one minor  $\gamma$ -transition at +26.18°C, which is related apparently to some relaxations in the polymer bulk of one of the binders. Glass transition temperature  $T_g$  was not detected by DSC since cured SURPHEX™ films represent highly miscible blends of several chemically compatible polymers. Between -40°C and +105°C cured SURPHEX™ film is thermally stable. Above +110°C DSC film sample begins to soften and at +145°C it becomes slightly brownish, which can be attributed to the decomposition of the film at +153.57°C.

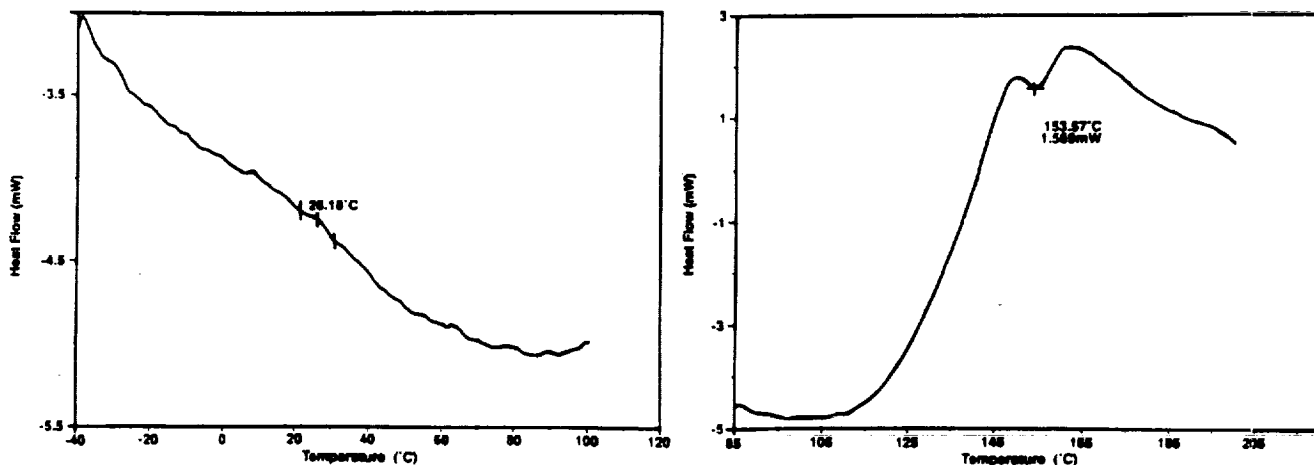


Figure 4. SURPHEX™, cured film: differential scanning calorimetry curve

## PERFORMANCE OF SURPHEX™ REPLICAS

Several qualification tests have been performed on the SURPHEX™ replicas made by DPE technology. Results from these accelerated life tests are summarized in **Table 2**. Dimensional stability test was performed during spinning test in which DPE replica was optically aligned on a high-speed motor by viewing cross-scan dot placement (200 times magnified) on a TV monitor. The replica was spun at **10.000 rpm** in enclosed box at constant temperature of **35°C** for **200 hours** and following data was measured at **24-hour** intervals while keeping laser current and diode laser temperature constant:

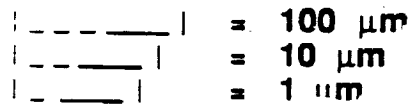
- physical changes to the DPE replica at visual inspection
- dot size (micrometers) in three meridians -
  - 1 - zero degrees or cross-scan
  - 2 - forty-five degrees (clockwise)
  - 3 - ninety degrees or in-scan
- diffraction efficiency
- dot movement

A number of environmental tests were run on open and sealed surface relief micro structures of the SURPHEX™ replicas and main results from these tests are shown in **Table 2**. As a general comment to the presented performance parameters data it can be said, that DPE technology produces replicas which have optical performance comparable to performance of the original Master-DOE, and environmental properties similar or better than other known polymeric materials used in conventional DOE replication processes.

