

Photoconductor Fatigue. 3. Effect of Polymer on the Photooxidation of the Charge-Transport Layer of Organic Layered Photoconductors

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The photochemistry of hydrazone-based hole-transport molecules such as *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH) in organic photoconductors gives rise to fatigue of their initial electrical properties. These include an increase in dark decay rates and dark voltage drops and residual surface voltages after light decay. The type of electrical fatigue and its extent are strongly mediated by the polymeric host chosen for the charge-transport layer. We find that polymers such as polycarbonate or polymethacrylate are passive toward DEH photochemistry; in these materials the photochemical rate is high, resulting in large increases in residual voltage. Conversely, DEH photochemistry in polyesters affects the dark electrical properties to the extent that the photoconductor becomes persistently conductive. Acidity in the charge-transport layer and terephthalate versus isophthalate linkages in the polyester are important parameters; the terephthalate linkages exhibit considerable reduction of DEH photochemistry.

Introduction

Electrophotography is the process by which an electrostatic image, formed on the surface of an organic layered photoconductor, is transferred and developed onto paper.¹ During the electrophotographic process a layered organic photoconductor is repeatedly subjected to corona discharges, light used to discharge the photoconductor, heat (primarily generated by the heat required to fuse toner to paper), and light emitted from fluorescent lights in the work environment (room light). Although the accumulative incident dose received from both room light and light used to discharge the photoconductor appears to be innocuous, of the order of 1 J/cm², nevertheless the photocurrents generated during the discharge process are very small and subject to significant changes if the incident dose is translated into photochemical changes. From a different point of view, a photoconductor, in order to have commercial value, must maintain constant electrical properties for many charge and discharge cycles. We label the deviations in the electrical properties of the photoconductor with time as fatigue; electrical fatigue has many sources, as alluded to above, and in addition depends on the particular organic materials used to fabricate the photoconductor. In recent reports^{2,3} a model photoconductor was used that clearly exhibits electrical fatigue as a result of photochemistry from room light, hereafter referred to as blue light fatigue (because this is due to the blue component of the light emitted from fluorescent lamps), and discharge light, hereafter referred to as yellow light fatigue (because the spectral output of discharge lamps used in copiers and printers is >520 nm).

The blue light fatigue was attributed to the effect of photochemistry² of a charge-transport molecule, *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH), on the electrical properties of an organic layered photoconductor. The photochemical reaction was characterized spectroscopically, and the photoproduct identified. In addition, the concentration of the photoproduct in the charge-transport layer (CTL) was correlated to specific changes in the electrical properties of the organic layered

photoconductor. Yellow light fatigue was attributed to a solid-state photochemical reaction³ that is diffusion controlled; the reaction occurs at the interface of the charge-generation and charge-transport layers and involves both the carrier generation dye, such as chlorodiane blue or substituted squaraines, and hole transport molecules such as DEH.

The requirements for high-volume printing capabilities (500 000 copies/month) on organic layered photoconductors puts stringent requirements on their durability. Thus fatigue studies of organic layered photoconductors are important, and in this paper we present the effect of the choice of polymeric matrices in the charge-transport layer (CTL) upon the photooxidation of DEH and its subsequent effect on the electrical properties of the photoconductor. We find that DEH photooxidation is strongly dependent upon the polymer matrix in which it is molecularly doped, so that in the presence of an appropriate polymer combination in the charge-transport layer, DEH photochemistry may be significantly retarded, which in turn minimizes the residual charge problems associated with organic layered photoconductors. A full description of the chemical composition and spectroscopic properties of a model organic photoconductor based upon the charge-generation molecule chlorodiane blue and the hole-transport molecule DEH has been given in the previous article,³ and thus no reiteration is necessary here.

Experimental Section

DEH, chlorodiane blue, hydroxysquarilium, polyester (PE), and polycarbonate (PC) were obtained from commercial sources. The chemical structures of the polymers are shown in Figure 1. Photoconductors were prepared as described previously.³

Synthesis of MPE. The acid end groups of PE (polyester) were converted to methyl ester groups by reacting it with diazomethane. Diazomethane was prepared in the usual manner⁴ using a Diazald kit obtained from Aldrich. Thus, in a round-bottomed flask, 0.1 g of KOH was dissolved in 0.15 mL of H₂O, and 0.6 mL of ethanol added. This was heated in a water bath to 65 °C, and from a dropping funnel was added dropwise a solution of 0.45 g of Diazald (Aldrich) in 4.5 mL of ether. The diazomethane so prepared was codistilled in ether and collected in a flask charged with 1.5 g of polyester in 120 mL of 17% (by volume) ether in tetrahydrofuran. After all of the diazomethane was codistilled with ether, the collection flask was stirred addi-

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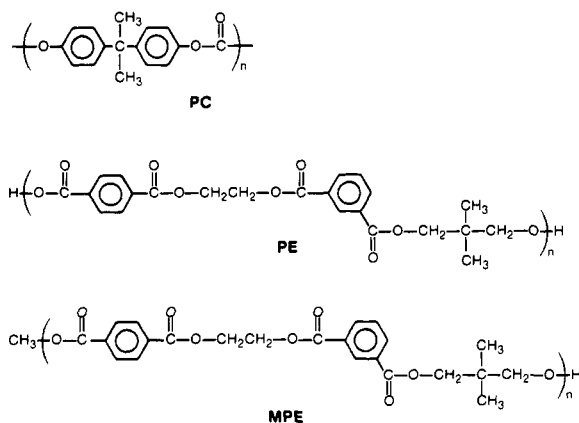


Figure 1. Polymers used in the charge-transport layer.

