JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 40, Number 2, March/April 1996

Carrier Transport in Titanyl Phthalocyanine Pigment Dispersed in Binder Polymer

Takashi Kitamura*, Yasuaki Miyazawa, and Hiroshi Yoshimura

Image Science Department, Faculty of Engineering, Chiba University, Chiba, Japan

The carrier transport mechanism of a single-layered photoreceptor containing titanyl phthalocyanine pigment dispersed in an insulating binder polymer was investigated by the measurement of hole drift mobility, using the conventional time-of-flight technique. The transient waveform of the photocurrent exhibited a plateau and kink at higher electric field than 2×10^5 V/cm. The drift mobility for a titanyl phthalocyanine–polycarbonate polymer layer varied from 1.2×10^{-6} to 7×10^{-5} $cm^2 V^{-1} s^{-1}$ as the concentrations changed from 20 to 50 wt% of pigment. The increase of dark conductivity and drift mobility in the range of pigment concentration higher than 20 wt% of pigments depended on the formation of pigment particle chains in the photoconductive layer.

Journal of Imaging Science and Technology 40: 171 – 174 (1996)

Introduction

An organic electrophotographic photoreceptor is a key device in the application of organic material for xerographic copy machines and modern non-impact printers. Both double- and single-layer photoreceptors are used in commercially available devices. The double-layer photoreceptor consists of a charge generation layer and a charge transport layer. In this photoreceptor, an organic photoconductive pigment and a charge transport material are used in the charge generation and charge transport layers, respectively.

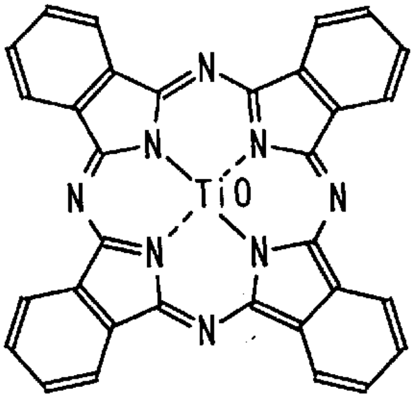
The single-layer photoreceptor consists of the organic photoconductive pigment dispersed in a binder polymer. A single-layer type organic photoreceptor is characterized by a simple structure, positive-charge capability, high gamma photodischarge, and a simple manufacturing process. The organic photoconductive pigment has the roles of charge generation and transport through the layer in a single-layer photoreceptor. The photocarriers generated by illumination are transported through the photoconductive pigments dispersed in the insulating polymer.

Xerographic characteristics of single-layer organic photoreceptors consisting of metal-free phthalocyanine pigment,[1,2] copper phthalocyanine pigment,[3] and titanyl phthalocyanine pigment[4] have been reported. Titanyl phthalocyanine–binder polymer photoreceptor exhibited high sensitivity. However, the mechanism of the charge transport for the single-layer photoreceptor has not been understood, because physical values such as drift mobility and carrier lifetime could not be measured accurately on account of the spatial distribution of photogenerated carriers dispersed in the layer, nonuniformity of hopping distance, and trapping of charge in the bulk and at the surface of the pigment. Recently, however, drift mobilities were reported for titanyl phthalocyanine pigment[5,6] and X-type metal-free phthalocyanine pigment[7] dispersed in binder polymer.

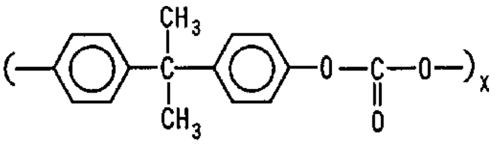
In this study, the hole drift mobility of the single-layer photoreceptor measured by the conventional time-of-flight technique is reported, and the mechanism of carrier transport through the layer at the point of particle contact between the photoconductive pigments is discussed.

