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EVALUATION OF A NEW PHOTOPOLYMER HOLOGRAM RECORDING MEDIUM

by

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ABSTRACT

The holographic-recording characteristics of a very sensitive photopolymer recently made available to CRC for trial by E.I. duPont de Nemours are discussed. Upon exposure a latent image forms in the material which is then photically processed to produce a final image in terms of refractive-index variations. The material is thus extremely well suited to the recording of volume phase holograms. The principles of operation of the material and its properties pertaining to holography are reviewed. Experimental data are given which confirm the theoretical prediction that 100 per cent diffraction efficiencies can be approached with this type of material. The photopolymer seems well suited to holographic applications where *in situ* development or extremely high diffraction efficiency is required.

1. INTRODUCTION

Since the invention of holography, there has been considerable effort expended by many research groups to find suitable materials on which to record holograms[1-5]. Most image-recording media, developed for photographic use, exhibit two disadvantages of significance in holographic applications. The first of these disadvantages is that in order to exhibit high sensitivity they require development and fixation processes which are difficult to perform *in situ*. Silver halide emulsions, photoresist and diazos all require processing in appropriate fluids, which cannot be conveniently handled on an optical table. While the necessity for moving the plate to another apparatus for

* This report is not to be considered an endorsement of any product.

processing is not of great moment in photography, it can be a serious problem in certain holographic applications, such as wavefield encoding[6], since the processed plate must be repositioned with extreme accuracy. Present methods use high precision kinematic plate mounts, or circumvent the problem by the use of elaborate pumping systems with the aid of which the plate can be developed on the holographic table. Simplified methods of emulsion processing in which development and fixation are performed by the same solution have also been investigated[7]. Post distortion of the holographic record caused by the processing is the second major disadvantage of most present materials. This problem is particularly troublesome when phase holograms are desired. Dichromated gelatins swell[8] and bleached emulsions shrink[9] with processing, thereby changing the wavelength required for reconstruction of phase holograms recorded throughout the volume of the material in order to achieve maximum reconstruction efficiency. Thin phase holograms in which distortion effects are not as severe can be made in emulsions and in lithographic photopolymers by using the surface-relief effects these materials exhibit. This type of hologram, however, is less efficient than the volume phase hologram, and also can exhibit enhanced nonlinearity noise if there is bulk absorption at the reconstruction wavelength. Such noise is associated with the effectively complex nature of the amplitude transmittance response[10].

This report presents an assessment of an experimental holographic photopolymer which will soon be available commercially from E.I. duPont de Nemours and Company. This photopolymer has been designed specifically for holography[11-13]. It has the high sensitivity which is associated with the development of a latent image produced by a low-energy exposure. In addition, the processing is entirely accomplished by light, so that the plate need not be moved from the location where it was exposed. The hologram formed in this recording medium can be a volume phase hologram recorded as refractive index variations and therefore can have a theoretical maximum efficiency of 100 per cent. Distortion of the material during processing is insignificant. In general, the photopolymer appears to be an excellent candidate for read-only optical memories, holographic interferometry, white-light Bragg-Lippmann holograms, wavefield encoding and other similar applications.

2. PRINCIPLE OF OPERATION

The photopolymer material consists of a photopolymerizable acrylate monomer, an initiator which serves to extend the intrinsic spectral sensitivity of the monomer (330-360 nm) into the visible, to about 550 nm, and a cellulose polymer binder which forms a matrix to hold the liquid monomer. The material is supplied coated on glass plates to a thickness of approximately 100 μm and covered by a protective Mylar sheet which is stripped off before exposure.

As with silver halide emulsion, the image-forming process consists essentially of three steps - formation of a latent image, development to produce a visible image, and fixation to remove the light sensitivity. With the photopolymer, however, the individual steps can occur simultaneously. There exists two general regimes of exposure under which the operation of the material may be described-short, high intensity exposures and long low intensity exposures.