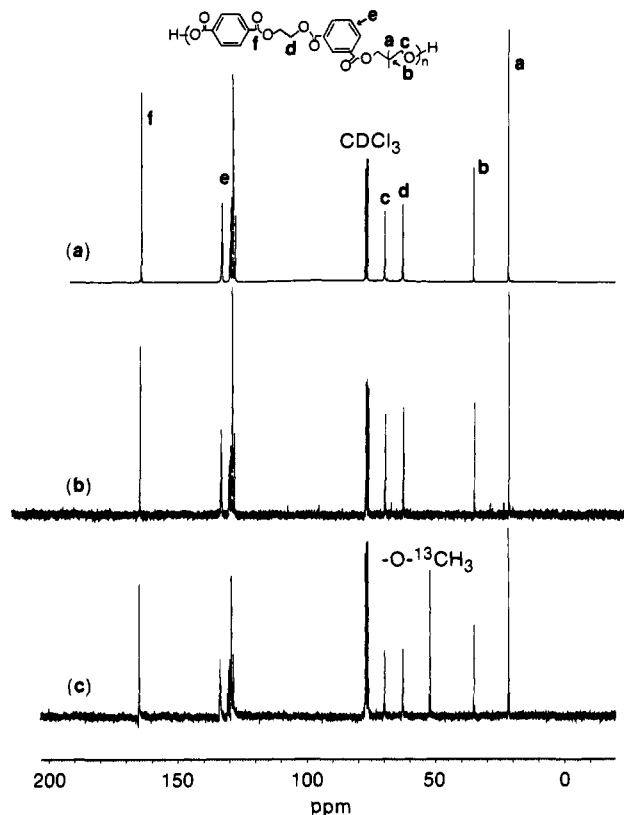


Figure 2. ^{13}C NMR spectrum of (a) PE, (b) MPE, the methyl ester of PE, and (c) the ^{13}C -enriched methyl ester of PE.

tionally for several hours. The solvent was then removed (rotovap) to leave the methylated polyester, MPE. MPE was redissolved in tetrahydrofuran and fractionated from methanol several times and then dried in a vacuum oven at 60°C for 1 week prior to use.

The esterification of polyester was verified by using NMR spectrometry. The ^{13}C spectrum of PE is shown in Figure 2a, and the assignments are made based on analogous compounds. The spectrum of PE after treatment with diazomethane is shown in Figure 2b. No substantial differences between the spectra before and after methylation are observed because the relative concentration of acid end group carbon atoms to carbon atoms in the polymer is exceedingly small. To alleviate this problem and to confirm methyl esterification, ^{13}C -enriched diazomethane was prepared and the methylation repeated. The spectrum of this polymer, ^{13}C -enriched MPE, is shown in Figure 2c. Note the presence of a new resonance band at 52.3 ppm not observed previously in either polyester (PE) or methylated polyester (MPE). This band was confirmed with the ^{13}C NMR spectra of dimethyl isophthalate and dimethyl terephthalate, both of which have their methyl ester carbon resonance at approximately 52 ppm. These data substantiate that MPE has been methylated and that the