**Table 2.** Accelerated life tests of SURPHEX™ replicas

• dimensional stability (SURPHEX™-P)	no visual physical changes and no losses in optical performance after 200 hours of a spinning test at 10.000 rpm and 35°C
• UV exposure stability (SURPHEX™-P)	no physical or spectral changes after >1 year of the accelerated sun test in the exposure unit SUNTEST CPS
• high power resistance, qualitative test (SURPHEX™-G)	replicas made on quartz substrate sustained diffraction limited focal spot sizes under illumination 5x5 mm laser beam with 10 W CO <sub>2</sub> laser with power density of ~ 200 W/cm <sup>2</sup>
• environmental stability	
- open gratings (SURPHEX™-P)	no physical or spectral changes and no losses in optical performance after >1 year of normal storage at ambient conditions
- sealed gratings (SURPHEX™-P)	no physical or spectral changes and no losses in optical performance after storage at -20°C in 85% RH for 100 hours and at +60°C in 85% RH for 100 hours

Optical and scanning electron microscope inspections confirm that original DOE surface relief profiles are being transferred to the SURPHEX™ photopolymer layer with a very high fidelity. Several examples of the replicated surface relief microstructures with different width/depth aspect ratios are shown in Figures 5, 6, and 7. Broad range of the width/depth aspect ratios recorded in original HOE have been faithfully reproduced in the DPE replicas and features from 0.1 μm to 3.5 μm were precisely replicated. DPE technology covers full range of the grooves width/depth aspect ratios to produce different types of high quality surface relief or embossed holograms. All presented SEM photographs have the same size code to scale properly dimensions of the original and replicated microstructures. This code can be followed by observing the scaling white dashed line located under magnification number in the lower left corner on every SEM photograph. One can scale replicated microstructures referring to the following size code and by measuring the length of the last bigger dash shown in the scaling line under magnification index 'kx':



Detailed optical microscope scanning profilometry of the DOE shown in Figure 5 demonstrated that the average difference in the top surface profiles between the original DOE (a) and replicated microstructures of the SURPHEX™ replica (b, c, and d) constitutes only several hundred angstroms.