When the photopolymer is given a short exposure to a high intensity holographic fringe pattern, amounts of the photopolymer proportional to the local intensity of illumination are polymerized. The resulting condition is analogous to the silver halide latent image. Immediately on cessation of the exposure, the unpolymerized monomer begins to diffuse into the exposed regions as a result of the monomer concentration gradients established by the exposure, and the fact that the mobility of the monomer in the matrix is considerably greater than that of the polymer. When the diffusion process is completed, the plate is re-exposed, this time to a uniform illumination, until the remaining monomer is photopolymerized. These two steps combine the development and fixation of the holographic record, which exists in terms of the refractive index changes caused by polymerization. After fixation, continued exposure bleaches the yellow-coloured initiator until the final hologram is clear and colourless.

Observation of the holographic diffraction efficiency during these stages indicates that a hologram begins to form almost immediately upon exposure. The diffraction efficiency rises quickly, and peaks at a small value, at which time the exposure should be stopped. During the subsequent diffusion period, the diffraction efficiency falls to zero, then rises slowly to reach, after a few minutes, a maximum which is higher than at the end of the exposure stage. Thus the diffusion has an effect analogous to photographic development. During the final re-exposure to uniform illumination, the diffraction efficiency again rises quite sharply, to reach in a few seconds a very high value. Then it falls off somewhat, yielding finally a hologram of efficiency very much greater than was the case at the end of the exposure. During the re-exposure also, the remaining monomer is photopolymerized, so that development and fixation are combined in the re-exposure processing stage.

When the material is given a long exposure at low intensity the formation of the latent image, diffusion, and fixation all occur simultaneously, producing a temporally dependent value of diffraction efficiency which rises slowly to a saturation value over a few minutes.

A hypothesis has been offered and experimentally justified by Colburn and Haines[11], to explain the mechanism of hologram formation in the photopolymer. They note that at typical holographic spatial frequencies no surface relief is observed. This can be interpreted to mean that in the relatively thin (100 μm) films of the material used in holography, the shrinkage associated with photopolymerization is less than occurs with polymerization of the bulk material. The result of exposure of a thin film of the material to a fringe pattern is that the polymerized regions exhibit a decrease in refractive index rather than the increase that would occur on polymerization of the bulk material. Since refractive index increases with molecular density and since polymerization reduces the absolute number of molecules in a region, if the exposed regions are constrained from shrinking by the unexposed regions, then the refractive index must fall with polymerization in the exposed regions.

Since the polymerized regions are constrained from shrinking it follows that the unpolymerized regions, which form the constraining structure, undergo some shrinkage during the exposure. This shrinkage increases their refractive index. The net result of exposure to a holographic fringe pattern is a lowered refractive index in the exposed regions and a raised index in the unexposed regions. The variation in refractive index, δ, is defined as the difference