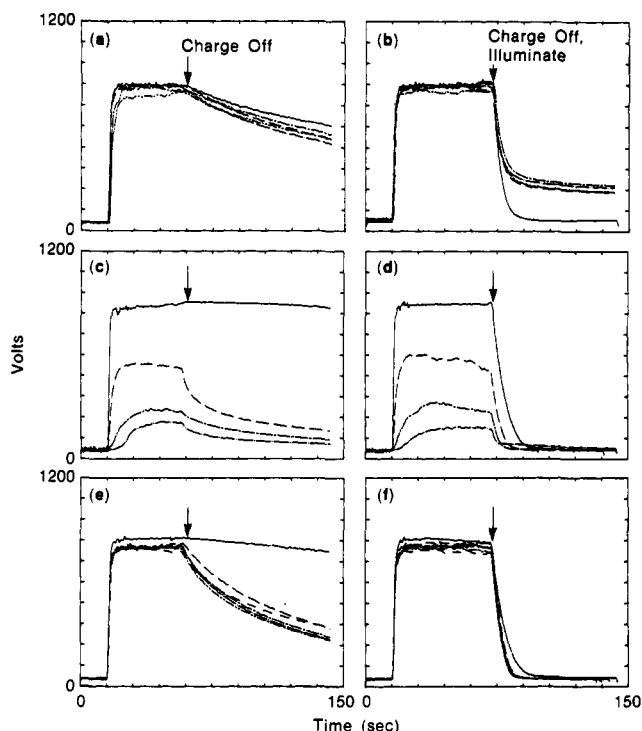


Figure 3. Effect of incident blue light ($0.22\text{ mW}/\text{cm}^2$, λ 400–480 nm) on the dark and light electrical properties of organic photoconductors: (a) and (b) 40 wt % of DEH in PC; 0 (—); 0.8 (---); 2.4 (---); 4.0 (---); and $15.8\text{ J}/\text{cm}^2$ (---). (c) and (d) 40% DEH in PE; 0 (—); 1.5 (---); 3.9 (---); and $15.5\text{ J}/\text{cm}^2$ (---). (e) and (f) 40% DEH in MPE; 0 (—); 0.8 (---); 1.5 (---); 2.3 (---); $3.9\text{ J}/\text{cm}^2$ (---); and $16.3\text{ J}/\text{cm}^2$ (---).

esterification has taken place on an aromatic carboxylic acid.

Fatigue Studies. For blue light fatigue studies of the electrical properties of the photoconductors, the sample photoconductors were first exposed to blue light in air at room temperature, and then their electrical properties measured. For light exposures, a fluorescent desk lamp (light source Inter-World 8CW) with a spectral output $\approx 400\text{--}800\text{ nm}$ was used. To isolate blue light, the lamp was filtered with Corning CS 4-72 and 7-59 filters in tandem to allow transmission of light between 400 and 480 nm. The incident energy on the sample surface was measured with a United Detector Technology Model 371 optical power meter equipped with a Model 262 head assembly; the blue light incident power was $0.22\text{ mW}/\text{cm}^2$. The electrical properties of the photoconductors were investigated on a rotating disk electrometer; a full account of the rotating disk electrometer has been given in a recent publication.⁵ The photoconductors in the rotating disk electrometer were discharged with long-wavelength light (520–800 nm) with an incident energy of $20\text{ }\mu\text{W}/\text{cm}^2$.

For optical absorption studies of DEH photooxidation in the charge-transport layer, $0.3\text{-}\mu\text{m}$ CTL films were spin coated on optically flat quartz substrates and exposed to blue light. Exposures were carried out in air at room temperature using a Xe arc lamp filtered with 8 cm of water and CS 4-72 and 7-59 filters. The incident power was $11\text{ mW}/\text{cm}^2$. UV-visible measurements were carried out using a Perkin-Elmer Lambda Array UV-visible spectrophotometer equipped with a Model 7700 computer.

Results and Discussion

Changes in Electrical Properties. The dark and light decay curves for a photoconductor formulation composed of a CTL of 40% (by weight) of DEH in polycarbonate (PC) are shown in Figure 3. The initial electrical properties of such a photoconductor, before its exposure in air to blue light (λ 400–480 nm), reveal that the dark decay curve holds charge (negative corona, 900 V), and when the

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corona is turned off, it has a dark decay rate of several V/s. Upon exposure to a discharge lamp (i.e., light decay curve), the surface potential drops from 900 to ≈ 50 V, and we observe no residual surface voltage. This is characteristic of a normal photoinduced discharge curve for organic layered photoconductors, which act as electrical insulators in the dark and as conductors in the light. When the electrical properties of the organic layered photoconductor are measured as a function of incident blue light, the dark decay curves remain largely unchanged, but the light decay curves are observed to change significantly: there is evolution of residual surface potential as a function of incident energy, increasing from 50 to ≈ 250 V after less than 1 J/cm^2 is incident upon the organic photoconductor. The onset of the residual surface voltage evolution is rapid and appears to reach a limiting value as a function of incident energy. The origin of the electrical fatigue, as discussed in detail previously,² is attributed to the photooxidation of DEH to an indazole derivative in the charge-transport layer of the organic photoconductor. The indazole derivative photoproduct is 1-phenyl-3-(4-(diethylamino)-phenyl)-1,3-indazole and was isolated by chromatography, and its chemical structure identified by X-ray crystal structure determination, elemental composition analysis, and standard analytical spectroscopy.^{6,7}

