Photoconductor Fatigue. 2. Effect of Long-Wavelength Light on the Electrical and Spectroscopic Properties of Organic Layered Photoconductors

J. Pacansky,* R. J. Waltman, and R. Cox

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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Electrical fatigue as a result of exposure to light emitted from lamps used to discharge photoconductors is a problem that limits the longevity of commercial organic photoconductors. We present data herein on a model organic layered photoconductor showing that the light initiates a solid-state photochemical reaction that is diffusion controlled and depends on the polymers used in the charge-transport layer. Most importantly, the reaction occurs at the interface of the charge generation and charge transport layers, between the hole-transport molecule *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH) and the carrier generation dye chlorodiane blue. The resultant photochemistry renders the organic photoconductor useless with regard to electrical properties. Depending upon the polymer chosen for the hole-transport layer, evolution of residual voltage during light decay, or an electrically conductive photoconductor in the dark, arises. Acidity in the hole-transport layer also appears to degrade the dark electrical properties upon exposure to discharge lamps.

Introduction

Organic photoconductors are central in electrophotographic applications such as electronic publishing, and with high-volume printing systems (500 000 copies/month) in demand, the search for robust photoconductors is an ardent endeavor of research.[1] To develop extended-life photoconductors for future applications, it is important to understand the parameters that limit the useful lifetimes of present organic photoconductors. In pursuit of this goal, we have fabricated a model organic layered photoconductor to study. From this system it is clear that several mechanisms are operative that undermine the lifetime of organic photoconductors: they include photochemistry of the charge-transport molecule and light-induced fatigue of the charge generating dye.[1] Both mechanisms cause fatigue of the electrical properties of organic photoconductors and have different origins. The first is a result of exposing the photoconductor to the blue component of light emitted from fluorescent lamps; it is alluded to as room light fatigue and, unless one operates in spectral regions where the photoconductor does not have absorption, will always be present. The second is a necessary consequence of operating the photoconductor: a discharge lamp that emits toward the red end of the visible spectrum is used to induce photocurrent. The material in the photoconductor that is responsible for absorption of light in this region is the dye in the charge generation layer (CGL). The changes in electrical properties as a result of exposure to the discharge light is commonly referred to as light fatigue.

A detailed study of the blue-light-induced photochemical effect on the electrical properties of organic layered photoconductors using hydrazone-based transport molecules such as *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH) has revealed a photocyclization and oxidation reaction of DEH to an indazole derivative as responsible in the adverse development of excessive residual surface charges during light decay.[2,3] Residual surface charges give rise to poor image contrast and memory effects; resolution of this problem was achieved by identifying the active transport site of DEH[4] and, subsequently, by suitable chemical derivatization of DEH away from the active hole-transport center to inhibit the photocyclization and oxidation reaction without sacrificing its original hole-transport properties.[3,5] This will have broad applications in hole-transport molecules used by the industry because of the striking structural similarity of present hole-transport molecules used in the industry. Conversely, investigation into the origins of discharge light-induced fatigue of the charge generation layer is a formidable task because of the generally intractable nature of the pigment or dye used in the charge generation layer and that basically it is a solid-state chemical reaction dependent upon the proximity of reactants and products. To our knowledge, there is a paucity of such studies in the literature, and the data base must be increased before reasonable conclusions are made. Accordingly, in this paper, we present some preliminary investigations into the long-wavelength-light-induced fatigue of photoconductors derived from the bisazo pigment chlorodiane blue. In the article immediately following, a discussion of the effects of blue light on the electrical properties of organic photoconductors is considered. Here we find that the origin of electrical fatigue is a long-wavelength-light-initiated photochemical reaction at the interface of the charge-generation (CGL) and charge-transport layers (CTL). Upon exposure of the photoconductor to long-wavelength light, the electrical properties are observed to change deleteriously concomitant with optical bleaching of the bisazo pigment, chlorodiane blue. To observe dye bleaching, hole-transport molecules are required at the CGL/CTL interface, suggesting a photochemical reaction between it and the dye are operative. The extent of the observed electrical fatigue is additionally strongly dependent upon the choice of the actual hole-transport molecule and the polymeric binder used in the charge-transport layer. When certain hole-transport molecules or polymeric binders are used, dye bleaching can actually be slowed or inhibited.

Structure of the Organic Layered Photoconductor

In the work presented here and in subsequent reports, a model photoconductor is used whose composition and structure is well-established. The overall composition of the photoconductor follows those used commercially and thus should serve as a useful test model from which relationships of electrical properties on organic materials may

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[1] Nguyen, K. C.; Weiss, D. S. *Electrophotography* 1988, *27*, 2.

[2] Pacansky, J.; Coufal, H.; Brown, D. W. *J. Photochem.* 1987, *37*, 293.

[3] Pacansky, J.; Waltman, R. J.; Grygier, R.; Cox, R. *Chem. Mater.* 1991, *3*, 454.

[4] Pacansky, J.; McLean, A. D.; Miller, M. D. *J. Phys. Chem.* 1990, *94*, 90.

[5] Pacansky, J.; Waltman, R. J.; Cox, R. Manuscript to be submitted.

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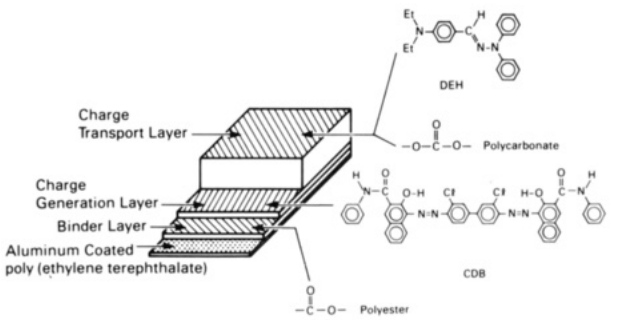

Figure 1. Compositional profile of an organic layered photoconductor.

be understood. A brief summary of the structure of the model organic layered photoconductor is presented here. As shown in Figure 1, the model organic photoconductor is composed of several key layers. Aluminum-coated ($\simeq$300 Å) poly(ethylene terephthalate) serves as a substrate and electrical ground. A binder layer, a polyester, is coated atop the aluminized polymer substrate and serves to adhere the next layer, the charge-generation layer (CGL). The CGL is composed of an organic dye such as chlorodiane blue, which absorbs visible light in the presence of a strong electric field to generate free carriers. Atop the charge generation layer is the charge-transport layer (CTL), composed of a charge-transport molecule such as the hydrazone DEH, dispersed typically to 40% by weight in a polymeric matrix. While Figure 1 is representative of typical commercial formulations for organic layered photoconductors, a variety of materials may be used as charge-generation and charge-transport molecules. A summary of the types of molecules used by various groups have been given by Nakanishi.[6]

The optical absorption spectrum of the organic layered photoconductor is shown in Figure 2. The CTL absorbs light $\lambda < \simeq 500$ nm, which in this case mandates that longer wavelength light must be used to expose the CGL for carrier generation. Once the absorption characteristics of the photoconductor have been determined, at this point it is convenient to express the spectral dependence of the light-induced fatigue in more familiar terms; the portion of the light emitted from fluorescent lamps that is absorbed by the CTL lies in the blue region of the visible; henceforth, we will refer to the electrical fatigue that results from absorption in this spectral region as "blue light fatigue". The spectral output of discharge lamps used to expose and generate charge in the CGL is in the longer wavelength region of the visible spectrum and has a yellow color; hence, electrical fatigue that thus results is referred to as "yellow light fatigue".