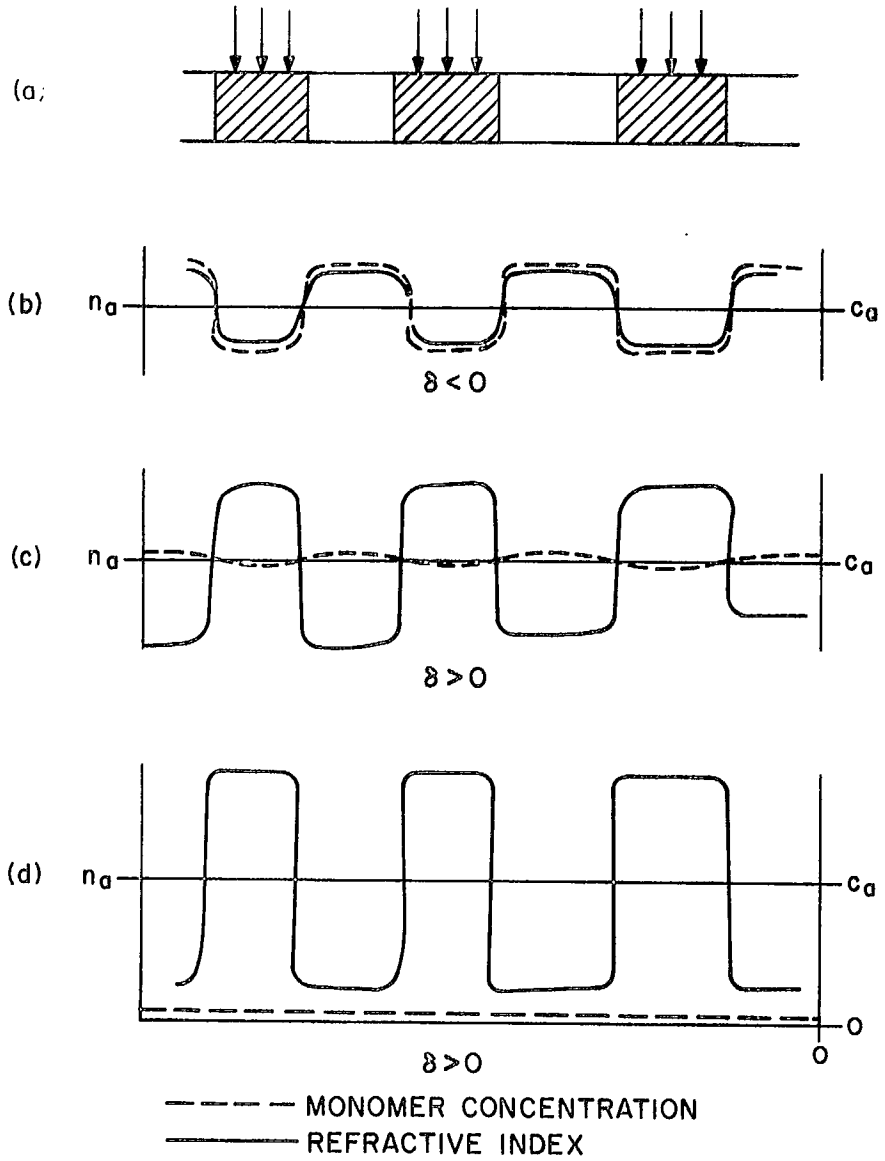

Fig. 1. Refractive index and monomer concentration distributions after each stage of the processing.

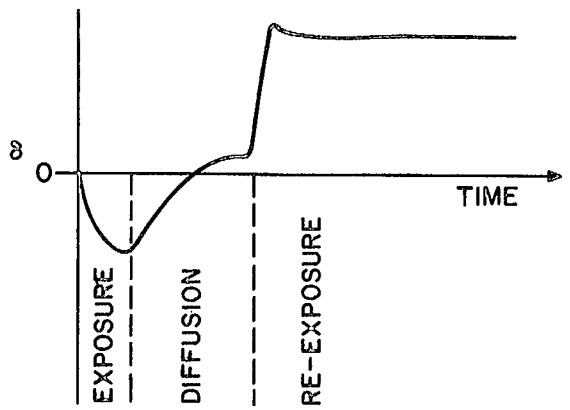

Fig. 2. Variation of δ with time.

between the refractive indices of an exposed area and an unexposed area of the plate. The situation immediately after exposure is shown in Figure 1(a) and (b). Part (a) of the figure is a diagram of the intensity distribution of the illumination and shows the polymerized areas crosshatched. Part (b) of the figure shows the variations of refractive index and monomer concentration about their unexposed values n_a and c_a.

Following the exposure the monomer diffuses from the unexposed regions to the exposed regions. This process raises the molecular density and hence the refractive index of the exposed regions and lowers them in the unexposed regions. The refractive-index difference δ increases from its negative value, passes through zero and may reach a positive value. The situation after diffusion is shown in Figure 1(c). At this stage, the concentration of monomer is returned to a nearly uniform distribution and the absolute value of δ can be higher than at the end of the exposure.