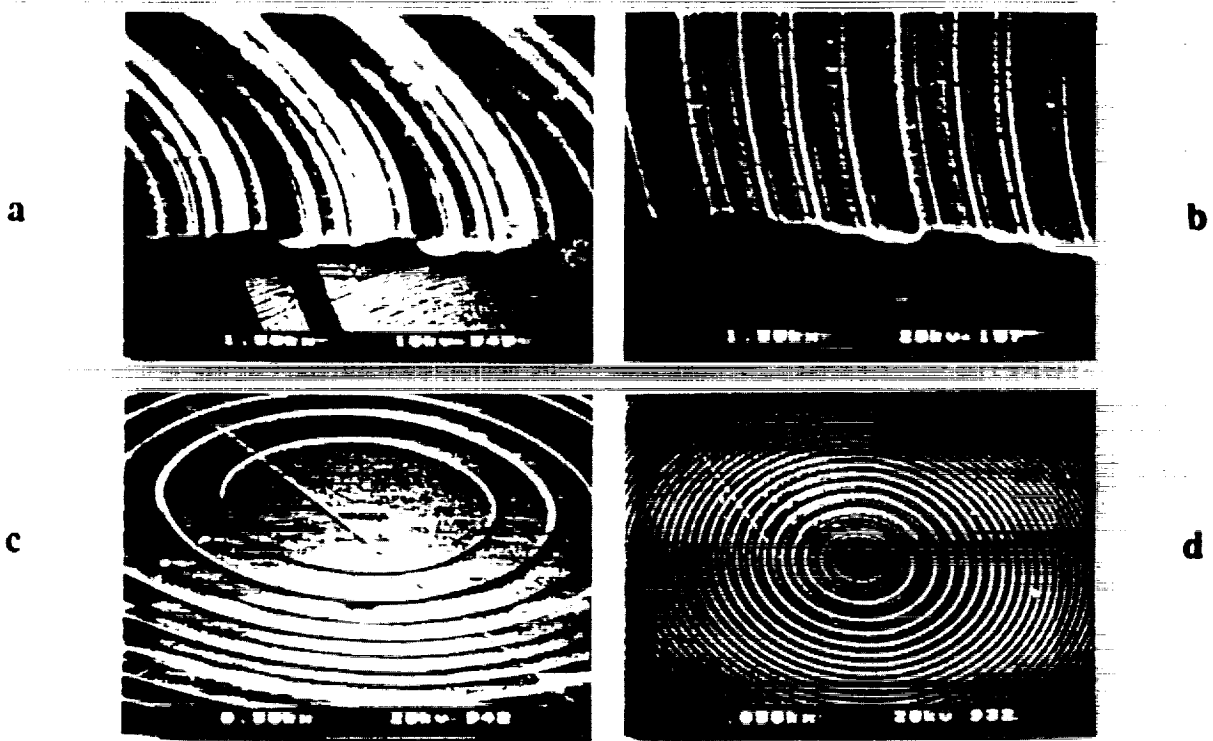


Figure 5. SEM of original DOE (a) and DPE replica (b, c, and d): width/depth aspect ratio - 1:10

Figure 6 shows SEM of the DPE replica with the width/depth aspect ratio in the groove of 1:20, where width at the bottom of the groove is ~0.1 μm and depth of the same groove is ~2 μm. Also, as one can see, quite sophisticated curved microstructures of this DOE were faithfully replicated.