Since the charge-transport layer has significant absorption out to $\simeq$480 nm (in the blue region) photochemical changes in the CTL occur; this has been shown to be a direct result of the high quantum yield for photochemistry exhibited by the charge-transport molecule, DEH,[7] absorbing light at these wavelengths. The source of the yellow light or discharge light fatigue is caused by absorption of longer wavelength light, $\lambda > 520$ nm, by the dye chlorodiane blue at the CGL/CTL interface; this is the topic of the present paper.

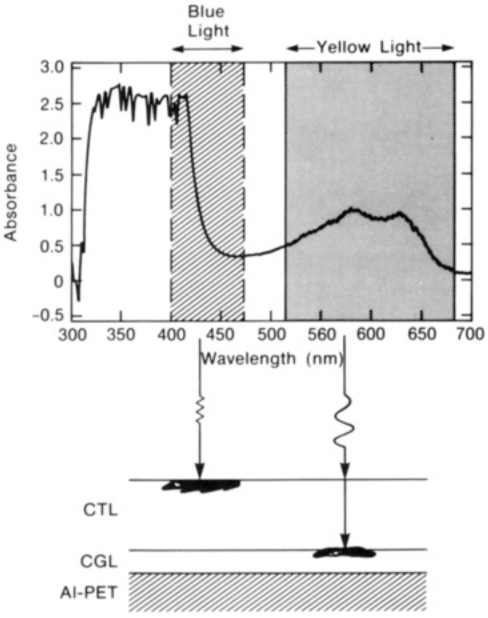

Figure 2. Optical absorption spectrum of an organic layered photoconductor depicted in Figure 1. The intense, broad absorption band between 320 and 450 nm is attributed to the CTL (40% DEH in polymer, 20 μm thick), while the broad bands between 500 and 680 nm is due to the CGL (chlorodiane blue, $\simeq$0.1–0.2 μm thick). Blue light absorption by the CTL (DEH) results in photochemistry at the air/CTL interface, while yellow light absorption by the CGL results in photochemistry initiated at the CGL/CTL interface.

Experimental Section

Chlorodiane blue, polyester, and polycarbonate were obtained from commercial sources. The synthesis of DEH and its derivatives are fully described in ref 5. Photoconductors were formulated in the following manner: coating sequentially, a 0.1-μm binder layer of polyester on aluminized poly(ethylene terephthalate) was coated from tetrahydrofuran. The charge-generation layer was next coated, chlorodiane blue from ethylene diamine to a thickness of 0.1–0.2 μm. The charge-transport layer was next coated, 40 wt % DEH in polymer(s) from tetrahydrofuran to a thickness of 20 μm. All layers were coated by using the draw coating technique.

For yellow light fatigue studies of the electrical properties of the photoconductors, a fluorescent desk lamp (light source Inter-World 8CW) with a spectral output of $\simeq$400–800 nm was used. To isolate yellow light, the lamp was filtered with a Corning CS 3-69 filter to allow transmission of light between 520 and 800 nm. The incident energies were measured with a United Detector Technology Model 371 optical power meter equipped with a Model 262 head assembly: yellow light (incident power = 1 mW/cm^2).

For the electrical fatigue studies, the photoconductor was first exposed to yellow light in air at room temperature, and then the electrical properties were measured by using a rotating disk electrometer modified for computer-controlled data acquisition, as described in detail previously.[8] For light discharge of the photoconductors in the rotating disk electrometer, an erase lamp fitted with a CS 3-69 filter was used; the incident energy on the photoconductors was $\simeq$20 μW/cm^2. For UV–visible studies of dye bleaching, exposures were carried out using a Xe arc lamp filtered with 8 cm of water and CS 3-69 and 1-57 filters in tandem. The incident power was 25 mW/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 charge-transport layer of 40% by weight of DEH in polymer (34% polycarbonate, 16% polyester, 10% polyacrylate/polymethacrylate copolymer) and a charge-gen-

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(6) Nakanishi, K. *Nikkei New Mater.* **1987**, *41*.

(7) Pacansky, J.; Coufal, H.; Waltman, R. J.; Cox, R.; Hsing, H. *Radiat. Phys. Chem.* **1987**, *29*, 219.

(8) Pacansky, J.; Waltman, R. J.; Coufal, H.; Cox, R. *Radiat. Phys. Chem.* **1988**, *31*, 853.

eration layer (CGL) of chlorodiane blue, are shown in parts a and b of Figure 3, respectively. A blend of polymers in the charge-transport layer (CTL) is commonly used in the industry to optimize various properties, e.g., mechanical properties, of the layered photoconductor. Before exposure (in air) to "yellow light", i.e., white light filtered to transmit in the range λ = 520–800 nm, the dark decay curve is observed to hold charge and, upon exposure to a discharge light (i.e., light decay curve), the surface potential drops to ambient, ≃50 V; thus there is initially no evolution of residual surface voltage. When the organic layered photoconductor is exposed to yellow light and its electrical properties are measured, the dark and light decay curves are observed to change dramatically as a function of incident energy. The dark decay rate increases significantly to the point where the photoconductor becomes persistently electrically conductive; it no longer exhibits the required property of being an electrical insulator in the dark. Consequently, a latent electrostatic image cannot be formed with adequate contrast, and the photoconductor becomes completely unacceptable for electrophotographic applications. We coin the acronym "yellow light fatigue" to characterize this behavior. We observe that approximately several J/cm^2 of incident energy is all that is required to observe yellow light fatigue. In a typical application of organic photoconductors such as in copying, the incident energy of a discharge lamp erase station is of the order of 20–200 μJ/cm^2; consequently, the number of cycles a photoconductor may endure before fatigue (defined at say, 1 J/cm^2) necessitates replacement at 5000–50 000 copies, far short of the extended-life goal of more than 500 000 copies alluded to in the Introduction. As shown in Figure 3c,d, the initial electrical properties of the photoconductor may be recovered by annealing the organic photoconductor at a temperature close to its glass transition; the number of such "recoveries" is finite and has its origins from refreshment of the photoconductor interfaces by diffusion. Recovery of the initial electrical properties will be discussed in a later section.

Polymer Matrix Effects. Electrical Properties as a Function of Polyester in the CTL. While polymer blends are often used in commercial photoconductors as the polymer matrix in the charge-transport layer, we have observed during the course of the experiments that useful information may be garnered by observing light-induced electrical fatigue in individual polymers. For example, persistent dark conductivity or evolution of residual voltage after light decay may predominate depending upon the chemical composition of the polymer host. In this section, light-induced electrical fatigue as a function of polymer composition in the charge-transport layer (CTL) is investigated.