Finally the hologram is given a uniform re-exposure which polymerizes the remaining monomer. Because of the transport of monomer during the diffusion into the regions polymerized by the original exposure, the result after re-exposure has polymerized the entire film is that there is a higher concentration of polymer, and hence a higher refractive index, in regions which received strong illumination during the first exposure. The situation after the re-exposure is shown in Figure 1(d). The refractive-index modulation constituting the hologram after the re-exposure can be of the order of 3×10^{-3}. For this modulation, 100 per cent diffraction efficiency can theoretically[14] be reached in a volume hologram 100 μm thick, which corresponds to the thickness of the film as it was made available to us.

The entire hologram formation process can be represented by a sketch of the variation of δ with time during the stages of the exposure, as shown in Figure 2. The observed diffraction efficiency varies temporally as the square of the refractive index difference. The measured temporal dependence of diffraction efficiency confirms the behaviour postulated for δ on the basis of the stated model for hologram formation in this material.

For low-intensity exposures when exposure times are longer than the diffusion times, monomer is continuously being polymerized as it diffuses into the illuminated regions. In this case the value of δ slowly rises due to the increase in the polymer concentration in the exposed regions, until all the monomer available is polymerized. This behaviour is seen in Figure 5 which shows an experimental determination of diffraction efficiency for a long, low intensity exposure.

3. CHARACTERISTICS OF THE MATERIAL

3.1 Spectral Response

The material is about twice as fast in the blue near 450 nm as at 515 nm. Generally, however, the higher power of the argon ion laser in the line at 514.5 nm makes operation in the green advantageous. The sample made available to us exhibited no red sensitivity, which made it possible to monitor diffraction efficiency during hologram formation using the 632.8 nm line of a He-Ne laser.

3.2 Spatial Resolution

The manufacturer quotes a 50 per cent fall-off in diffraction efficiency beyond 3000 ℓ/mm, but some sensitivity extending beyond 3500 ℓ/mm. We have found that formation of Lippmann-type holograms with fringe spacing corresponding to 3890 ℓ/mm was only partially successful. At present therefore, a practical upper limit on the spatial resolution seems to be about 3500 ℓ/mm.

The mechanism of operation at low spatial frequencies changes somewhat, since the fringes tend to be spaced farther apart than the diffusion length for the monomer. Below 100 ℓ/mm the volume refractive index variation becomes insignificant and surface-relief effects play a major role. This is evidenced by the appearance of multiple orders as Bragg order-selection effects decrease and the surface-relief hologram becomes significant.

The fall-off in volume sensitivity for low spatial frequencies is a useful characteristic. The intermodulation noise which occurs as a result of nonlinear recording response arises from self-interference of the object-wave components, and is associated therefore with low spatial frequencies. Discrimination against low spatial frequencies in the recording response of the material will therefore tend to reduce the effect of the shape-dependent noise components[15] which are the sources of the most severe noise in recording materials with nonlinear response characteristics. In order to realize the benefit of the poor low-spatial-frequency volume response, however, the material must be used in an index-matching gate to eliminate the effect of the surface-relief response.

3.3 Photometric Sensitivity

The material requires a total exposure of from 10 to 25 mJ/cm^2 at 514.5 nm. In terms of energy required, it is about two hundred times slower than the fine-grain silver halide emulsions commonly used in holography. The slower speed may not be very significant, considering that the power available in the argon ion lasers which are required to expose the polymer is generally greater by a factor of about twenty than the power available from the small helium-neon lasers now in widespread use for holography. The material is considerably faster than presently available resist-type photopolymers. Exposures of 150-200 mJ/cm^2 at 457.9 nm are required for the formation of surface relief holograms in Shipley AZ-1350 photoresist[16].

The DuPont photopolymer exhibits an induction period (see Figure 5) at the beginning of the initial exposure during which no change occurs. The effective sensitivity of the material can be increased by pre-exposing the plate to complete the induction period before the hologram exposure is made. As pre-exposure lowers the effective holographic recording beam-ratio[16], this technique may also prove useful in dealing with the significant material nonlinearity of the photopolymer, which is discussed later. The threshold intensity for exposing the material is 0.15 mW/cm^2 at 514.5 nm.

