

Free-Volume Trapping in Multiactive Photoconductors

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Introduction

The concept of free-volume trapping was first reported for single-layer aggregate (SLA) photoconductors.[1,2] The drying of SLA films, at temperatures above the glass transition temperature T_g of the SLA's amorphous phase, followed by rapid cooling, generates excess free volume. It was proposed that excess free volume in the photoconductor film can act as a physical barrier to transport, amplifying hole range limitations.

The results reported in this paper concern a study of the free-volume phenomenon in multiactive photo-conductors.

Experiments

Figure 1 shows the structure of the multiactive photoconductors used in this study. We used a cylindrical 60 mm aluminum drum. All three layers were dip coated at 0.3 ips, dried at 100 °C for 30 minutes, and allowed to cool to room temperature in the dark. For aging studies, the coated drums were heated at 110 °C for 30 minutes in a Blue M oven, and allowed to cool to room temperature in the dark for 2 hours. At that time the drum was tested by low intensity continuous exposure (LICE) at four different wavelengths, 540, 600, 680, and 780 nm.

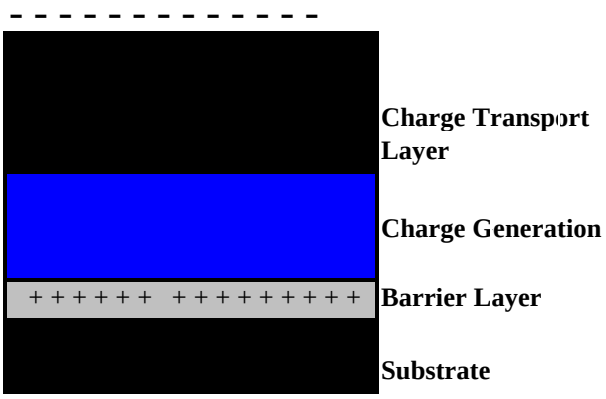


Figure 1. Structure of multiactive photoconductors.

Results

In SLA photoconductors, drying at temperatures above Tg and rapid cooling generate dramatic sensitivity loss. This was explained by the creation of excess free volume in the film. Elimination of the excess free volume through either aging or annealing restores the film inherent electrophotographic sensitivity. These effects are more pronounced at strongly absorbed wavelengths. Surface generation of carriers resulting in longer travel distances for photoholes can account for this observation.

The multiactive photoconductors used in this study are described in Table 1-3. Charge generation layers 1-3 use a 6-micron aggregate composition similar to the SLA except that a titanyl phthalocyanine pigment is included in various concentrations to impart infrared sensitivity. The charge transport layers use a combination of three transport materials, tri-p-tolylamine, TTA, 1,1-bis (4-p-tolylamino-phenyl) cyclohexane, TAPC, and bis (4-diethylamino-phenyl) diphenylmethane, DAPM.

Table 1. Charge Transport Layer Variations.

	CTL-1 wt%	CTL-2 wt%	CTL-3 wt%
Binder	**60**	**60**	**60**
TTA	**19**	**18**	**19.9**
TAPC	**19**	**18**	**19.9**
DAPM	**2**	**4**	**0.2**
TOTAL	**100**	**100**	**100**

Table 2. Charge Generation Layer Variations.

	CGL-1 wt%	CGL-2 wt%	CGL-3 wt%	CGL-4 wt%
Lexan	45	37.5	33.5	50
TTA	40	37.5	33.5	0
Dye1	6.4	6.4	6.4	0
Dye2	1.6	1.6	1.6	0
IR Pigment	5	15	23	50
Others	2	2	2	0
TOTAL	100	100	100	100
Top 1-micron absorption				
540nm	29%			57%
600nm	60%			93%
680nm	100%	100%	100%	97%
780nm	17%	79%	79%	100%

Table 3. Multiactive Photoconductor Variations.