The dark and light decay curves as a function of incident energy for an organic photoconductor with a CTL composed of 40% DEH in polycarbonate are shown in Figure 4a,b. Two changes are observed as a function of incident energy: there is a modest decrease in the dark voltage and, most importantly, evolution of residual voltage becomes evident during light decay which was not observed previously in the photoconductor whose charge-transport layer was formulated from a polymeric blend (Figure 3). In a DEH/polycarbonate based CTL, the dark voltage decrease is minimal and only decays by ≃5% after 20 J/cm^2 of light energy are incident on the photoconductor, in contrast to the 35% drop observed in Figure 3a for the polymer blend. The dark decay rate remains relatively constant at ≃2–3 V/s even after yellow light exposure of incident energies up to 20 J/cm^2, under these conditions.

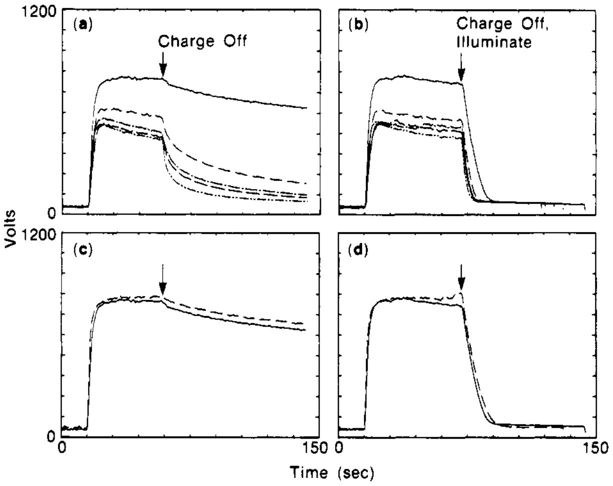


Figure 3. (a) Dark and (b) light decay curves as a function of incident yellow light (1.09 mW/cm^2, 520–800 nm) for an organic photoconductor derived from a CGL composed of chlorodiane blue, and a CTL of 40% by weight of DEH in a polymer blend (34% polycarbonate; 16% polyester; 10% polyacrylate/polymehacrylate copolymer). For (a) and (b), 0 (—), 4 (– – –), 8 (– - –), 12 (–·–), and 20 J/cm^2 (– - - –). Figures c and d illustrate the effect of annealing (T = 60 °C for several hours) the photoconductor sample previously exposed to 20 J/cm^2 of yellow light. The annealed sample (– – –) is compared with a virgin photoconductor sample (—).

When polyester is formulated into the DEH/polycarbonate charge-transport layer such that it comprises a weight concentration of 9%, the dark and light decay curves as a function of yellow light change dramatically (Figure 4c,d). First the dark voltage drops by ≃15% after 20 J/cm^2. Second, the initial dark decay rate increases to ≃10 V/s after only 4 J/cm^2 incident energy. Thus, addition of polyester into the polycarbonate-based charge-transport layer has the effect of increasing the dark electrical conductivity of the organic photoconductor after it is exposed to yellow light. The increase in the electrical conductivity does, however, eliminate also the residual voltage that would otherwise develop in a photoconductor with a polycarbonate-based CTL after exposure to yellow light.

When the concentration of the polyester is increased in the polycarbonate-based charge-transport layer to 26% by weight, the dark electrical conductivity of the photoconductor after yellow light exposure increases further, with the dark voltage after 20 J/cm^2 dropping by ≃18%, and the initial dark decay rate after 4 J/cm^2 of incident energy increasing to ≃15 V/s (Figure 4e,f). Residual voltage during light decay is absent up to 20 J/cm^2 incident yellow light.

Finally, when the polymer used in the charge-transport layer is composed entirely of polyester, the electrical conductivity of the CTL increases significantly as a function of yellow light (Figure 4g,h). The dark voltage drop after 20 J/cm^2 is ≃44%, and the initial dark decay rate is ≃140 V/s. There is no residual voltage during light decay even after 80 J/cm^2. Thus we observe that as the relative concentration of the polyester is systematically increased in the charge-transport layer formulation, so is the drop in dark voltage and increase in dark decay rates. A summary of these changes as a function of ester content, and after exposure to yellow light of 20 J/cm^2, is shown in Figure 5. A persistently electrically conductive state is approached with increasing ester content, after yellow-light-induced fatigue of the organic photoconductors.

The chemical structures of the polyesters used in these studies are shown in Scheme I.

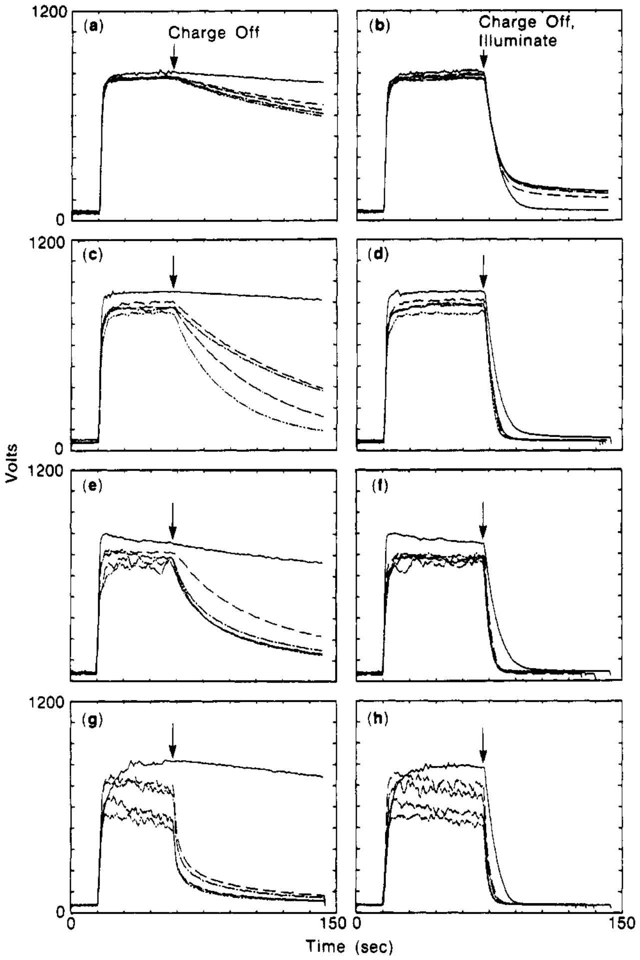


Figure 4. Comparison of the dark and light decay curves for photoconductor samples with varying CTL formulations as a function of incident yellow light (1.09 mW/cm^2; 520–800 nm). (a) and (b) 40% DEH, 60% polycarbonate; (c) and (d) 40% DEH, 9% polyester, 51% polycarbonate; (e) and (f) 40% DEH, 26% polyester, 34% polycarbonate; (g) and (h) 40% DEH, 60% polyester. For all samples, the incident exposures were 0 (—); 4 (---); 8 (- - -); 12 (-•-); and 20 J/cm^2 (----).

