

Laser Marking in Dye-Polymer Systems

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Synopsis

Light-induced marking in dye-polymer systems based on dye diffusion was investigated. It was demonstrated that when a dye film coated on an appropriate polymer substrate is exposed to a laser beam, marked areas are obtained. In the exposed areas the dye melts and diffuses into the substrate and also flows laterally. The dye, when diffused into the polymer, shows altered spectral characteristics, and significant changes of optical densities can occur in the marked areas. A direct optical marking process based on these phenomena is described. Good spatial resolution and adequate marking sensitivities were demonstrated as submicron marks and energy density requirements below 100 mJ/cm² were obtained.

INTRODUCTION

The increasing interest in high-resolution information storage devices and high-sensitivity direct marking processes led to the exploration of the processes based on light-induced dye-polymer interactions. Several investigators have studied light-induced transfer of volatile organic dyes from one polymer substrate to another.^{1,2}

This paper presents some initial results obtained during an exploration of laser-induced dye diffusion in polymer-dye systems. The process is based on the principle of simultaneously exposing and fixing a pattern by inducing dye diffusion on and into the same substrate on which it is coated. In the area exposed to the laser beam the dye absorbs light, melts, diffuses into the polymer substrate, and also flows in the lateral direction. The dye diffused into the polymer exhibits spectral characteristics that differ from those of a solid dye layer. These include spectral shifts and a sharpening of the absorption features both of which are associated with the transition from a solid dye to a molecularly dispersed system. This process can produce significant changes in the optical densities in the marked areas.

EXPERIMENTAL

Materials

Derivatives of 1,4-diaminoanthraquinone and methine disperse dyes were investigated in this study. The data obtained with ICI Disperse Red 11, Du Pont Disperse Blue 60, and Eastman Disperse Yellow 88 dyes³⁻⁵ are presented and discussed. The thermal and spectroscopic properties of these dyes are most relevant to our study. The melting temperature T_m , the latent heat of fusion, ΔH , and the specific heat C_p of these dyes were determined by differential scanning calorimetry using a Du Pont 990 Thermal Analyzer. The data obtained are presented in Table I. The thermal stability of the dyes was investi-

TABLE I
 Properties of Dyes

Dye	T_m , °C	ΔH , J/g	C_p at 160°C, J/g·°C	$\epsilon_{\text{max}}^{\text{solid film}}$, (liter/mole-cm) $\times 10^4$
Disperse Blue 60	206	36	1.80	0.4
Disperse Red 11	250	120	1.74	0.9
Disperse Yellow 88	189	52	1.88	3.6

gated using a Pyroprobe Pyrolizer fitted with a platinum ribbon probe. No decomposition products were detected on heating the dyes for a duration of 20 msec at 600°C.

A biaxially oriented 50- μm film of polyethyleneterephthalate (Du Pont's Mylar) was used as the substrate in most of the experiments. The dyes were evaporated onto this polymer substrate in a Varian/NRC vacuum coater system at a vacuum better than 10^{-5} Torr and at a rate of 10–20 Å/sec. The thickness of the dye film was determined with a quartz crystal digital thickness monitor (Sloan Model DTM-200), and the thicknesses of the dye layers were typically between 0.05 and 0.2 μm even though dye films up to 1.0 μm were sometimes used. The absorption spectra of the dyes in the visible region were measured with a Cary 17 spectrophotometer. A Zeiss scanning microdensitometer was used to record spectra from areas down to 1 μm^2 .

Marking Systems

The laser marking system was described in Reference 6. The system is adjusted to have a beam size of 1 μm (at $1/e$ points) and can deliver up to 32 mW at the film surface for 5145-Å light from an argon ion laser. It can automatically scan the substrate, focus the laser beam, and control the power and also the ex-