It should be noted that in the UV spectral region near 364 nm the material is faster than it is in the green by a factor of about ten. The advantage may be offset somewhat by the fact that the stronger scattering and absorption in the UV region may limit the hologram formation to a layer less than the full thickness of the film and thereby reduce the ultimate diffraction efficiency which can be obtained.

3.4 Diffraction Efficiency

The diffraction efficiency depends upon the film thickness and the refractive index modulation. For a given thickness the index modulation can be optimized by controlling the object-to-reference beam intensity ratio. The manufacturer claims that 100 per cent diffraction efficiency can be obtained in the films as supplied to us. This appears not unreasonable. We have consistently attained efficiencies over 75 per cent even though the beam ratio was not optimized.

3.5 Nonlinearity of Response

In addition to the intrinsic nonlinearity of phase-recorded holograms the material exhibits a fairly strongly nonlinear response of refractive index to exposure, and material nonlinearity becomes significant at diffraction efficiencies of one to two percent. As has been mentioned, this behaviour may be partially compensated by the poor low spatial frequency response.

3.6 Bulk Scattering Effects

The manufacturer claims that the noise due to scattering within the material is less than one tenth that of Kodak 649-F plates. We have not yet verified this claim experimentally. Such low scatter is, however, typical of photopolymer recording materials in general as a consequence of the homogeneity of the material.

There is some tendency of the material to crystallize during prolonged storage. The samples we received had visible evidence of crystallization, which would degrade the excellent low-scattering properties of the photopolymer recording material. It should however, be noted that the films tested were an experimental batch. Production of films would be carried out in a clean room thus reducing dust contamination which forms nucleation centers of crystallization.

4. EXPERIMENTAL

The diffraction efficiency was monitored during hologram formation using the apparatus shown in Figure 3. Typical experimental plots of diffracted intensity versus time are shown in Figure 4 for a short exposure and Figure 5 for a long exposure.

The short exposure intensity was standardized at an illumination of 6 mW/cm^2 and an exposure time sufficient to reach the peaking condition of diffraction efficiency when initial polymerization is completed. These exposure times were of the order of two to three seconds, for a total exposure of 12 to 18 mJ/cm^2 which is in agreement with the manufacturer's exposure data.

The long exposure intensity level was established by inserting a neutral density filter into the argon ion laser beam before the beam-splitter to reduce the intensity of exposure by a factor of 10. Again diffraction

efficiency peak was reached. These exposures were about 40 sec long; which is somewhat higher than would be expected from the data for short exposures. It is possible that exposing to the levelling-off condition of diffraction efficiency yields over-exposure for low light levels. The slow drop in diffraction efficiency during fixing shown in Figure 5 is a result of slight over-exposure.