Experimental

Sample and Measuring Apparatus. A sandwich-type sample of the photoconductive layer was prepared for the measurement of hole drift mobility. Titanyl phthalocya-



Titanyl phthalocyanine (TiOPc)



Polycarbonate polymer (PC)

Figure 1. The molecular structures of titanyl phthalocyanine and polycarbonate polymer.

Original manuscript received August 17, 1995.

* Senior Membership IS&T

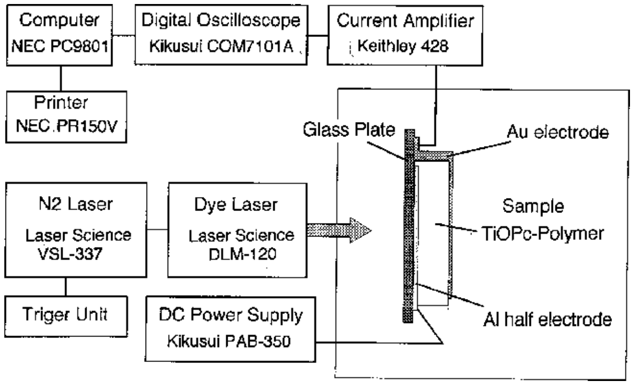


Figure 2. The TOF measuring apparatus.

nine (TiOPc) was used as the photoconductive pigment in the sample. The crystal form of TiOPc pigment is alpha type. Polycarbonate (PC, Teijin Kasei Co. Ltd., Panlite 1300) was used as the binder polymer. The molecular structures of the TiOPc and the PC polymer are shown in Fig. 1. The mixture of TiOPc pigment and PC polymer was dispersed, using an ultrasonic dispersion technique for 1 h. The composition was typically 30 wt % pigment. The emulsion was coated on a glass substrate with a semi-transparent aluminum electrode. The thickness of the photoconductive layer was 5 μm. After the samples had been dried in vacuum for 2 h, a gold top electrode of 200-Å thickness was vapor deposited on the surface of the photoconductive layer.

The measuring apparatus for the transient photocurrent, using the conventional time-of-flight (TOF) technique is shown in Fig. 2. The sandwich sample was connected to a measuring electric circuit, and the aluminum electrode was biased positively for the measurement of hole drift mobility. The sample was illuminated through the aluminum electrode by a light pulse from a dye laser (Laser Science Inc., VSL-337 and Dye Laser Module). The wavelength and pulse width of incident light were 610 nm and 3 ns, respectively. The transient photocurrent was amplified (Keithley, Current Amplifier 428) and monitored on a digital memory oscilloscope (Kikusui Elec. Co., Ltd., COM 7101A). After the data had been fed to the computer memory through a GP-IB bus, the transit time and drift mobility were calculated. The temperature of the sample was maintained by a temperature controller.

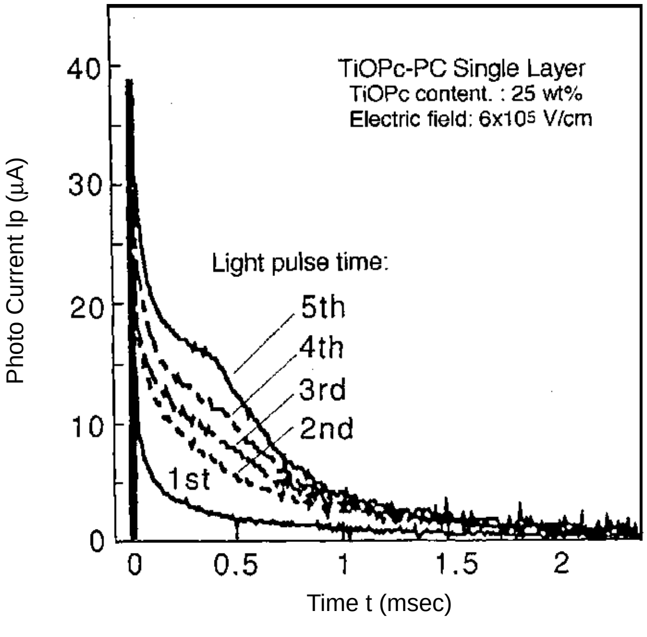


Figure 3. TOF waveforms for the TiOPc–PC sample exposed to several laser pulses.