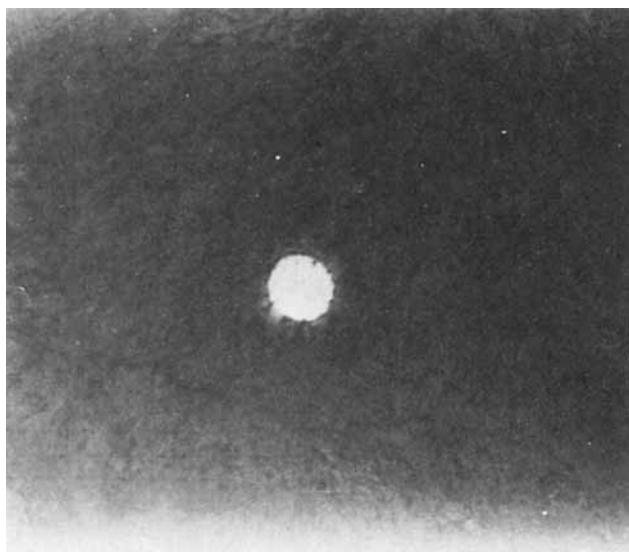


Fig. 1. Optical micrograph of a laser-induced mark with Disperse Red dye on polyethyleneterephthalate. The picture was taken with a red bandpass filter. The spot size is about 100 μm in diameter and was produced with an energy of $\sim 0.5 \mu\text{J}$.

posure time. Usually at least 30 bits were recorded at constant power levels and exposure times. Larger marks (up to $100\ \mu\text{m}$) were produced with a high-power argon ion laser ($\sim 2\ \text{W}$ at $5145\ \text{\AA}$) having the appropriate beam size at the substrate.

Analysis

The recorded bits were examined by optical and scanning electron microscopy to determine the geometry and size of the marks. The optical size of the bit decreases on moving perpendicular to the surface from outside the dye film toward the polymer substrate. This is expected for a diffusion process. The marked regions extend up to about $1\ \mu\text{m}$ in a direction perpendicular to the surface and up to several times the beam diameter in the direction parallel to the surface for micron-size bits. The optical bit sizes were measured at the surface.

RESULTS AND DISCUSSION

Spectral Investigation

Significant changes in color due to laser-induced dye diffusion are readily observed. Figure 1 shows an optical micrograph of a laser-diffused dye mark surrounded by a film of unexposed solid Disperse Red dye. Changes in the visible absorption spectra in the area exposed to the laser beam were observed in all samples examined. Typical absorption curves obtained using the spectrophotometer and the microdensitometer are presented for the Disperse Red

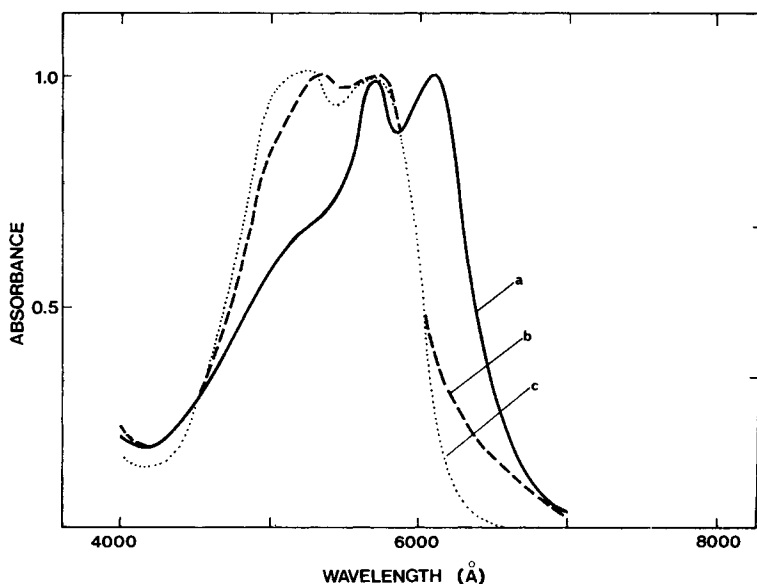


Fig. 2. Optical absorbance of a solid film of Disperse Red 11 on polyethyleneterephthalate. The visible spectra of this dye after thermally- and laser-induced dye diffusion into the polyethyleneterephthalate are also included: (a, —) solid film; (b, ---) thermally diffused; (c,) laser diffused.