A completely different response to blue light is observed when the polymer matrix of the charge-transport layer (CTL) is changed from polycarbonate to polyester in our organic layered photoconductor. As with polycarbonate (PC), the initial electrical properties are indistinguishable; the photoconductor acts as an insulator in the dark and a conductor when exposed to light. However, when the organic photoconductor with a CTL derived from 40% DEH in polyester is exposed to blue light, the organic layered photoconductor responds by becoming persistently electrically conductive in the dark, and no evolution of residual surface voltage is observed during light decay, under these conditions (Figure 3c,d). Thus, for the example shown, the dark voltage after 1.5 J/cm^2 drops 39%, from 885 to 539 V, and the dark decay rate increases from ≈ 0 to 40 V/s, at least over the time scale measured. With additional blue light exposure, the dark electrical properties continually degrade, as vividly illustrated in Figure 3c. The light decay curves, in contradistinction to the photoconductor with a polycarbonate-based charge-transport layer, exhibits no residual voltage even after $\approx 20 \text{ J/cm}^2$ of blue light exposure and is attributed to the persistently conductive state developed by the photoconductor after blue light exposure. During the course of the experiment, we have correlated the rapid decay of the dark electrical properties after blue light exposure to acidity of the polyester. When the acid end groups in the polyester (Figure 1) are "capped" with a methyl ester group and formulated into a charge-transport layer (CTL) with DEH, the persistent electrical conductivity observed above by using ordinary polyester is virtually eliminated; these data are summarized in Figure 3e,f and should be compared with Figure 3c,d. Thus the surface potential, as a function of blue light exposure, remains essentially at the initial level although the dark decay rate does increase modestly from 2 to 10 V/s after 1 J/cm^2 . Most significantly, no evolution of residual voltage is observed after light decay, after 20 J/cm^2 . Thus we observe that modification of the polyester with diazomethane improves the resistance of the photoconductor to blue light exposure, i.e., the pho-

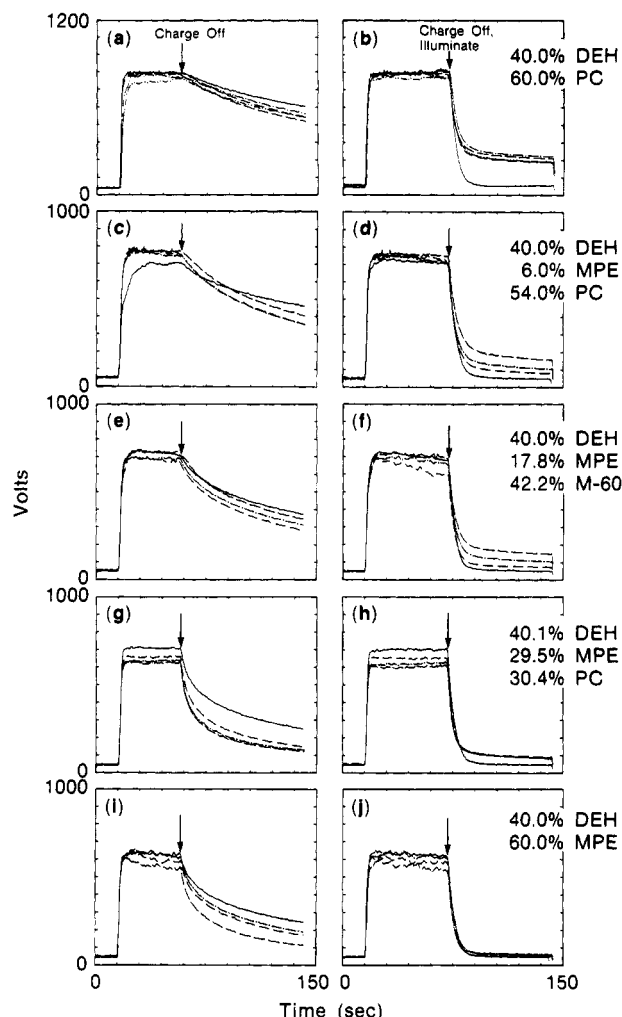


Figure 4. Effect of incident blue light (0.22 mW/cm^2 , λ 400–480 nm) on the dark and light electrical properties of organic photoconductors, as a function of polyester content in a 40 wt % DEH/polycarbonate-based CTL. (a) and (b): 0 (—); 0.8 (---); 2.4 (---); 4.0 (---); and 15.8 J/cm^2 (---). (c)–(j): 0 (—); 0.8 (---); 2.4 (---); and 4.0 J/cm^2 (---).

tochemistry of the hole-transport molecule DEH is significantly retarded. Consequently, the dark electrical properties approach the more ideal polycarbonate behavior, where the dark electrical properties are more resistant to blue light and, concomitantly, maintains the more favorable light decay characteristics of the polyester-derived photoconductor, i.e., no evolution of residual voltage as a function of incident blue light. Frequently, commercial preparation of the charge-transport layers involves using polymeric blends for the matrix in an effort to optimize both the dark and light electrical properties of the resultant photoconductor. As summarized in Figure 3, methyl esterification of polyester provides a facile approach by which both the dark and light electrical properties of the photoconductor may be optimized.