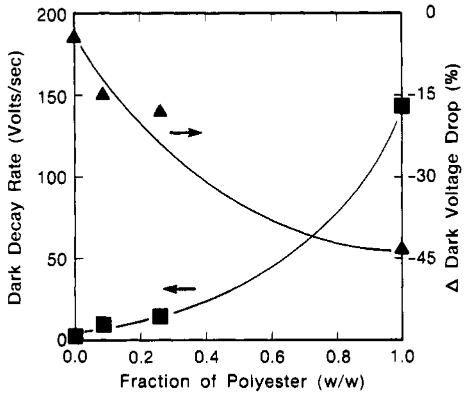
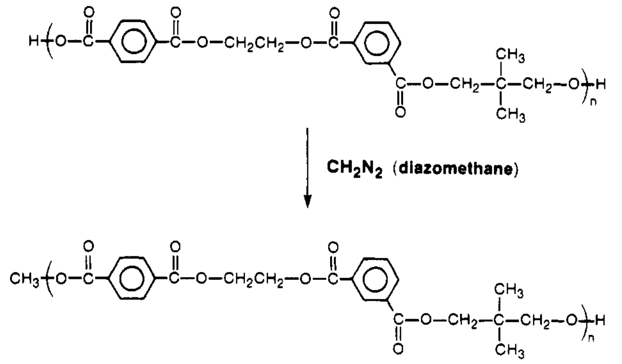


Figure 5. Summary from Figure 4: the effect on the dark electrical properties of photoconductors exposed to yellow light after 20 J/cm^2 incident energy, as a function of ester content in the charge transport layer.

The persistently conductive state developed in the photoconductor as a result of yellow light exposure is attributed to acid content in the polyester; thus acidity can deleteriously affect longevity of the electrical properties of organic photoconductors which are subject to discharge light, and a detailed discussion follows.

Scheme I



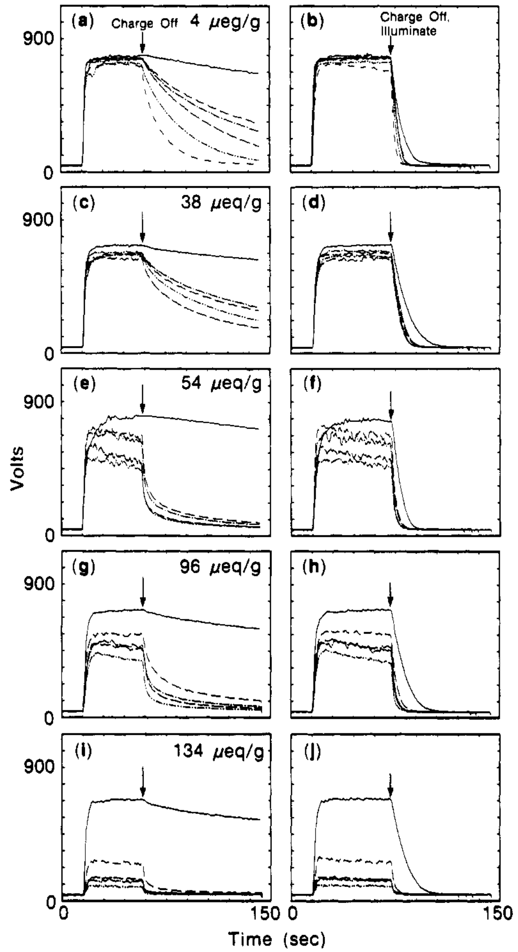


Figure 6. Dark (left column) and light (right column) decay curves for photoconductors as a function of incident yellow light (1.09 mW/cm^2, 520–800 nm). The charge-transport layer is composed of 40% DEH in polyester; the acidity of the polyester (microequivalent/gram) is varied and is specified in the appropriate figures. For (a)–(j) the incident energies are 0 (—); 4 (---); 8 (- - -); 12 (-•-); 20 (----) J/cm^2; additionally, and only for (a) and (b), 80 J/cm^2 (---).

The dark and light decay curves for photoconductors with CTLs derived from DEH/polyesters of varying acidity are shown in Figure 6. The degree of acidity in the polyester was controlled in several ways: first, to remove acid, the polyester was treated with diazomethane[9,10] to "cap" the acid with a methyl ester. Second, the molecular weight of the polyester was decreased to increase the number of acid end groups, and/or the polymerization was terminated by addition of acid anhydrides to create acid functional groups. The acid number of each polyester was then de-

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(9) *Aldrichim. Acta* **1983**, *16*, 3.

(10) Pacansky, J.; Waltman, R. J. *Chem. Mater.*, following article in this issue.

Table I. Acid Number and Molecular Weight of the Polyesters

polym	acid no., μequiv/g titrated	acid no., μequiv/g calcd	M_n
PE-4	4	40	25 000
PE-38	38	59	17 000
PE-54	54	71	14 000
PE-96	96	118	8 500
PE-134	134	172	5 800

termined by titration, and these data are summarized in Table I. The abbreviation used in Table I for the various polyesters merely defines the experimentally derived acid number values, i.e., PE-4 is the polyester with an acid number of 4 microequiv/g. Inspection of Table I reveals that, for the samples investigated herein, the acid content correlates with the molecular weight of the polymer. Thus by decreasing the molecular weight of the polyester, smaller chains and therefore more acid end groups are present. Organic photoconductors were then formulated by using exclusively in the CTL 40 wt % DEH in each of the polyesters shown in Table I below. In Figure 6, the dark decay curves as a function of exposure to yellow light and of acid content in the CTL clearly illustrate the effect of the acid on the yellow-light-induced fatigue of the dark electrical properties: the greater the acid content in the CTL, the faster the drop in dark voltage and increase in dark decay rate. No residual voltage during light decay is observed here, under these conditions. Since the drop in dark voltage is small for low acid numbers, increasing the molecular weight of the polyester may effectively control acidity to the point where it approaches the diazomethane-treated polyester. Conversely, they can be simply capped with diazomethane treatment. We note that there is a difference between the measured and calculated (from the measured M_n) acid values. This may be due to systematic experimental error in the titrated values for the acid numbers and the molecular weight determinations or that some of the end groups are not acid but rather some other functional group. Most importantly, the trend of increasing acidity in the charge-transport layer correlates with the increase in the electrical fatigue of the photoconductors.

The photoinduced discharge curves, shown in Figure 6, are indeed very revealing. Initially, when the photoconductors are not exposed to yellow light, the dark and light decay curves are essentially indistinguishable for the various charge-transport layer polyesters. The decay in the electrical properties manifest themselves only after the photoconductors are exposed to yellow light. Thus, as the acid number of the polyester used in the CTL is increased, the dark voltage decreases and the dark decay rates increase; the photoconductors become persistently conductive and no longer hold charge. These studies conclude that acidity in CTL polyester will have deleterious consequences upon the electrical properties of the photoconductor after exposure to long-wavelength light-discharge lamps. Finally, it is important to compare Figure 6a,b with Figure 4a,b. In Figure 4a,b we observed that a CTL derived from DEH/polycarbonate resulted in evolution of residual voltage as a function of incident energy, during light decay. In comparison, a charge-transport layer derived from DEH/PE-4 revealed good dark charge acceptance despite exposure to light, with no evolution of residual voltage.