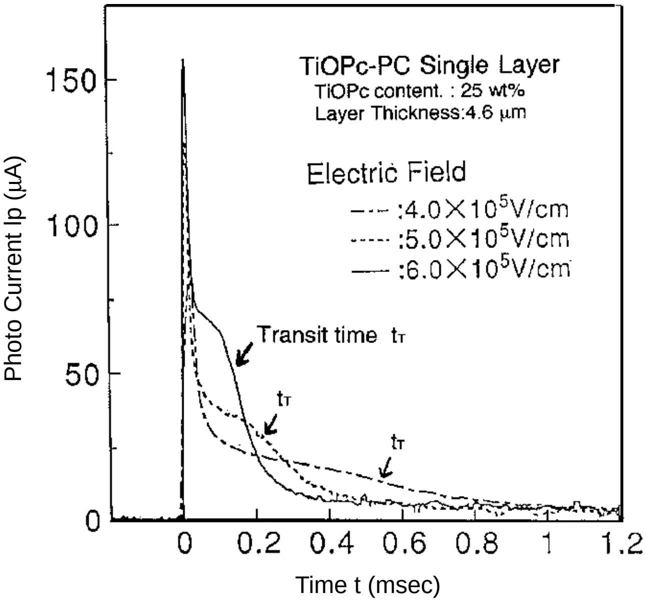


Figure 4. The typical waveform of the transient photocurrent for the Al/TiOPc–PC/Au device as a function of electric field.

Results and Discussion

Transient Photocurrent. To measure drift mobility, we must first decrease the carrier trapping in the bulk of the layer. The kink in the waveform of transient photocurrent cannot be observed for a single-layer organic photoreceptor with a large number of carrier traps. The transient photocurrents can be measured after several TOF measurements to exclude the carrier trapping effects. Figure 3 shows the transient photocurrents when the Al/TiOPc–PC/Au sample was exposed for several laser pulses. At first exposure, the waveform of the transient photocurrent exhibited simple decay. The values of photocurrents increased with increasing times of pulse illumination, and the kink was observed after four exposure pulses. These experimental results implied that the photogenerated carriers were trapped and the space charges were accumulated in the layer. In this measurement, however, the transit time was not changed by the space charge formation because a small fraction of carriers was trapped in the bulk during the TOF operation.

Figure 4 shows the typical waveform of the transient photocurrent having the cusp in electric fields higher than 4×10^5 V/cm. These curves show the plateau and slow decay. The transit time was determined by the peak position of a differential curve of transient photocurrent waveform. The hole drift mobility was calculated, using the values of the transit time, layer thickness, and applied voltage.

Concentration of TiOPc Pigment. Figure 5 shows the electric field dependence of the drift mobility as a function of the weight percentage of TiOPc pigment in the TiOPc–PC photoconductive layer. Drift mobility was calculated using the value of transit time obtained by the log I–log t plot, because the transient waveform exhibited simple decay at electric fields lower than 1×10^5 V/cm. The transient waveform having the plateau and slow decay was observed at electric fields higher than 2×10^5 V/cm. The photogenerated carrier could not move through the layer