To illustrate these effects more systematically, Figure 4 shows the effect of adding the methylated polyester, MPE, into a polycarbonate-based charge-transport layer (with 40% by weight DEH). The changes in the electrical properties as a function of blue light exposure and of ester content in the CTL are shown in Figure 4. The decay curves reveal several trends as a function of blue light: with increasing ester content (MPE) in the CTL, dark voltage is observed to drop increasingly, but not more than $\approx 14\%$ after 4 J/cm^2 , and in the light decay curves, evolution of residual surface voltage decreases systematically

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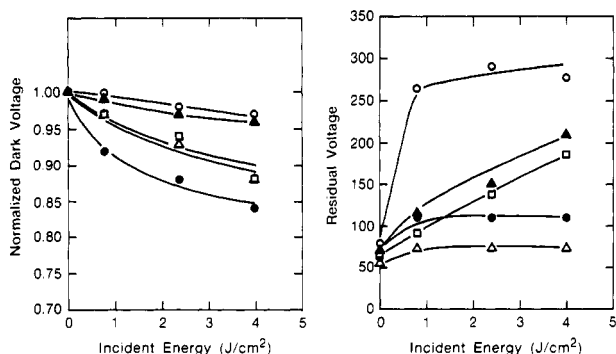
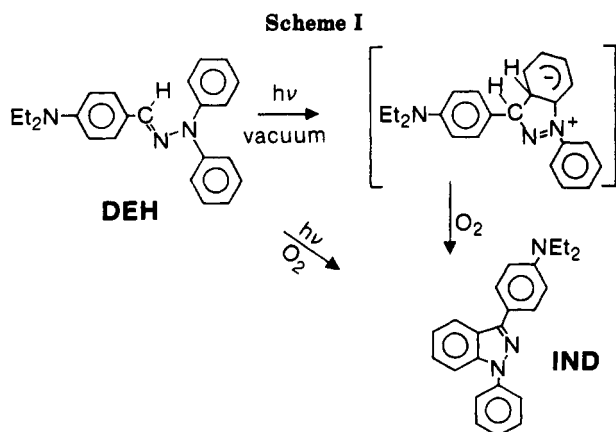


Figure 5. Normalized dark voltage drop (left figure) and evolution of residual voltage on photoconductor (right figure), as a function of both incident blue light (0.22 mW/cm^2 , λ 400–480 nm) and CTL formulation: (○) 40% DEH, 60% PC; (▲) 40% DEH, 6% MPE, 54% PC; (□) 40% DEH, 18% MPE, 42% PC; (●) 40% DEH, 30% MPE, 30% PC; (△) 40% DEH, 60% MPE. All concentrations are percent by weight.



with increasing MPE content in the polycarbonate-derived charge-transport layer. For a CTL formulation of DEH entirely in MPE polyester, no residual voltage is observed even after 57 J/cm^2 is incident on the photoconductor. These data are summarized in Figure 5, which clearly illustrates the effect of adding methylated polyester into polycarbonate: the dark electrical properties remain unaltered within 15%, and residual voltage is completely eliminated.

In the next section, optical absorption studies are used to investigate the possible origins of the polyester effect.

Optical Absorption Studies of DEH Photochemistry in Polymers. The optical absorption spectra of $\approx 40\%$ DEH separately in polycarbonate and polyester are shown in Figure 6a,b, respectively. When DEH is molecularly doped in polycarbonate and exposed to blue light in air at room temperature, DEH is photochemically converted to an indazole derivative (IND) by the reaction pathway illustrated in Scheme I.² Thus, the optical density of the 368-nm band maximum attributed to DEH, decreases as a function of incident energy, and there is a gradual shift of the (368 nm) band maximum to shorter wavelengths, to $\approx 350 \text{ nm}$. Concomitantly, a new band at 263 nm emerges, attributed to the indazole derivative (IND). The latter two bands are characteristic of authentic IND.⁵ Figure 6a also reveals the presence of an isosbestic point at $\approx 300 \text{ nm}$, which is indicative of a single photo-reaction pathway, that of DEH to an indazole derivative (IND).

On the other hand, the absorption spectrum of DEH doped in polyester and exposed to blue light behaves considerably different from the DEH/polycarbonate system (Figure 6b). First, the optical decay of the DEH band

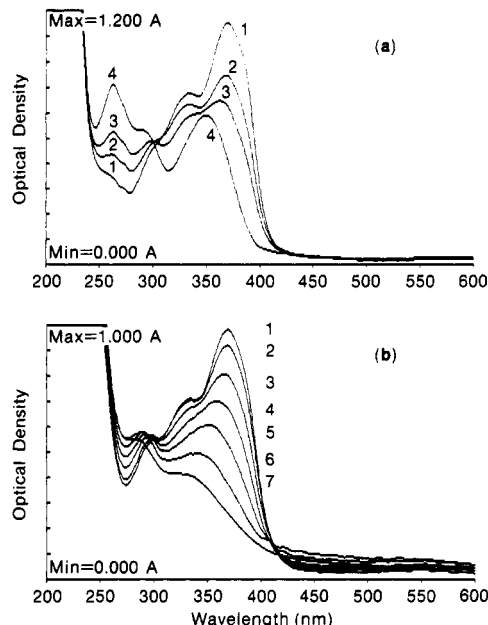


Figure 6. Optical absorption spectra of (a) 40% (by weight) DEH in PC and (b) 40% DEH in PE as a function of incident blue light (10.9 mW/cm^2 ; λ 400–480 nm). For (a), traces 1–4 are 0, 3.3, 7.9, and 19.6 J/cm^2 , respectively; for (b), traces 1–7 correspond to 0, 8, 39, 86, 166, 333, and 605 J/cm^2 , respectively.