(Fig. 2) and for the Disperse Blue dyes (Fig. 3). Comparison of the absorption of the solid Disperse Red dye film (curve a, Fig. 2) with the absorption of the dye after exposure to the laser beam (curve c, Fig. 2) reveals the important spectral shift. The 6100-Å peak is shifted to 5750 Å and the 5650-Å peak is displaced to 5350 Å. An absorption curve of the same dye film after thermal diffusion (heating at 180°C for 3 min) is presented in Figure 2(b). A blue shift occurs for both the thermally and laser-diffused dye. Minor differences between the laser and thermally diffused dye spectra are observed in the blue and red regions. These differences could be due to some subsidiary photochemical reaction despite the known light stability of the dye.^{4,5}

In Figure 3 the absorption spectrum of the solid Disperse Blue dye (curve a) is compared with the absorption spectrum of the diffused dye (curve b). A considerable difference between the two spectra is evident. The spectrum of the solid dye film on the polyethyleneterephthalate substrate shows little structure, having almost uniform absorption over the whole visible region. This may be partially due to diffuse scattering of the rough dye surface which is observed with scanning electron microscopy. The dye diffused into the polymer substrate has a drastically different spectrum. The absorption at 6800 Å after dye diffusion is about 40 times larger than that of the solid dye. A spectrum of a thermally diffused dye is shown in Figure 2(b) and agrees with the laser-diffused spectrum. The solid Disperse Yellow 88 dye has a relatively narrow absorption peak with a maximum at 4480 Å, while the thermally or laser-diffused absorption maximum shifts to 4610 Å with further narrowing.

The spectra of the laser and thermally diffused dyes in polyethyleneterephthalate (Figs. 2 and 3) are in agreement with the spectra of the dyes dissolved in a solvent. This suggests that the dyes diffuse at a molecular level forming a

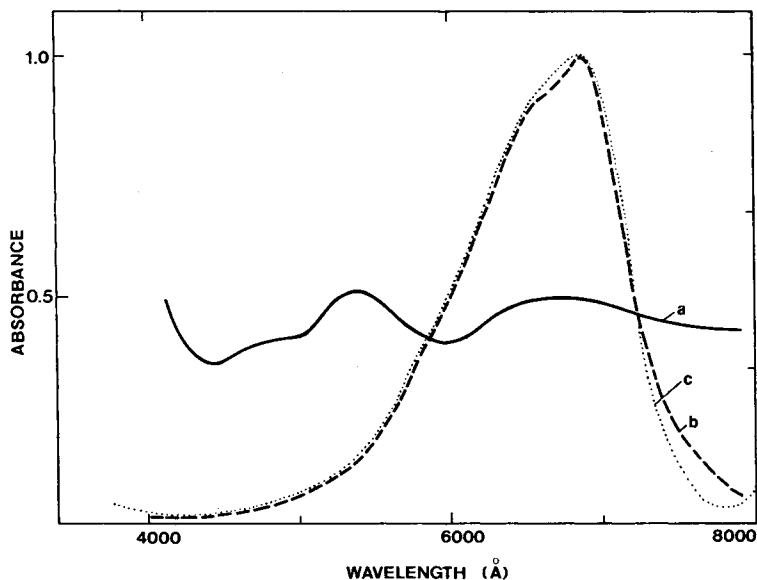


Fig. 3. Optical absorbance of a solid dye film of Disperse Blue 60 on polyethyleneterephthalate. Some apparent absorption is due to diffuse scattering of the rough solid surface. The visible spectra after laser and thermal diffusion of this dye into polyethyleneterephthalate are also shown: (a, —) solid film; (b, ---) thermally diffused; (c,) laser diffused.

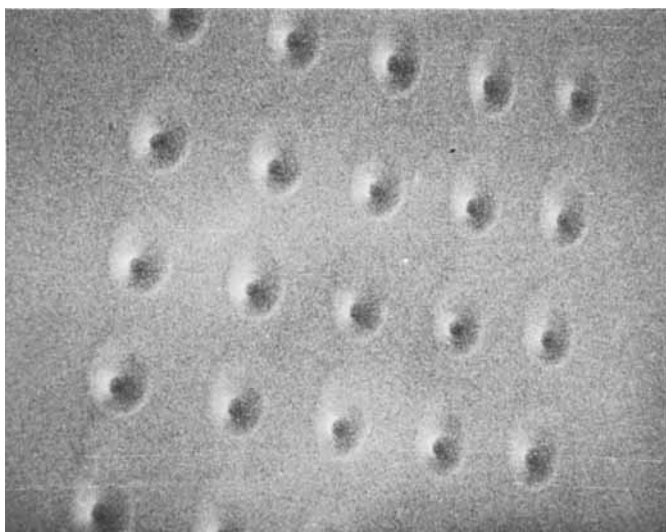


Fig. 4. Scanning electron micrograph of the marked bits on the Disperse Red 11-polyethyleneterephthalate system. The spots were marked at a power of 32 mW and an exposure time of 1 μ sec. The magnification was 6000 \times .