We make one additional and important comment here. All of the deleterious effects on the electrical properties of the organic photoconductor caused by exposure of the photoconductor to yellow light is initiated by absorption of the yellow light by the dye chlorodiane blue. In particular, when the charge-transport layer is coated directly upon the aluminized polymer substrate, without the charge-generation layer, and subsequently corona charged in the dark or light, there is no charge decay. Prolonged exposure of the dyeless photoconductor to yellow light does not change its insulating electrical properties in any way. When such a photoconductor is corona-charged negatively, the charges remain on the surface of the charge-transport layer and decay at the same rate as the unexposed, dyeless photoconductor. Thus the origin of yellow-light-induced electrical fatigue in the conventional organic photoconductor is not due to any bulk effects induced in the charge-transport layer exclusively but rather is an interfacial process between the charge generation and transport layers. The dye absorbs the light first and, after excitation, interacts with hole-transport molecules nearby and undergoes photochemistry. These aspects will be discussed in greater detail below.

In conclusion, the electrical properties as a function of polymer in the CTL have revealed that electrical fatigue after light exposure is extremely sensitive to the particular polymer. Depending upon the polymer and/or acid content in the CTL, dark or light decay curves may be adversely affected. Even in the best cases, the formulations used in these studies have exposure lifetimes of several J/cm^2 before replacement must be considered. In the next section, the origins of light induced fatigue are investigated.

Evidence for Chlorodiane Blue Dye Bleaching. It is important to consider that the changes observed in the electrical properties as a function of incident yellow light energy are yellow light driven; thus a reasonable starting point is to investigate the effect of yellow light on chlorodiane blue, both in the presence and absence of a charge-transport layer overcoat.

The changes in the UV-visible absorption spectrum of chlorodiane blue as a function of charge-transport layer polymer and exposure temperature are shown in Figures 7 and 8. For $T < \simeq 50$ °C, the changes in the absorption spectrum as a function of yellow light were too slow to complete the experiment in a reasonable time and were therefore excluded; however, these may be extrapolated from the higher temperature results. Even at $T = 53$ °C the photoconductor must be exposed to light of the order of kJ/cm^2, to observe small changes in the optical absorption spectrum of the dye. Only when the exposures are performed at a higher temperature, e.g., at $T = 102$ °C, do the changes require less energy and less time, allowing conclusion of the experiments in a reasonable time limit. From a discussion of the electrical fatigue data, it is apparent that less than 10 J/cm^2 is required to cause significant fatigue of the electrical properties at room temperature. Clearly, electrical properties are much more sensitive to small changes of the structure in the photoconductor, particularly at the interface of the charge-generation layer (CGL) and the charge-transport layer (CTL) because only molecules at the interface need be affected. If the molecules at the CGL/CTL interface are destroyed, carrier generation and injection will be affected. We can estimate the changes in optical density expected as a result of destroying dye molecules at the interface. Consider a sample of chlorodiane blue dye of 1 cm^2 area, with a 0.1-μm-thick layer ($\rho = 1.2$ g/cm^2; MW = 802 g/mol). The total number of molecules contained in a 0.1-μm-thick film of unit area (1 cm^2) is approximately 9.0×10^{15}. If we assume that one chlorodiane blue molecule occupies 500 Å^2, then there are (in 1 cm^2) $\simeq 2 \times 10^{13}$ molecules of chlorodiane blue at the interface. If we

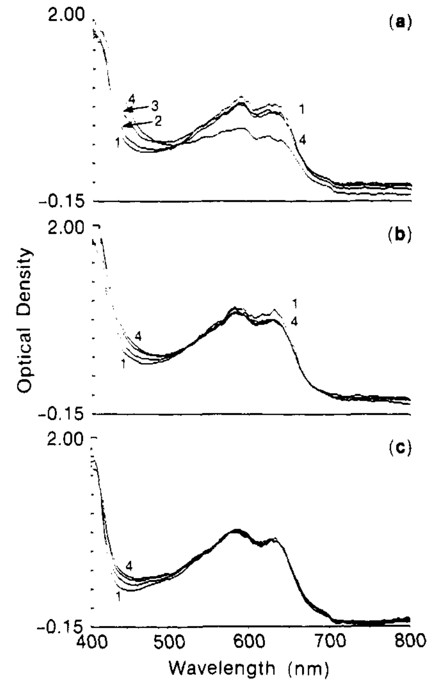


Figure 7. Optical absorption spectra as a function of incident yellow light (25 mW/cm^2; 520–800 nm) at T = 53 °C for: (a) 40% DEH in PE-54; (b) 40% DEH in PE-4; (c) 40% DEH in PC. For all curves, traces 1–4 correspond to 0, 2.4, 4.1, and 6.3 kJ/cm^2, respectively.

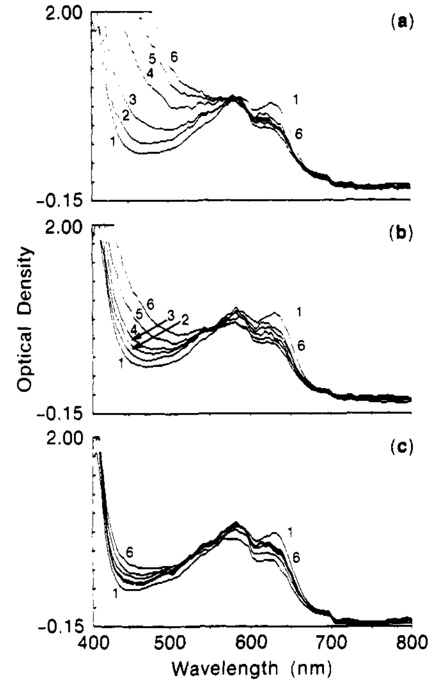
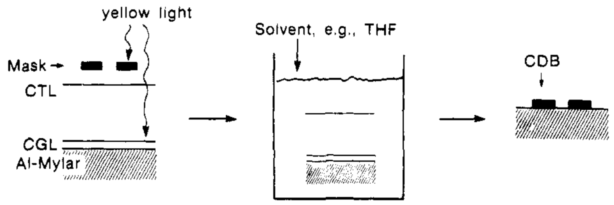


Figure 8. Optical absorption spectra as a function of incident yellow light (25 mW/cm^2; 520–800 nm) at T = 102 °C for: (a) 40% DEH in PE-54; (b) 40% DEH in PE-4; (c) 40% DEH in PC. For all curves, traces 1–6 correspond to 0, 180, 275, 410, 640, and 870 J/cm^2, respectively.

conservatively assume that all of the chlorodiane blue molecules at the interface must be destroyed to observe a significant barrier to charge injection (and therefore residual voltage), then the fraction of molecules destroyed is 0.002. This represents too small a change to observe with any degree of accuracy in the optical absorption spectrum (see Figure 2). Thus while electrical damage may be extensive, optical damage would appear small. Thus it becomes necessary to expose a photoconductor much longer to yellow light, i.e., much greater than several tens of J/cm^2, to observe significant changes in the optical absorption spectrum. Alternatively, the temperature at which yellow light exposure of the photoconductor is performed may be raised to increase diffusion and therefore the rate of photochemistry. Thus the data presented above represent an upper limit of photochemical fatigue.