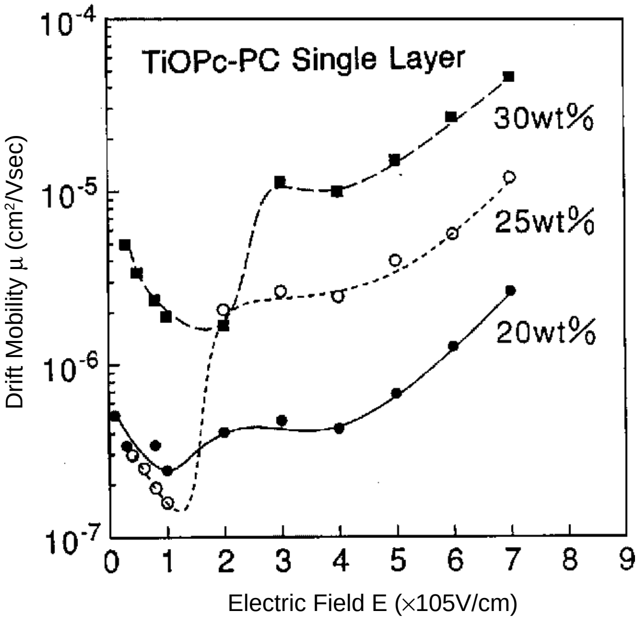


Figure 5. The relation of electric field intensity and hole drift mobility for the single-layer photoreceptor as a function of pigment percentage.

and arrive at the counterelectrode, because the value of $\mu\tau E$ (μ, τ, and E are drift mobility, carrier lifetime, and electric field intensity, respectively) was smaller than the layer thickness at the low electric field. The drift mobility increased with increasing intensity of electric fields higher than 2×10^5 V/cm. The true values of hole drift mobility for the sample were obtained in a high electric field range. There were complicated changes of drift mobility in the low electric field range. These experimental results implied that the energy barrier for hole conduction existed at the interface between the photoconductive pigments, because the drift of photogenerated carriers was accelerated by electric fields higher than 2×10^5 V/cm.

Figure 6 shows the relation between the concentration of TiOPc pigment and hole drift mobility. The drift mobility

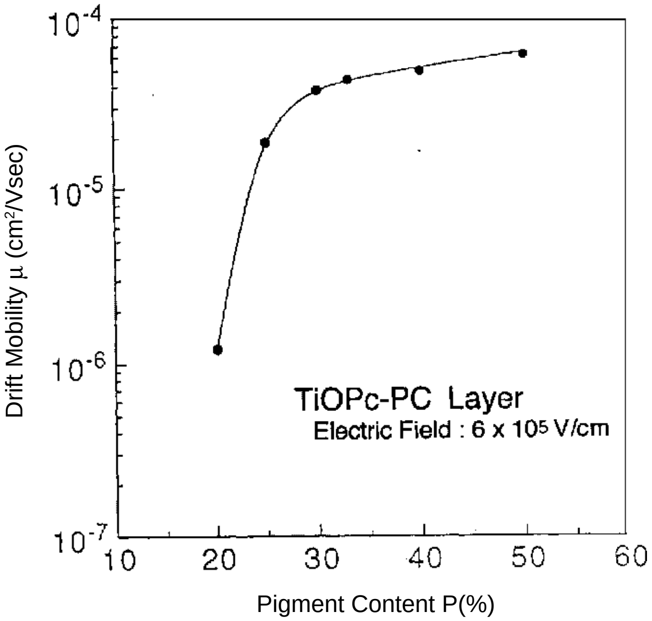


Figure 6. The relation between the concentration of TiOPc pigment and drift mobility.