solid solution with the polymer. The spectra presented above were generally taken in areas between 10 and 100 μ m in diameter which were marked at the lower-power densities (10^3 W/cm²) and at longer exposure times (a few msec). The spectra of marks as small as 1 μ m were also measured using the microdensitometer, and these agreed, within accuracy of the measurement, with the spectra found for large spots. The optical densities in the center of the marked areas were only $\sim 25\%$ of those of the solid films, indicating that lateral flow of the melted dye plays an important role in marking micron areas.

In Figure 4 a scanning electron micrograph shows the surface relief in the dye resulting from diffusion and flow of the dye in the area exposed to the laser beam.

Marking Results

The extent of the dye diffusion and flow is laser-power and exposure-time dependent. The marked areas obtained under different conditions are plotted in Figure 5. Their size varies from below a micron to several microns. Increasing the laser beam power or the exposure time increases the diffused area. The minimum power required to induce dye diffusion, the power threshold P_T , is readily obtained by extrapolating the curves in Figure 5 to zero marked area. The threshold powers for all three dyes on polyethyleneterephthalate increase linearly with decreasing exposure times below 1- μ sec exposures. This shows that in this range the marking energy requirements are independent of exposure time. At longer exposure times deviations from this reciprocity are observed. Larger marking energies are required above 1- μ sec exposures, indicating the importance of thermal losses due to heat conduction.

The energy density required for marking E_D , can be determined from the equation

$$E_D = Pt/A \quad (1)$$

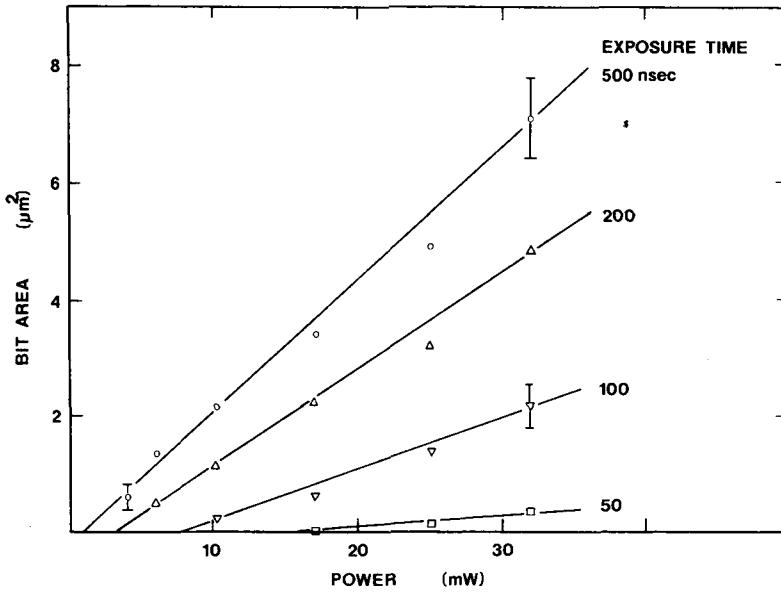


Fig. 5. Spot sizes as a function of laser power at different exposure times for Disperse Red 11 dye ($0.2 \mu\text{m}$) on polyethyleneterephthalate. The intercepts with power axis indicate the threshold powers required for marking at the given exposure times.

where P is the laser power, t is the exposure time, and A is the area of the marked spot. The marking energy density requirements were found to be $100 \text{ mJ}/\text{cm}^2$ for the Disperse Red dye. The marking energy densities for Disperse Blue were higher, around $500 \text{ mJ}/\text{cm}^2$, mainly because this solid dye has a low extinction coefficient. Marking on Disperse Yellow was made at a wavelength where this dye absorbs only a small fraction of the incident energy, and thus the apparent marking sensitivity was low. However, with marking wavelengths near the absorption maximum, energy density requirements below $50 \text{ mJ}/\text{cm}^2$ are antici-