Scheme II



As will be discussed below, accompanying the exposures of the photoconductor to yellow light is a gradual change of the blue color of the CGL, due to chlorodiane blue, to an overall red-brown color of the photoconductor giving rise to a broad absorption band that covers the wavelengths from approximately 400 to 600 nm. At T = 53 °C, the UV-visible absorption spectrum as a function of yellow light for photoconductor formulations with CTLs derived from DEH/PE-54, DEH/PE-4, and DEH/polycarbonate are shown in Figure 7a–c. The spectrum of the photoconductor with a CTL of DEH/PE-54 at various exposures to yellow light reveal that the absorption due to chlorodiane blue dye decrease and a new, broad absorption band at ca. 400–500 nm becomes evident. When PE-54 is replaced by PE-4 or polycarbonate, dye bleaching is observed to proceed comparatively more slowly. At T = 102 °C, the relative rates of photochemistry are clearly discernible (Figure 8); the changes in the absorption spectra are fastest for DEH in PE-54, slowest for DEH in polycarbonate, and intermediate for DEH in PE-4. Thus the photochemistry, much like the electrical fatigue, is apparently accelerated by the presence of acid in the CTL. We conclude from Figures 7 and 8 that yellow light causes the chlorodiane blue dye to be consumed in a solid-state photochemical reaction. When DEH was removed from the charge-transport layer and the chlorodiane blue exposed to yellow light under identical conditions but with only a polymer overcoat, either polycarbonate or polyester, no dye bleaching was observed. When a 0.6-μm-thick polymer film was placed in between the charge-generation layer and the DEH-containing CTL, no dye bleaching was observed. Thus we conclude that DEH must also be involved in the photoreaction. As further investigation, a standard photoconductor formulation with a CTL of 40% DEH/polymer blend and a CGL of chlorodiane blue on aluminized polymer substrate was exposed to yellow light through a mask, as shown in Scheme II.

The total exposure was 10 kJ/cm^2 at 80 °C; the regions of the photoconductor covered by the mask remained blue but the exposed regions colored red-brown. The photoconductor was then washed with tetrahydrofuran solvent, and it was found that the dye in the unexposed regions covered by the mask remained insoluble whereas the exposed regions became soluble. This clearly shows that the yellow light photochemically transforms the dye and, for it to have become completely soluble in a solvent, drastic changes in its chemical structure have occurred.

In view of the optical bleaching experiments discussed above, we may now rationalize the thermal recovery of the initial electrical properties observed in Figure 3c,d. The bleaching studies concluded that a solid-state photochemical reaction between chlorodiane blue and DEH destroys the CGL/CTL interface by introducing photoproducts. By annealing the photoconductor to a temperature near or above its glass transition temperature, the CGL/CTL interface is refreshed by the diffusion of photoproduct away from the interface. Since the concentration of photoproducts is initially small, this is enough to recover most of the initial electrical properties. However, since repeated exposure to yellow light and annealing eventually reacts most of the chlorodiane blue with DEH, the number of such "recoveries" of the initial electrical properties is finite. In this case, the electrical properties eventually degrade because (1) not enough carrier generation molecules are left for efficient hole injection into the charge-transport layer and (2) traps in the charge-transport layer inhibit carrier flow.

Chlorodiane Blue Bleaching Experiments with and without DEH. In the previous section, it was shown that upon exposure of the photoconductor to yellow light, a photochemical reaction is initiated that consumes chlorodiane blue. The experiments described below uncover more details about the nature of this reaction. When chlorodiane blue is coated with a charge-transport layer that *does not* contain DEH, that is, only polyacrylate, polyester, and polycarbonate, either as a mixture or individually, and the standard bleaching experiments are repeated, the absorption spectrum of chlorodiane blue does not change even after extensive exposure. In the presence of the above listed polymers, chlorodiane blue bleaching is observed only when a hydrazone is incorporated into the formulation. It is also pertinent to add that amines (depending on basicity) whether in the form of organic molecules in the normal molecular weight range, or part of polymer chain also induce chlorodiane blue bleaching when incorporated in a CTL formulation.

Thus, the results implicate DEH as a partner in the photochemical reaction that is responsible for chlorodiane blue bleaching. While on one hand it is gratifying that the source of the yellow light fatigue is identified, however, on the other hand, DEH and chlorodiane blue molecules must come into contact at the CGL/CTL interface for charge injection to occur; the most important step in the electrophotographic process involves fatigue. The obvious solution to this problem is inversely related to the efficiency of the photoconductor; to reduce the chlorodiane blue bleaching, separate DEH from chlorodiane blue, but this reduces charge injection because molecular contact is required.

Quantum Chemistry: DEH–Chlorodiane Blue Interaction. When a CTL is coated onto the CGL, intramolecular interaction between DEH and chlorodiane blue determine the eventual structure of the materials. It is important to understand how the molecules are oriented relative to each other because (1) charge injection depends on this geometry and (2) it provides an understanding for where the reactive sites of chlorodiane blue and DEH might occur. This will be discussed in more detail in a subsequent report; here, we discuss some general aspects of the chlorodiane blue structure and provide quantum chemical calculations for their charge distributions. This involved geometry optimizations for both chlorodiane blue and DEH and, due to the size of the molecule, were limited to the semiempirical AM1 calculations[11] using the IBM vectorized version of GAUSSIAN 88 computer code.[12]