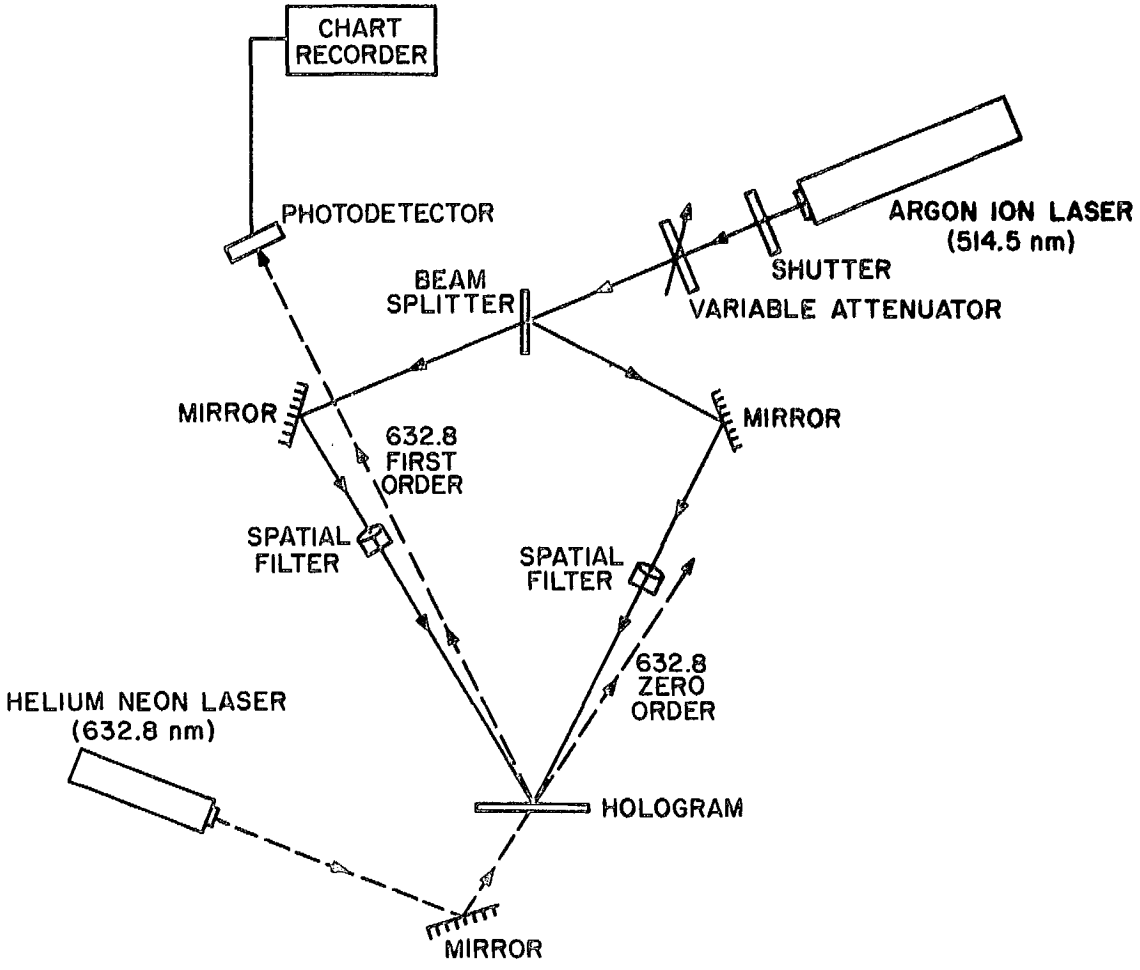

Fig. 3. Experimental arrangement for measuring diffraction efficiency variations.

The induction period is a pronounced feature of the long exposure diffraction efficiency data.

The intensity ratio between the object and reference beams for the diffraction efficiency tests was set at 2:1 by the use of beam expanders of different focal lengths. This beam ratio is closer to the ratios typical of holography than is the 1:1 beam ratio which gives maximum fringe contrast. Nevertheless, well-exposed holograms yielded 75 per cent diffraction efficiency. The spatial frequency of the fringe pattern recorded was approximately 500 mm^{-1}, which is also typical of holography.