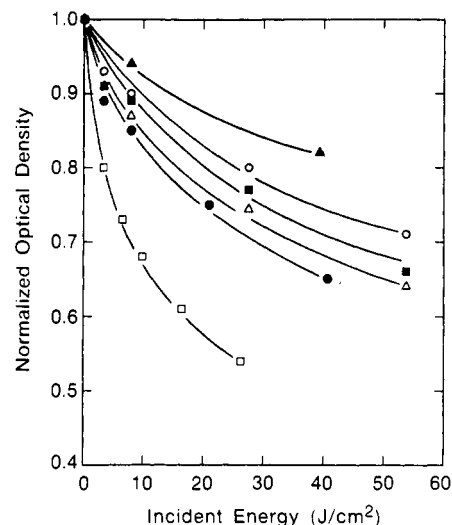


Figure 7. Summary of the blue-light-induced decay of the DEH band maximum (370 nm): (▲) 40% DEH, 60% MPE; (○) 40% DEH, 30% MPE, 30% PC; (■) 40% DEH, 18% MPE, 42% PC; (△) 40% DEH, 12% MPE, 48% PC; (●) 40% DEH, 6% MPE, 54% PC; (□) 40% DEH, 60% PC. Incident blue light: 10.9 mW/cm^2 ; λ 400–480 nm. All concentrations are percent by weight.

maximum at 368 nm requires significantly more energy in the polyester matrix. Second, the isosbestic point observed previously for DEH in polycarbonate is absent, suggesting more complicated photochemistry than simply DEH to an indazole derivative. Finally, polyester absorption out to 320 nm complicates interpretation of the short-wavelength spectral region, and it is not clear whether or not IND (263 nm) is photochemically produced at all, under these conditions. Attempts to obtain difference spectra between the DEH/PE and PE systems are complicated by the intense polyester absorption; presently we conclude only that the photochemical pathway of DEH in polyester is affected by the presence of the polyester and differs from DEH in polycarbonate. Figure 7 summarizes the relative decay of the 368-nm band maximum of DEH when molecularly doped in various polymeric blends of polycarbonate with

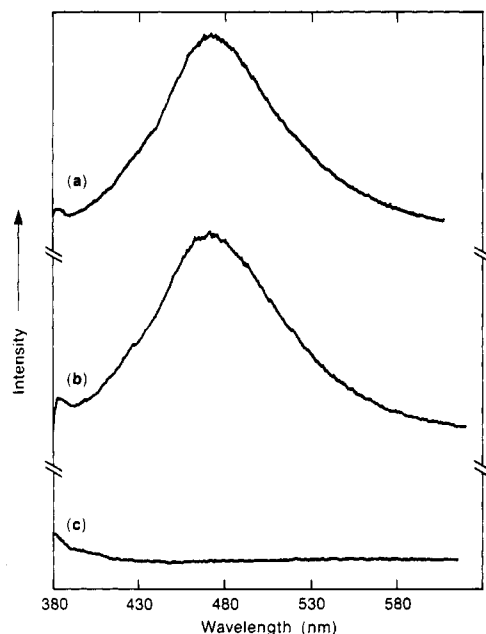


Figure 8. Emission spectra from 40 wt % DEH in (a) polymer blend of polyacrylate/polymethacrylate, (b) polycarbonate, and (c) polyester. Excitation wavelength = 360 nm.

polyester. The trend is clear; increasing the polyester content in the CTL inhibits DEH photochemistry to the indazole derivative. In Figures 4 and 5, we observed previously that residual surface voltage on photoconductor formulations incorporating polyester in the CTL reduced residual voltage after light decay. We conclude that DEH photocyclization to IND may be responsible for the residual voltage effects and increasing the polyester content in the charge-transport layer inhibits DEH photochemistry.

In a previous paper,² we reported an emission spectrum of DEH in CTL samples; the lifetime of the excited state, which was measured and found to be about 10^{-6} s, indicated that the emission was most likely due to a delayed fluorescence phenomenon. Exposure of the CTL film to blue light converted the DEH fluorescence spectrum to that of the indazole derivative. Figure 8 shows the fluorescence spectra of 40 wt % DEH in polycarbonate, a copolymer of polyacrylate/polymethacrylate, and polyester, respectively, using an excitation wavelength of 360 nm. As revealed in Figure 8, emission from DEH is observed in the polycarbonate and polyacrylate/polymethacrylate films but not in the polyester film. Further corroboration is presented in Figure 9, where emission from DEH is gradually quenched with increasing addition of polyester in DEH. Thus, we observe that in the presence of the polyester (1) DEH emission is quenched, (2) the efficiency for photodecomposition of DEH is dramatically reduced, and (3) different photoproducts are produced.