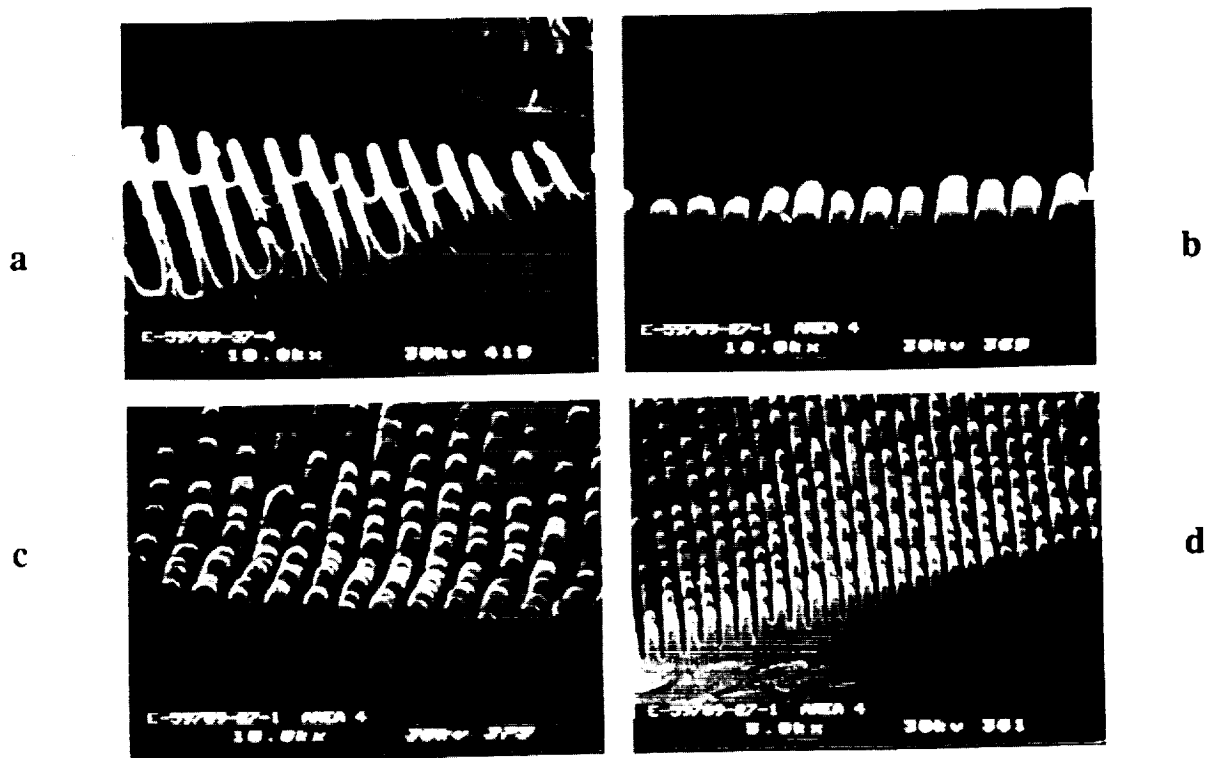


Figure 6. SEM of DOE stamper (a) and DPE replica (b, c, and d): width/depth aspect ratio - 1:20

Figure 7 demonstrates SEM of a cross-section of the SURPHEX™ replica from a DOE with a saw-tooth type surface relief profile. This microstructure, which has repeatable small negative curvatures (side pockets of ~50 nm), was precisely replicated by DPE technology into the SURPHEX™-P25 (25 μm thickness) film laminated to a polycarbonate (PC) sheet substrate.



Figure 7. SEM of SURPHEX™ replica of a saw-tooth microstructure: depth - 0.7 μm, pitch - 2μm

## CONCLUSIONS

Novel Dry Photopolymer Embossing technology and SURPHEX™ dry photopolymer films can be successfully utilized to replicate different types of surface relief microstructures with a definite advantage in replication of the deep groove surface relief DOE. For each specific DOE application properties of the SURPHEX™ type formulations can be optimized and processing parameters for the DPE replication process can be adjusted to meet required performance specifications. Comparing DPE technology with existing conventional replication processes, such as thermo-embossing, injection molding, wet photo-polymerization (2P-process), and injection-reaction molding, the following advantages should be emphasized:

- *dry* UV curable materials improve handling and processing
- very precise replication of the deep groove DOE
- no need for an adhesive layer to mount DOE on a substrate
- wide range of polymeric and inorganic substrate materials
- no size or shape limitations for the SURPHEX™ replica
- potential economical advantage for a *continuous* DPE process

## ACKNOWLEDGMENTS

Formulations improvements, coating, imaging and processing techniques were developed in collaboration with Dr. A. L. Shobert, Mr. D. G. Gray, and Mr. W. J. Morgan. Continuous and dedicated assistance in the laboratory by Mr. J. M. Brawdgers is greatly appreciated.

## REFERENCES

1. S. Hasegawa, F. Yamagishi, H. Ikeda, and T. Inagaki, "High Resolution Line Scanner for Use in Diode Laser Printers," *Proceedings of SPIE on Practical Holography II*, Vol. 747, 8-16 (1987).
2. Y. Komma, S. Kadowaki, Y. Hori, and M. Kato, "Holographic optical element for an optical disk head with spot-size detection servo optics," *Applied Optics*, Vol. 29(34), 5127-5130, 1990.
3. G. L. Swanson and W. B. Veldkamp, "Diffractive optical elements for use in infrared systems," *Optical Engineering*, Vol. 28(6), 605-608 (1989).
4. N. F. Borrelli and D. L. Morse, "Microlens arrays produced by photolytic technique," *Applied Optics*, Vol. 27(3), 476-479, 1988.
5. T. Shiono, M. Kitagawa, K. Setsune, and T. Mitsuyu, "Reflection micro-Fresnel lenses and their use in integrated focus sensor," *Applied Optics*, Vol. 27(15), 3434-3442, 1989.
6. F. P. Shvartsman, "Holographic optical elements by dry photopolymer embossing," *SPIE-'91 Proceedings*, Vol. 1461: Practical Holography V, 313-320, 1991.
7. F. P. Shvartsman, "Dry Photopolymer Embossing: Novel Photoreplication Technology for Surface Relief Holographic Optical Elements," *Proceedings of ECO4-'91*, Vol. 1507: Holographic Optics III: Principles and Applications, 383 - 391, 1991.