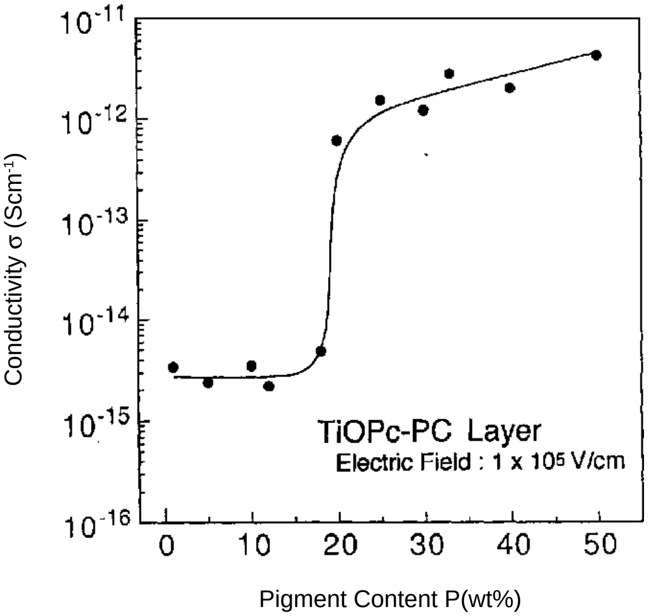
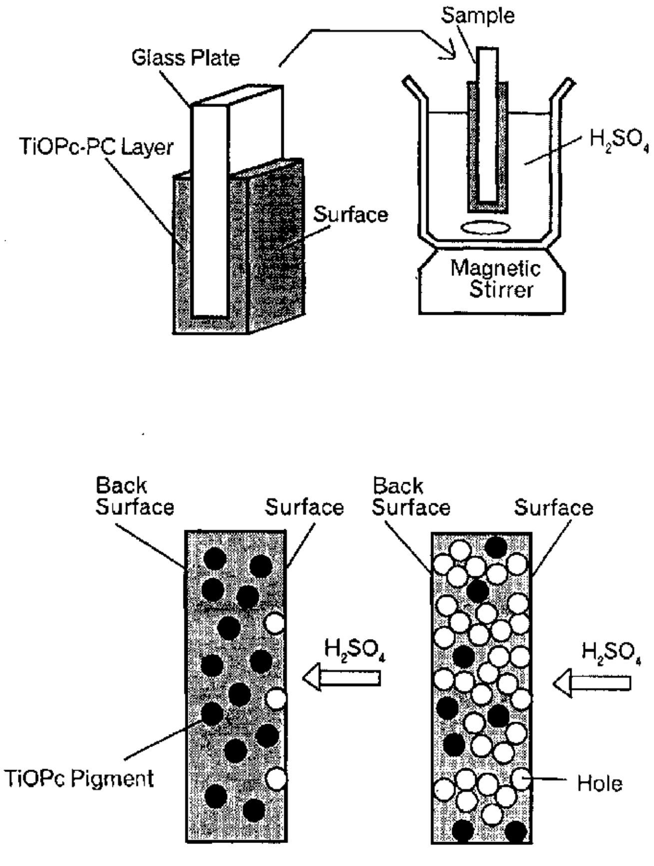


Figure 7. Dark conductivity of TiOPc–PC photoconductive layer.



(a) Low Concentration of TiOPc (b) High Concentration of TiOpc

Figure 8. TiOPc–PC sample in the sulfuric acid solution. (a) Low concentration and (b) high concentration of TiOPc. The open circles indicate holes left after the TiOPc pigment dissolved in sulfuric acid.

increased rapidly in the range of pigment concentration higher than 20 wt%, as did the dark conductivity shown later. We could not measure the drift mobility in the range lower than 20 wt% because the transient photocurrent was very small. The change of drift mobility is small in the range from 30 to 50 wt%.

Generally, the drift mobility can be expressed by the hopping conduction for the molecularly doped polymer. The distance between carrier transport materials is about 10 Å for the typical charge transport layer. It is very difficult to measure the separation distance between the pigment particles in the TiOPc–PC layer. The average separation distance of particles is estimated from the simple packing model for the single layer. It is supposed that the particle is a sphere with a radius of 150 Å and that the particles are dispersed uniformly in the layer. The estimated distance between the particles is very large for hopping conduction. It is implied that the photoconductive pigments were not dispersed uniformly in the layer.