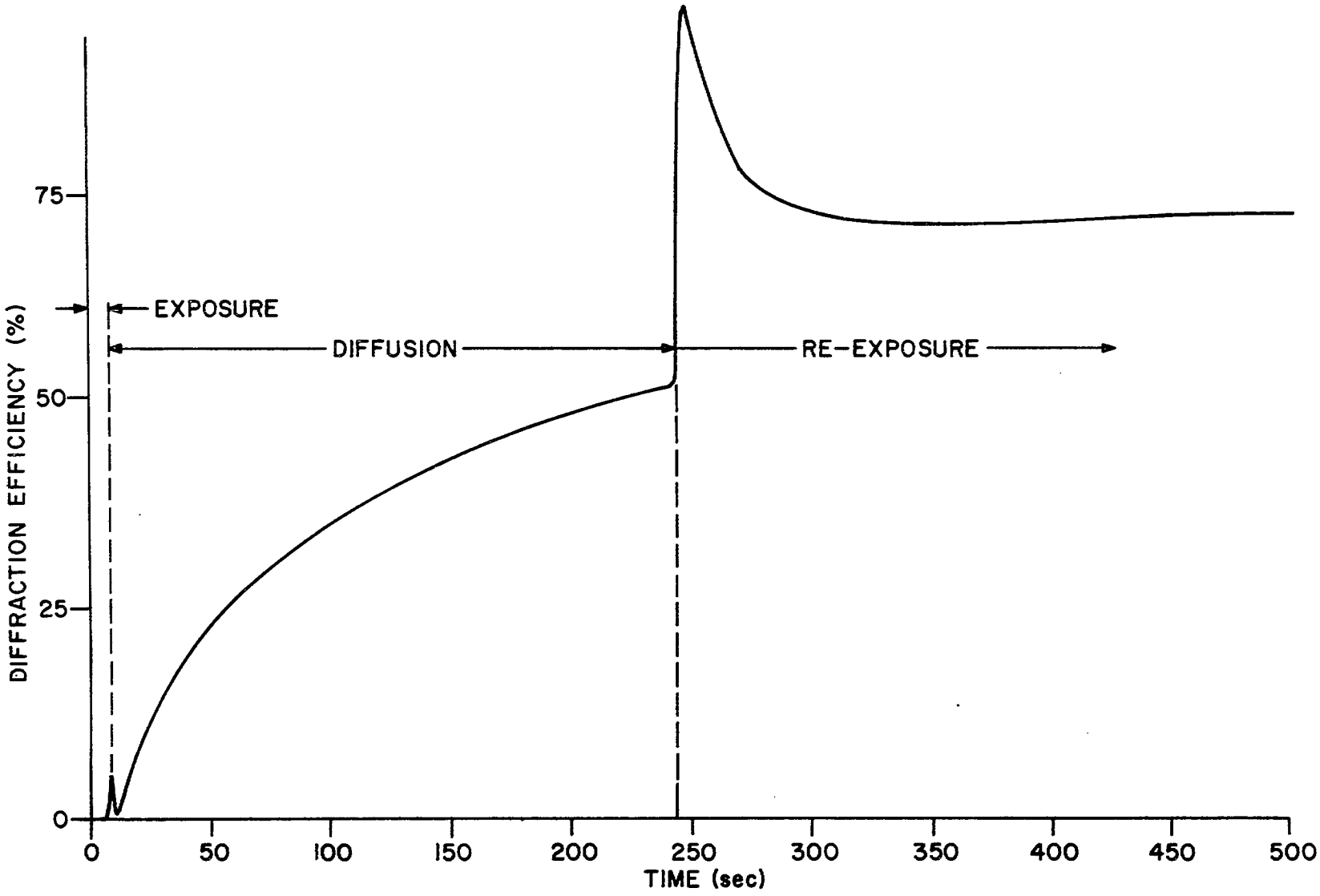

Fig. 4. Development of diffraction efficiency for a short exposure.