Photoconductor	Charateristic	CGL	CTL
Multiactive-1	5% Pigment/2% DAPM	CGL-1	CTL-1
Multiactive-1a	5% Pigment/4% DAPM	CGL-1	CTL-2
Multiactive-1b	5% Pigment/0.2% DAPM	CGL-1	CTL-3
Multiactive-1c	15% Pigment/2% DAPM	CGL-1a	CTL-1
Multiactive-1d	23% Pigment/2% DAPM	CGL-1b	CTL-1
Multiactive-2	50% Pigment/0.2% DAPM	CGL-2	CTL-3

The effect of incubation and aging on the sensitivity of the multiactive photocondutor using 5% pigment and 2% DAPM is shown in Figure 2. At 680 nm, no sensitivity loss occurs. The film reaches equilibrium sensitivity in less than 24 hours. On the other hand, at 780 nm and 540 nm equilibrium sensitivity is reached after more than 200 hours of aging. Moreover, the sensitivity loss is more pronounced at 780 nm.

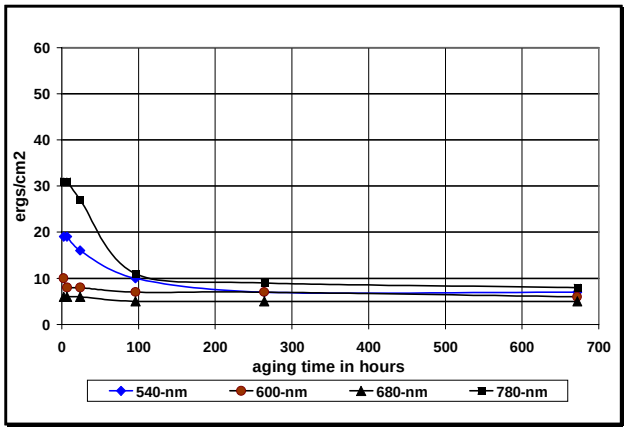


Figure 2. The effect of 110° C incubation on the LICE photosensitivity of Multiactive-1 photoconductor: 5% pigment & 2% DAPM.

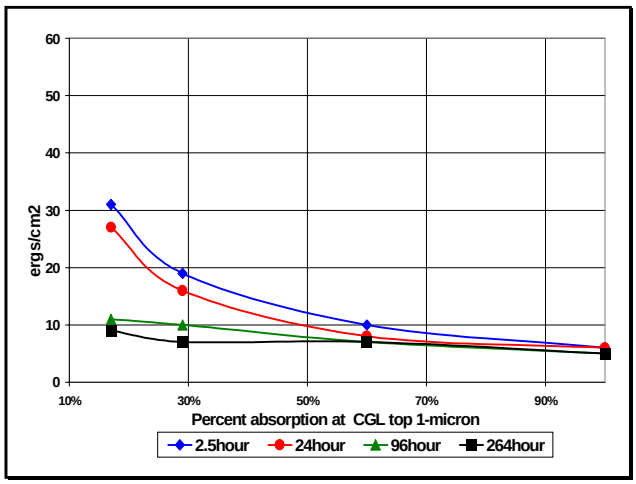


Figure 3. The effect of 100° C incubation on the LICE photosensitivity of Multiactive–1 photoconductor as a function of percent absorption at CGL top 1-micron.

The same data is re-plotted in Figure 3 as a function of percent absorption at the top 1-micron of the CGL. The data suggests that the weaker the absorption, the bigger the free-volume effect. In fact, at 100% top 1-micron absorption (680 nm), there is virtually no free-volume effect. This result is exactly opposite of that for single layer aggregate. The effect of light absorption was further investigated by varying the pigment concentration. This should particularly affect the 780 nm results.

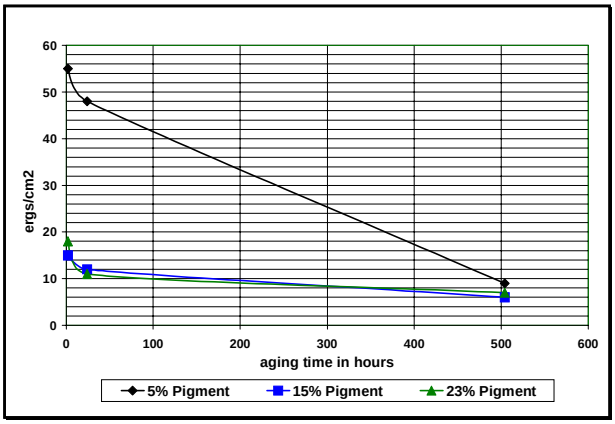


Figure 4. The effect of pigment concentration (CGL top 1-micron absorption) on free-volume effect.