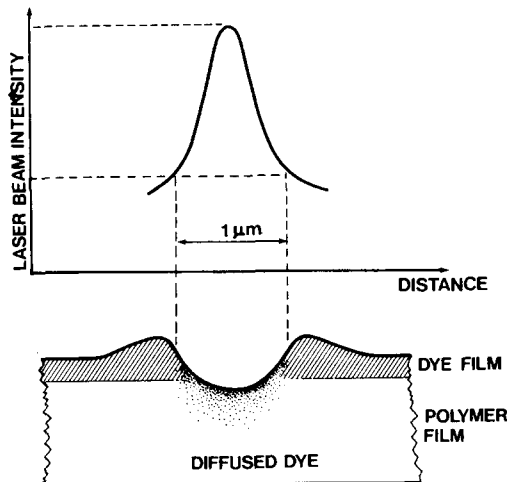


Fig. 6. Schematic representation of an area marked with a Gaussian laser beam. The marked area shows dye diffused into the substrate, laterally flowed dye, and the resulting surface relief in the dye film. Similar relief is also shown in the polymer substrate.

pated. The dependence of the energy densities on the power density and exposure time is discussed in another paper⁶ where conditions for optimum recording are also given.

Mechanism

It is proposed that the process described above involves the combined effect of heat and dye diffusion. This leads to changes in the spectral characteristics of the dyes, to surface relief and possibly to local changes in the structure of the polymer substrate.

In the exposed areas the dye absorbs the light which is then converted into thermal energy by nonradiative processes. This leads to local dye melting and heat transfer to the substrate and the surrounding dye. Near the dye-polymer interface a local increase in the temperature of the polymer occurs which can lead to changes in its structure, mainly in a decrease in the degree of orientation. This enhances penetration of liquid dye into the polymer substrate. Cooling and solidification of the diffused dye follows freezing of the locally changed polymer structure. Part of the melted dye flows laterally. The extent of dye diffusion and flow depends on the materials (dye and polymer), the light power, and the exposure time. An idealized representation of the marked area obtained with a Gaussian laser beam is presented in Figure 6.

To a first approximation heat and dye diffusion can be considered as independent processes as the thermal diffusivity κ ($\kappa = K/\rho C$, where K , ρ , and C are the thermal conductivity, density, and specific heat of the materials, respectively) is usually much greater than the dye diffusion constant D . The heat diffusion process can be described by the differential equation

$$\nabla^2 T = \frac{1}{\kappa} \frac{\partial T}{\partial t} \quad (2)$$

and dye diffusion by the similar equation with concentration c and diffusion constant D substituting for temperature T and diffusivity κ , respectively.

Taking into account the Gaussian profile of the laser beam and finite exposure time and neglecting the differences between thermal properties of dyes and polymer, the temperatures at any spatial point and time were determined from eq. (2).⁶ At threshold energies (less than 1 nJ/1 μm^2 area for Disperse Red) the temperatures at distances about 0.5 μm from the surface exceed the highest melting point of dyes used, i.e., 250°C. At the higher energies shown in Figure 5, the melting temperature is exceeded several microns from the surface. The temperatures exceed the melting point T_m of the dyes after the exposure is terminated and, at threshold energies, remains above T_m for several microseconds. After this time only slight temperature gradients exist between the surface and a point about 0.5 μm below the surface. At higher exposure energies diffusion can proceed for 5–10 μsec . We estimate that the diffusion coefficient of these dyes in polyethyleneterephthalate is of the order of 10^{-5} cm^2/sec near the dye melting temperatures. Therefore, it is expected that the dye diffuses over distances of 0.1–0.2 μm during the above times.

From the calculated temperature profiles the energy densities required for marking can also be evaluated. For 0.1–0.2 μm Disperse Red films we find $E_D \simeq 120$ mJ/cm^2 , in good agreement with experimental results.

Some side effects accompany the main diffusion mechanism. Polymer surface relief and photochemical reactions are possible. An increase in the temperature of the polymer above its melting point will lead to melting the substrate and produce a crater-like relief on its surface. This effect was observed, and it becomes pronounced when excessive powers or exposure times are employed. Furthermore, surface tension probably plays a role in the lateral flow of the molten dye.

In summary, a marking process in polymer-dye system was described, its optical and thermal characteristics investigated, and results of marking experiments presented.

References

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Received September 15, 1978

Revised January 30, 1979