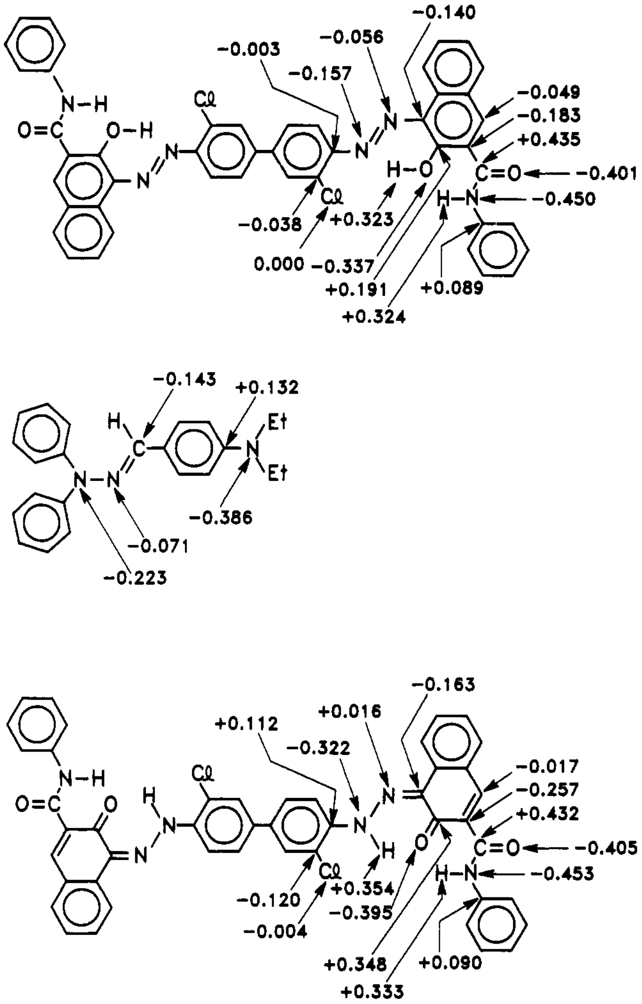
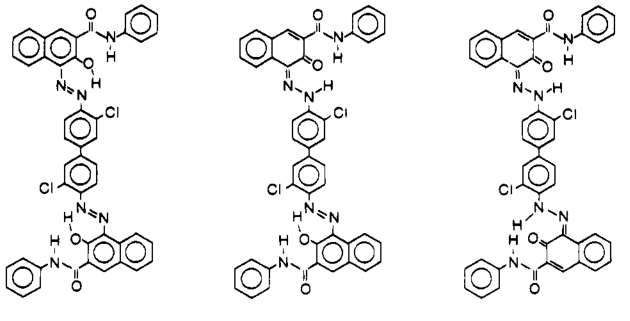


Figure 9. Semiempirical AM1 net charges on chlorodiane blue–AA, chlorodiane blue–HH, and DEH.

Chart I



CDB-AA CDB-AH CDB-HH

While chlorodiane blue is formally considered to be an azo dye, it in fact exists in several forms, an azo–azo form, a hydrazone–hydrazone form, and an azo–hydrazone form as shown in Chart I. The crystal structures for related azo dyes investigated by Whitaker[13] strongly suggest that in the solid state the hydrazone form is preferred. However, in solution the actual structure of chlorodiane blue is strongly dependent upon the polarity of the solvent,[13f] and because chlorodiane blue is solvent-coated, both forms were theoretically investigated. In Figure 9, net charges

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[11] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[12] Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. GAUSSIAN 88; Gaussian, Inc., Pittsburgh PA.

[13] (a) Whitaker, A. *Z. Kristallogr.* **1977**, *145*, 271. (b) Whitaker, A. *Z. Kristallogr.* **1985**, *171*, 17. (c) Whitaker, A. *Z. Kristallogr.* **1984**, *166*, 177. (d) Whitaker, A. *Z. Kristallogr.* **1981**, *156*, 125. (e) Whitaker, A. *Z. Kristallogr.* **1977**, *146*, 173. (f) Zollinger, H. *Azo and Diazo Chemistry*; Interscience: New York, 1961.

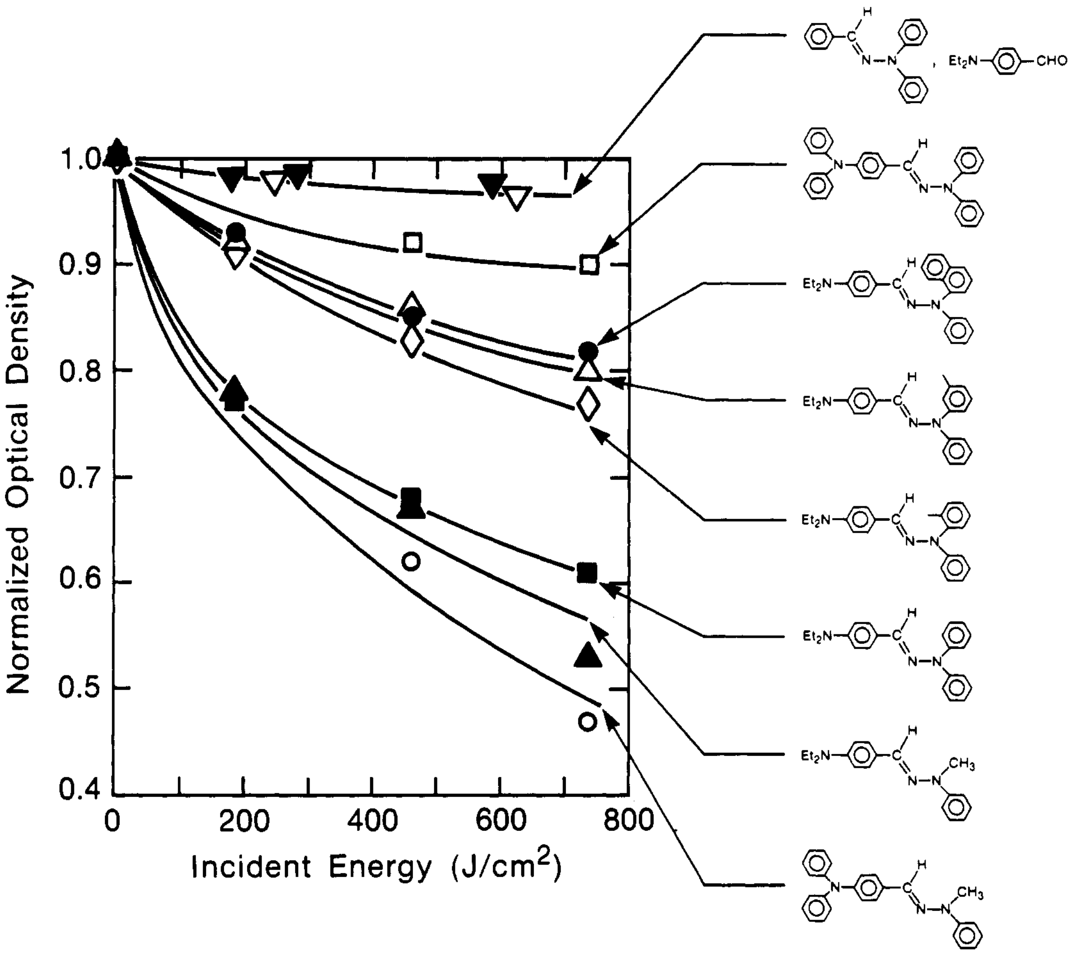

Figure 10. Normalized optical density of chlorodiane blue at 630 nm as a function of incident energy for photoconductors formulated from 40% by weight of DEH derivatives in polycarbonate, coated atop chlorodiane blue.

are tabulated for the azo–azo and hydrazone–hydrazone form of chlorodiane blue, along with the hole-transport molecule DEH; for the purpose of this report, only the pertinent atoms with large atomic charges are shown. Note that for DEH the aniline and the hydrazone amines are strongly negative; this is also true for hydrazone amine in chlorodiane blue and the amide nitrogen and oxygens in both the azo and hydrazone tautomer. The strongly positive centers are the carbon atoms in the amide groups in both tautomers. On the basis of the charges one would expect either or both amine nitrogen atoms of DEH to complex with the carbonyl groups of chlorodiane blue. In spite of the theoretical predictions, a DEH complex with the chlorinated biphenyl structure was expected. The rationale here was mostly prejudiced by past studies on photoinduced electron-transfer reactions between aniline and chlorinated biphenyls;[14] in this case photoexcitation of aniline initiates an electron transfer to the chlorinated biphenyl to form radical ions and ultimately HCl and other products. Consequently, a chlorodiane blue dye without Cl atoms on the biphenyl ring was prepared, a photoconductor prepared, and bleaching experiments conducted. These results were identical with those using chlorodiane blue, and as a consequence more credence was placed on the theoretical directions.