Since Figure 1 reveals that polyester (PE) contains two phthalate moieties, an isophthalate and a terephthalate linkage, the next set of experiments were performed to elucidate which portion of the polyester unit is important for quenching DEH photochemistry. The effect of doping the CTL formulation containing DEH in polycarbonate, with dimethyl isophthalate and dimethyl terephthalate, on the photochemistry of DEH was investigated. For these studies, a rather dilute concentration of DEH in polycarbonate (PC) was used, ≈ 5 wt % in PC, with an excess molar ratio of dimethyl terephthalate or dimethyl isophthalate to DEH of $\approx 40:1$. These data are summarized in Figure 10 along with a "control" CTL of 5% DEH/PC

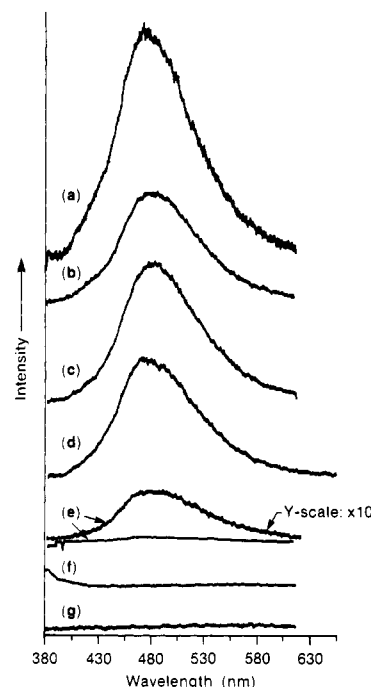


Figure 9. Quenching of the DEH emission by addition of PE (polyester); excitation wavelength = 360 nm. The weight percents of polyester in DEH are (a) 2, (b) 5, (c) 9, (d) 18, (e) 30, (f) 40, and (g) 60.

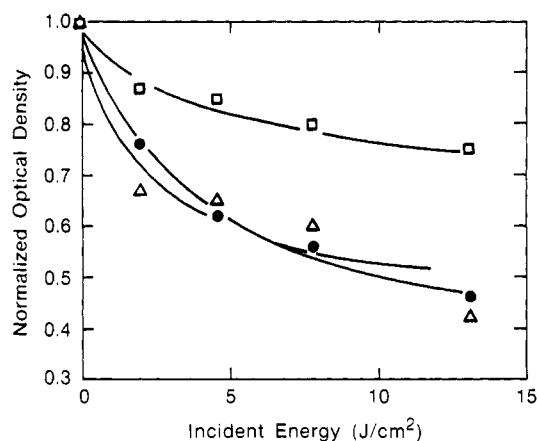


Figure 10. Plot for the normalized optical density versus incident blue light energy (10.9 mW/cm^2 ; λ 400–480 nm): (□) 0.51% DEH, 11.0% dimethyl terephthalate in polycarbonate; (Δ) 0.55% DEH, 12.3% dimethyl isophthalate in polycarbonate; (●) = 0.52% DEH in polycarbonate. All concentrations are percent by weight.

with no ester dopant. In this set of experiments, the optical density of the DEH band maximum at 368 nm in the various charge-transport layers was monitored as a function of incident blue light energy. These results clearly show the suppression of DEH photochemistry in polycarbonate when dimethyl terephthalate is incorporated into the CTL but not when dimethyl isophthalate is. Fluorescence studies were also performed on DEH/PC samples with dimethyl terephthalate or dimethyl isophthalate dopant to further investigate the effect(s) of polyester on DEH photochemistry. Figure 11 summarizes the results of the changes in the emission spectrum from DEH (excited by 360-nm light) as a function of dimethyl terephthalate or dimethyl isophthalate addition. The emission was spectrally analyzed from 380 to 600 nm; for DEH, emission onset occurs at 390 nm and the band maximum at 497 nm. These data reveal that the emission from excited DEH is increasingly suppressed with addition