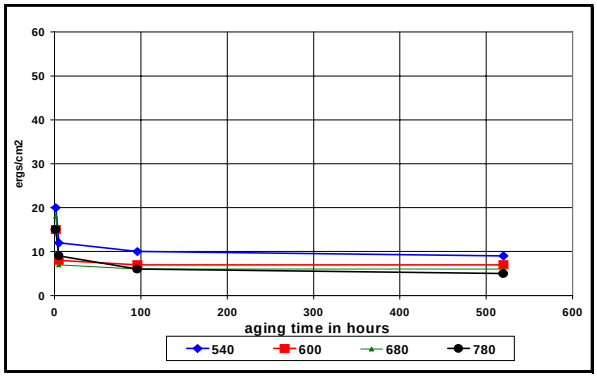


Figure 5. The effect of 110° C on the photosensitivity of Multiactive-2 photoconductor: 50% pigment & 0.2% DAPM.

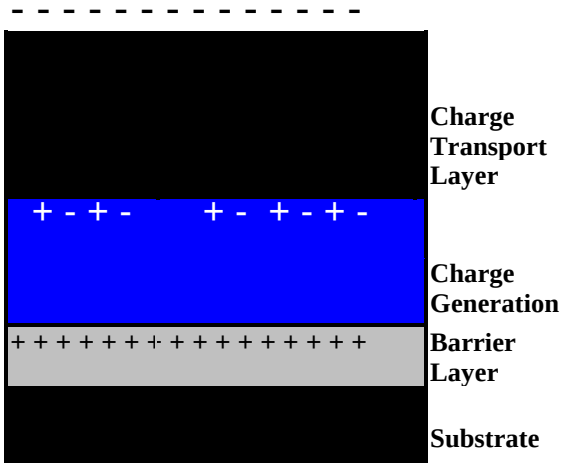


Figure 6. Surface charge generation at strongly absorbed wavelength

Indeed this is seen in Figure 4. The increased 780 nm absorption reduces the free-volume effect substantially. In Figure 5, the aggregate CGL layer was completely replaced by a 50/50-polymer/pigment mixture, coated at one micron. For all 4 wavelengths, equilibrium sensitivity is approached only after 5-hour of aging. Another important result is shown in Figure 6. The level of DAPM was varying from 0.2%, 2%, and 4%. The free-volume effect increased with increased concentration of DAPM.

Discussion

SLA versus Multiactive Photoconductors

The influence of light absorption at the CGL surface is opposite for SLA and multiactive systems. Strong surface absorption in SLA results in large free-volume effect, but strong surface absorption minimizes the free-volume effect in multiactive systems. Figure 7 shows that strong absorption at the surface of the CGL results in photogeneration at the CGL/CTL interface. The fact that free-volume effect is minimal in that instance suggests that the problem is associated with the CGL not in the CTL. That was further confirmed by the fact that increasing the glass transition temperature of the CTL above the incubating temperature did not impact the free-volume effect as was the case in SLA. Bulk generation at weakly absorbed wavelengths results in hole transport within the CGL providing for trapping opportunities in that layer.