Dark Electrical Conductivity. The dark electrical conductivity of the TiOPc–PC single layer was measured as a function of the concentration of pigment in the layer. The sandwich type cell was used for the measurement of dark conductivity. The dark conductivity increased rapidly at the pigment concentration of 20 wt%, as shown in Fig. 7. This drastic change of dark conductivity is a typical phenomenon for the conductive powder dispersed in the insulating polymer. It was thus expected that the particles of pigments were in contact with each other, forming chain networks in the layer at the range of pigment concentrations higher than 20 wt%.

Chain Formation of TiOPc Particles. To investigate the contact of pigment particles with each other, color and density changes at the surface and back surface of the TiOPc–PC photoconductive layer were observed after dipping the layer into a sulfuric acid solution. The single TiOPc–PC layer, which adhered to the glass substrate, was dipped into a sulfuric acid solution for 10 min, as is shown in Fig. 8. The optical density of the sample layer was measured after dipping. The optical density of the surface of the sample decreased because the phthalocyanine pigments dissolved in the sulfuric acid solution. If the phthalocyanine pigments are isolated from each other, the color of the back surface will not be changed, because the sulfuric acid cannot penetrate through the polymer layer. On the other hand, if phthalocyanine pigments are in contact with each other in the layer, the optical density of the back surface of the layer will decrease as does that of the front surface of the layer.

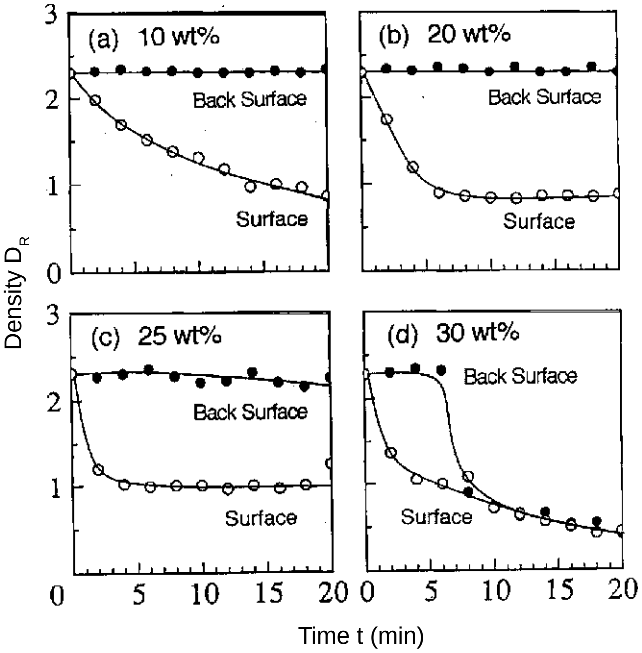


Figure 9. Color optical densities at the surfaces of TiOPc–PC layers dipped in sulfuric acid solution. D_r signifies measurement with red light.

Figure 9 shows the changes of optical densities of the front surface and back surface of TiOPc–PC layers containing 10 to 30 wt% TiOPc pigment during a 20-min dipping treatment. The changes of optical density of the front surface and back surface are shown as open circles and solid circles, respectively. The color of the back surface did not change for the sample containing 10 wt% TiOPc pigment after 20 min. The phthalocyanine pigments were thus isolated from each other in the sample containing 10 wt% pigment; the sulfuric acid therefore could not penetrate through the layer. The colors of both surfaces changed for a TiOPc–PC layer containing 30 wt% TiOPc pigment. We conclude that the phthalocyanine pigments were in contact with each other, because the sulfuric acid could penetrate the layer. From these simple experimental results, we determined that the phthalocyanine pigments formed chains in the layer in the range of concentrations higher than 20 wt% of phthalocyanine pigment.

The changes in surface potential, dark conductivity, and drift mobility are due to formation of particle chains in the layer. In other experiments, binder polymer had large effects on the drift mobility. There are also different values of drift mobility for single layers having different binder polymers. The wettability of pigment by the binder polymer and the method of dispersion are important factors in forming the particle chains. The pigments were aggregated and formed particle chains in the polymer used here, as is shown schematically in Fig. 10. From these experimental results, we find that the photogenerated carriers can be transported through the phthalocyanine pigment chains in the single-layer photoreceptor.