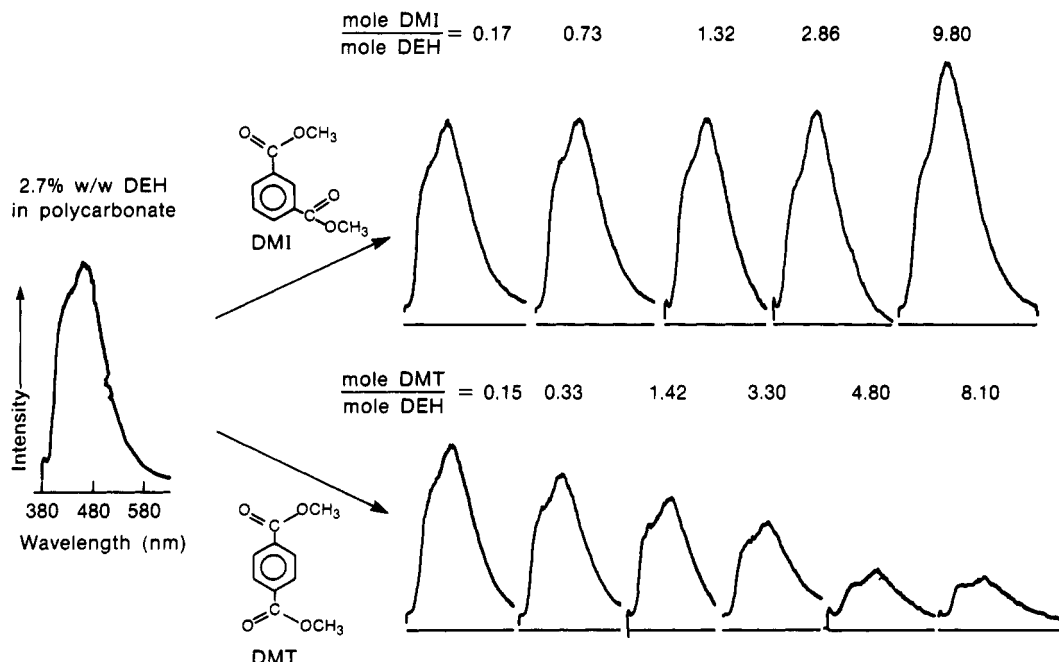


Figure 11. Emission spectra (excitation wavelength = 360 nm) from 3% DEH in polycarbonate mixtures, with addition of dimethyl isophthalate or dimethyl terephthalate. The number above each spectrum is the mole-to-mole ratio of the ester to DEH.

of dimethyl terephthalate but not with dimethyl isophthalate. Thus dimethyl terephthalate behaves as an efficient quencher for both the photochemistry and the fluorescence of DEH. From optical absorption measurements, the first excited singlet state of dimethyl terephthalate and dimethyl isophthalate (<300 nm or >4.15 eV), are well above that of DEH (≈ 370 nm = 3.4 eV). The lifetime for the DEH emission band ($\approx 10^{-6}$ s) suggests that the identity of the emitting species may be an excited singlet state of DEH; consequently, it is difficult to understand how DEH fluorescence is quenched by dimethyl terephthalate. However, the triplet energies of dimethyl terephthalate and dimethyl isophthalate are 3.16 and 3.33 eV, respectively,⁸ and the phosphorescent states of structurally related (substituted) dimethylanilines have triplet energies in the range 3.2–3.5 eV. Therefore, if DEH is considered to be primarily an aniline derivative, as has been demonstrated,⁹ then the lowest triplet state of DEH may be involved.^{10–14} Thus, we hypothesize that the photochemistry of DEH proceeds from a triplet state and that the emission is due to delayed fluorescence from S_1 , that is, thermally populated by the DEH triplet state. Polyester, with dimethyl terephthalate moieties, may then quench the photochemistry via triplet energy transfer and in doing so eliminate the channel for delayed fluorescence. One of the problems with this mechanism is that phosphorescence from a triplet state is not observed. Another possible mechanism may be that an exciplex is formed between excited DEH and dimethyl terephthalate, which decays nonradiatively; this latter mechanism may have more merit in view of the ineffectiveness of dimethyl isophthalate in quenching the emission from DEH. Here, it

is plausible that the geometry for a DEH–dimethyl terephthalate pair favors exciplex formation whereas that for DEH–dimethyl isophthalate does not. In view of the limited data presented here other reasonable mechanisms may be presented to explain the photochemistry; more work is presently in progress. Here, we have demonstrated that the electrical fatigue may unequivocally be attributed to DEH photochemistry, which in turn is moderated by the polymeric environment. The finding that polymer components in the charge-transport layer mediate photochemistry, and therefore the extent of photoconductor electrical fatigue and useful lifetime, is significant for the development of extended-life, robust photoconductors because attention will be required not only of initial electrical properties, to which present studies are largely limited, but also of long-term electrical properties after exposure to room light and light used to discharge organic photoconductors.

Concluding Remarks and Summary

Absorption of light by DEH, when formulated into the charge-transport layer of an organic layered photoconductor, induces profound changes in electrical properties called, in this case, blue light fatigue. The sometimes bizarre nature of the fatigue originates with DEH photochemistry, which is moderated by the particular polymeric environment of the CTL. We find that polycarbonate, polyacrylate, and polymethacrylate materials appear to be passive toward DEH photochemistry; in these materials the photochemical rate is the highest, resulting in a large increase in white voltage. Polyesters with acid end groups exhibit rapid increases in dark decay rate to the point where the photoconductor can no longer be charged; DEH photochemistry is implicated here but is different and involves carboxylic acid and the basic amine nitrogens of DEH. Polyesters consisting of terephthalate ester groups in the monomeric unit exhibit considerable reduction in DEH photochemistry; concomitantly, a negligible increase in residual voltage or other electrical properties is observed.

Registry No. PC, 24936-68-3; PE, 135928-57-3; MPE, 135928-58-4; *p*-(dimethylamino)benzaldehyde, 68189-23-1; chlorodiane blue, 41709-76-6; hydroxysquarylium, 63842-83-1.

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