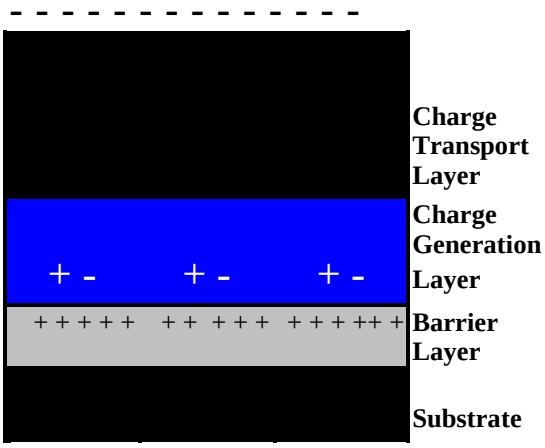
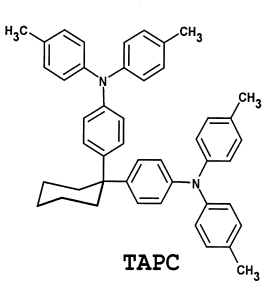
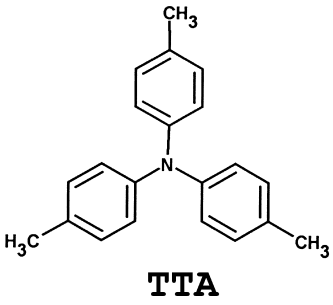


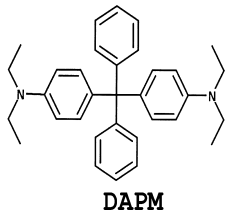
Figure 7. Bulk charge generation for weakly absorbed wavelength.

Effect of DAPM Concentration

DAPM typically is used in low concentration below 10% in combination with TTA and/or TAPC to improve film stability, especially toward corona chemistry; DAPM is an acid scavenger. Its oxidation potential is about 0.15 eV less TTA and TAPC. The results show that at a concentration of 0.2 wt% of DAPM free-volume effect was minimal; however, at 4 wt%, the free-volume effect increased significantly. These results suggest that excess free volume alone is not sufficient. The excess free volume appears to be amplifying the trapping ability of DAPM. Excess free volume decreases the probability of DAPM/TTA or DAPM/TPAC interaction, making DAPM a more efficient trap. Similar effect of free volume was seen for photopolymerizable/crosslinkable dry-film systems.[3]







Charge Transport or Charge Generation?

DAPM is actually coated in the CTL, but it has been shown that the transport materials migrate to the CGL establishing an equilibrium concentration in the two layers[4]. Thus DAPM should be as effective a trap in the CTL as in the CGL. However, the absorption dependence of the free-volume effect and its direction suggest that no effective trapping is manifested in the CTL. The fact that the free-volume effect seems to occur only with bulk charge generation tends to point to an association with the generation process. In the photogeneration process,[5] a bound electron-hole pair, or exciton, created by absorption of photon energy migrates to the charge generating material surface, where it either recombines or dissociates into a free electron and a free hole by an interaction with the donor component of the transport layer. We suggest that free-volume-enhanced trapping by DAPM at the surface of the CGM strongly contribute to recombination, effectively reducing photogeneration efficiency.

Summary & Conclusions

We have studied the free-volume trapping phenomenon in multiactive photoconductors with separate charge generation and charge transport layers, CGL and CTL respectively. We have found that trapping occurs in the CGL at weakly absorbed wavelength. We have identified the charge transport material DAPM as the source of the trapping. DAPM's oxidation potential is 0.15 eV less than TTA or TAPC. We propose that excess free-volume amplified trapping of DAPM at the surface of the charge generating material enhances recombination of the geminate hole pair, resulting in lower photogeneration efficiency. This problem can be eliminated, even with the low concentration use of DAPM, when the charge generation layer is optimized for full light absorption at the top 1 micron surface.

References

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Biography

Michel Frantz Molaire is currently a research associate, and project manager at Eastman Kodak with the Office Imaging Research and Development Group. He received his B.S. in chemistry, M.S. in chemical engineering and MBA from the University of Rochester. His research experience includes polymer synthesis, photopolymerization, organic monomeric glasses, optical recording materials, photoelectrophotographic masters, organic photoconductor formulation, and drum coating technology. Mr. Molaire is the recipient of twenty-eight US patents, over sixty-five foreign patents, and author of several scientific publications. In 1984, he received the Eastman Kodak Research Laboratories C.E.K. Mees award for excellence in scientific research and reporting. In 1994, he was inducted into the Eastman Kodak Distinguished Inventor's Gallery (Inventor Hall of Fame), for reaching the milestone of twenty or more patents. He is a member of the American Chemical Society, and the IS&T.