Conclusion

The drift mobility for the single-layer photoconductive layer containing titanyl phthalocyanine pigment dispersed in the insulating binder polymer was obtained, using the conventional TOF technique. The transient waveform of the

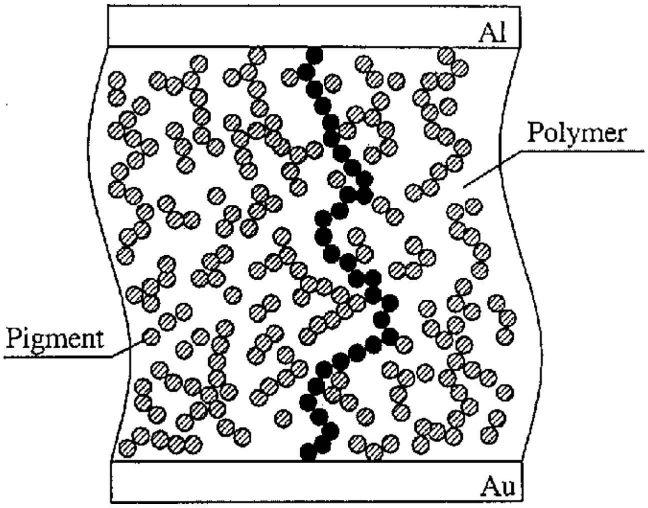


Figure 10. Formation of a pigment particle chain in the single-layer photoreceptor.

photocurrent exhibited a plateau and a kink at electric fields higher than 2×10^5 V/cm. The hole drift mobility for titanyl phthalocyanine–polycarbonate polymer layers varied from 1.2×10^{-6} to 7×10^{-5} $cm^2\ V^{-1}\ s^{-1}$ as the concentrations ranged from 20 to 50 wt% pigment. The increase of dark conductivity and drift mobility in the range of pigment concentration higher than 20 wt% of pigments depends on the formation of pigment particle chains in the layer.

References

1. J. Weigl et al., *Current Problems in Electrophotography*, Walter de Gruyter, Berlin, 1972, p. 287.
2. S. Tsuchiya, A. Omote, M. Murakami, and S. Yoshimura, *Proceedings of IS&T's 7th International Congress on Advances in Non-Impact Printing Technologies*, **1**: 336 (1991).
3. J. Decker, K. Fukae, S. Johnson, S. Kaieda, and I. Yoshida, *Proceedings of IS&T's 7th International Congress on Advances in Non-Impact Printing Technologies*, **1**: 328 (1991).
4. Y. Ide and T. Kitamura, *Proc. of Japan Hardcopy '91*, 305 (1991).
5. T. Kitamura and H. Yoshimura, *Proceedings of IS&T's 8th International Congress on Advances in Non-Impact Printing Technologies*, 237 (1992); T. Kitamura and H. Yoshimura, *Proc. Japan Hardcopy '92*, 54 (1992); T. Kitamura and Y. Miyazawa, *Proceedings of IS&T's 9th International Congress on Advances in Non-Impact Printing Technologies*, 619 (1993).
6. T. Enokida, *Proc. Japan Hardcopy '92*, 157 (1992); T. Enokida, *Proc. Japan Hardcopy '92*, 58 (1992); T. Enokida, *Proceedings of IS&T's 9th International Congress on Advances in Non-Impact Printing Technologies*, 615 (1993).
7. A. Omote, Y. Itoh, and S. Tsuchiya, *Proceedings of IS&T's 9th International Congress on Advances in Non-Impact Printing Technologies*, 623 (1993); A. Omote, Y. Itoh, and S. Tsuchiya, *J. Imaging Sci. Technol.*, **39**: 271 (1995).