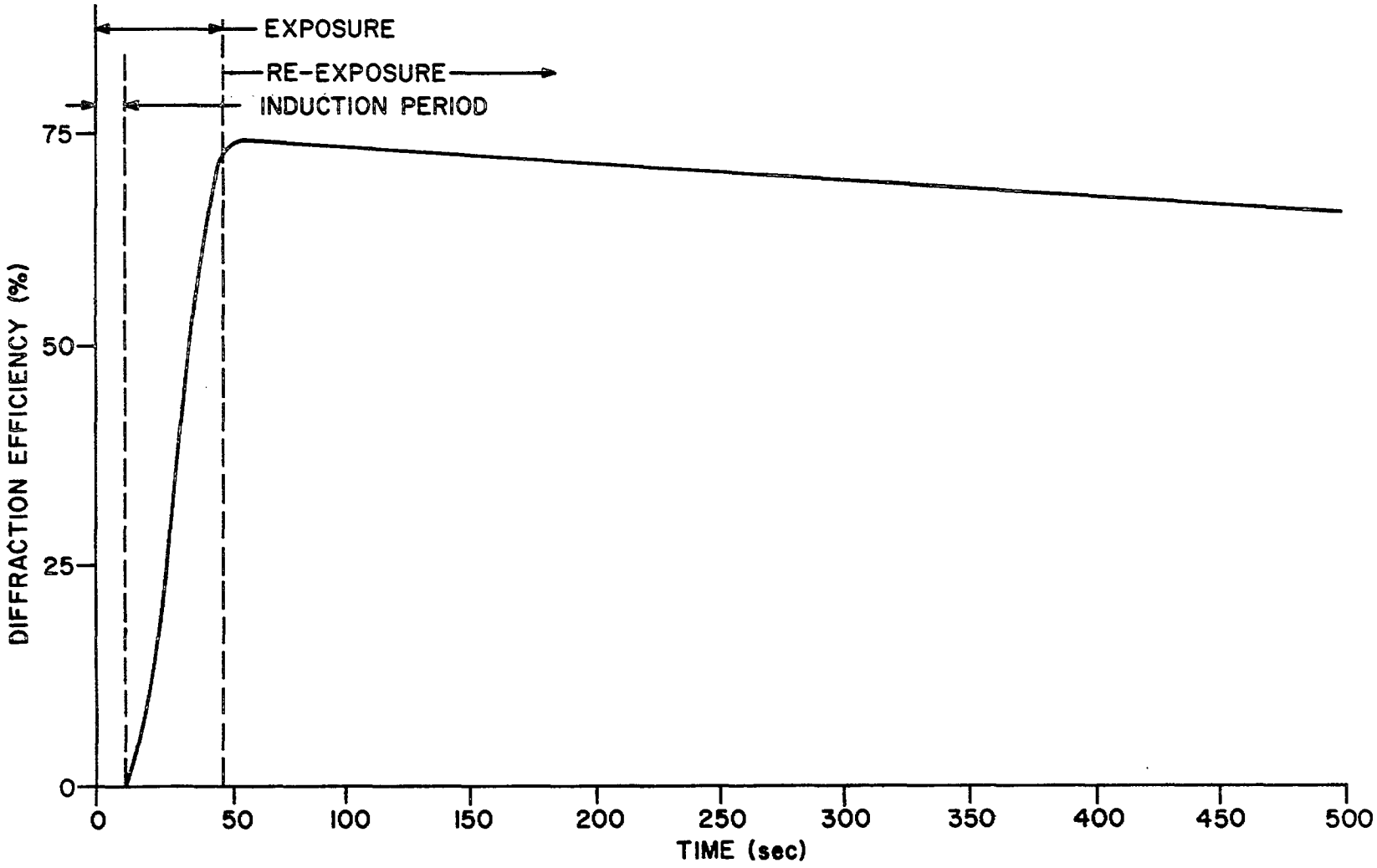

Fig. 5. Development of diffraction efficiency for a long exposure.

Fixation was accomplished using the reference beam alone, and was completed within three or four minutes at 4 mW/cm^2. Bleaching of the initiator was done by placing the plate in very close proximity to a pair of fluorescent lights. This process was lengthy because of the relatively low spectral power of these lamps in this portion of the spectrum - even after 24 hours some of the yellow colour of the initiator was still visible. It is also suspected that the crystallization of the films had some effect on the initiator, impeding the bleaching process.

5. CONCLUSION

The DuPont photopolymer is a material of great potential for many holographic uses. In general these would include all cases where extreme sensitivity is not required, and in particular, cases where very high efficiency or the benefits of *in situ* development are strong considerations.

6. ACKNOWLEDGEMENT

We wish to thank Dr. B. Booth of E.I. DuPont de Nemours & Company for providing us with samples of the photopolymer.

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