Altering the naphthamide part of chlorodiane blue proved to be problematic, mostly because the color of the dye is sensitive to structural changes in this part of the molecule; therefore, it was more attractive to consider DEH. Hence, a series of DEH derivatives were prepared to allow or hinder the approach of the DEH amine nitrogens toward chlorodiane blue. The chemical structures and acronyms for the DEH derivatives are summarized in Table II. If access to the basic amine nitrogen atoms could be hindered the light-induced photoreaction may be reduced, and an approach to understanding and modifying yellow light fatigue could be established. The results of the yellow light bleaching of the dye as a function of incident energy and of DEH derivatives is summarized in Figure 10. In general, it is observed that the bulkier the substituents around the aniline and hydrazone amine nitrogen atoms, the less extensive is the bleaching of the chlorodiane blue dye.

Comparison of Yellow Light Fatigue. Here, to complete a part of the yellow light fatigue saga, the effect of yellow light on the photoinduced discharge curves of photoconductors containing all of the DEH derivatives shown in Table II are discussed. In all cases, the charge-transport layer is composed of 40% by weight of the DEH derivatives in polycarbonate; the charge generation layer is chlorodiane blue. Evolution of residual surface voltage during light decay was observed only for DEH, DEH-DPA, and MPDEH-DPA, i.e., the latter two hydrazones containing bulky substituents on the aniline amine nitrogen atom. The residual voltages were observed after several J/cm² of yellow light was incident on the photoconductor samples. Many of the photoconductors also developed increased dark electrical conductivity as a function of yellow light exposure. The effect on the dark decay rate as a function of extent of chlorodiane blue

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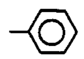
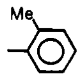
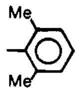
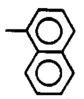
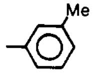
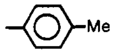
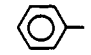
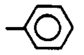
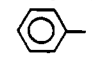
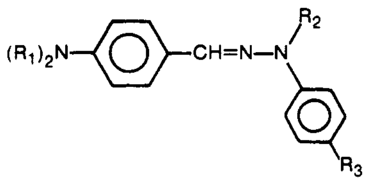
[14] (a) Chesta, C. A.; Cosa, J. J.; Previtali, C. M. *J. Photochem.* **1987**, *39*, 251. (b) Chesta, C. A.; Cosa, J. J.; Previtali, C. M. *J. Photochem.* **1986**, *32*, 203.

Table II. Chemical Structure of DEH Derivatives and Their Corresponding Abbreviations[a]

abbr	colloquial name	R_1	R_2	R_3
DEH	DEH	CH_3CH_2–		H
OMDEH	*o*-methyl-DEH	CH_3CH_2–		H
DOMDEH	di-*o*-methyl-DEH	CH_3CH_2–		H
1NDEH	1-naphthyl-DEH	CH_3CH_2–		H
MMDEH	*m*-methyl-DEH	CH_3CH_2–		H
DPMDEH	di-*p*-methyl-DEH	CH_3CH_2–		–CH_3
DEH-DPA	DEH–diphenylamine			H
MPDEH-DEA	methylphenyl–DEH diethylamino	CH_3CH_3–	–CH_3	H
MPDEH-DPA	methylphenyl-DEH diphenylamino		–CH_3	H

[a]


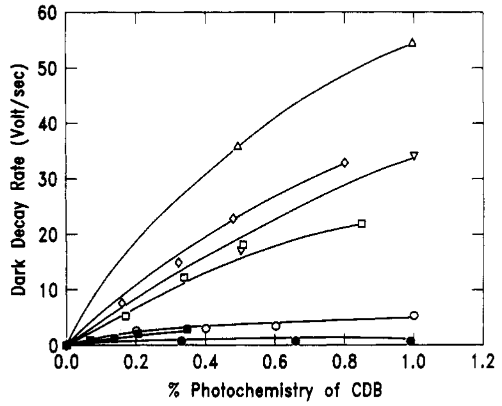


Figure 11. Changes in the dark decay rate of organic photoconductors as a function of chlorodiane blue photochemistry: MPDEH-DEA (△), 1NDEH (◇), DEH (▽), MMDEH (□), OMDEH (○), DEH-DPA (■), and MPDEH-DPA (●).

photochemistry is summarized in Figure 11. It is observed that the smallest increases in dark decay rate occur for the DEH molecules with the bulkier substituents on the aniline amine nitrogen atom. These results suggest that interaction between chlorodiane blue and the amine nitrogen atom of DEH may be sterically inhibited by the bulkier substituents; more work is presently in progress.

Concluding Remarks and Summary

Electrical fatigue as a result of exposure to light emitted from lamps used to discharge photoconductors is a problem that limits the longevity of commercial photoconductors. We present data herein on a model organic layered photoconductor showing that the light initiates a solid-state photochemical reaction that is diffusion controlled and depends on the polymers used in the CTL. Most importantly, the reaction occurs at the CGL/CTL interface and involves both the dye, chlorodiane blue, and the hole-transporting agent, DEH. Attempts were made to collect and separate the photoproducts, but due to the small amount of dye present and the complex nature of the photoreaction success was not possible. In lieu of this, theoretical calculations were performed to investigate where chlorodiane blue and DEH may complex; the salient results were that the amine nitrogens on DEH have a negative charge while the carbon atoms of carbonyl groups in chlorodiane blue are strongly charged positively. With use of this information DEH derivatives were synthesized to increase the distance between the negative centers on DEH and the positive ones on chlorodiane blue. Photoconductors were prepared that differed only by the respective DEH derivative and tested for their ability to bleach CDB upon exposure to yellow light. The bleaching studies revealed that as the size of the substituent increased the fraction of dye bleached as a function of incident energy decreased. This was also confirmed by measuring the amount of electrical fatigue as a result of the yellow light exposure, which showed the same trend with DEH derivative as determined for the bleaching results.

In summary, a source of photoconductor fatigue that plagues the copier and printer industry has been identified. In addition, a method is mapped out by which a problem may be investigated and solved.

Registry No. *p*-(Dimethylamino)benzaldehyde, 68189-23-1; chlorodiane blue, 41709-76-6.