Xerographic properties of metal/metal-free phthalocyanine composites in a double-layered photoconductor

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Abstract−The electrophotographic properties of a negatively charged double-layered photoconductor that consisted of y-type metal phthalocyanine (TiOPc) and x-type metal-free phthalocyanine (H$_2$Pc) composites were studied. The undercoating layer (UCL) was fabricated by a dip-coating method with Al$_2$O$_3$ and polyamide, and the charge transport layer (CTL) was prepared from N,N′-Bis-(3-methylpenyl)-N,N″-bis-(phenyl)-benzidine (TPD), polycarbonate (PC), and polyester (PE). In the charge generation layer (CGL), the dispersion state becomes more homogeneous with increasing amounts of non-metal phthalocyanine (H$_2$Pc). The electrophotographic properties of the photoconductor were obtained by using photo-induced discharge curves (PIDC) of charge acceptance, dark decay, photosensitivity, and photofatigue. It was found that the initial charge potential was not dependent on the compositional ratio of the charge generating material. However, the dark decaying rates and the photosensitivity were proportional to the content of TiOPc in the organic photoconductors.

Key words: Photoconductor, Phthalocyanine, Dip-coating, Charge Generation Layer, Charge Transport Layer

INTRODUCTION

The research on organic photoreceptors for electro-photography has undergone significant development during the last two decades. Electro-photographic technologies using photoconductivity involve the following series of steps (known as the Carlson process [1]): charging, laser scanning, developing, transferring, cleaning, erasing. Organic photoreceptors have been widely used in photovoltaic devices, copy machines, and laser beam printers. The machine efficiencies depend on the organic photoconductive materials and the structure of the photoreceptor.

General commercial photoconductors are double-layered devices composed of a charge generation layer (CGL) and a charge transportation layer (CTL) [2]. Typical charge-generation materials (CGMs) include phthalocyanine (Pc), and azo, squaraine, and perylene pigments. Azo and perylene pigments primarily absorb and photonically respond in the visible region (450-650 nm), i.e., they show high photosensitivity in the visible region, and are therefore particularly suitable for copiers where visible light sources operate. By contrast, some phthalocyanines and squaraines exhibit high photo sensitivity in the near-infrared (IR) region, and are therefore used for diode laser printers where near-IR light sources operate [3,4].

Phthalocyanines are being widely used as charge generation materials and are being intensely studied because of their thermal and chemical stability and photosensitivity. Phthalocyanines are usually classified as metal-free phthalocyanines (H$_2$Pc) or metal phthalocyanines (TiOPc) [5,6].

The basic requirements for electro-photographic photoconductors can be summarized as follows: a good charge acceptance (low dark discharge rate), a high photo generation yield of free carriers at the exposure wavelengths, adequate charge-transporting properties, and the ability to undergo many charging and discharging cycles. The last requirement also implies that no deep trapping of carriers and minimum photo-fatigue should be allowed [7,8].

In this paper, metal and metal-free phthalocyanines are blended in a single CGL, and N,N′-Bis-(3-methylpenyl)-N,N″-bis-(phenyl)-benzidine (TPD) was used as the charge transport material (CTM) to prepare a double-layered photoconductor. Furthermore, the electronic and aggregate structures of the composites were characterized by using FT-IR absorption spectroscopy, X-ray powder diffraction, and SEM. The electrophotographic properties, such as photosensitivity, dark decay, charging acceptance, and photo fatigue of the photoconductor were investigated with an electrical characteristics analyzer.

EXPERIMENTAL

1. Materials

Titanyl phthalocyanine (y-type TiOPc) and metal-free phthalocyanine (x-type H$_2$Pc) were used as the CGM, and were purchased from Syntec, Inc. (Germany), and Dainippon Ink and Chemicals, Inc. (Tokyo, Japan), respectively. The polymer binder used was polyvinylbutyral (PVB) (trade name BM-S; MW=80,000), which was obtained from Sekisui Chemicals, Inc. (Kyoto, Japan). N, N′-bis-(3-methylpenyl)-N,N″-bis-(phenyl)-benzidine (TPD) was the chosen CTM, and the CTL was dispersed on polycarbonate (PC) and polyester (PE). Nyron-6 polymer was used for the fabrication of the undercoating layer. The chemical formulae of the CGM and CTM used in the photoconductor layer are shown Fig. 1. The dual-layered photoreceptor device was made in the configuration shown Fig. 2.

2. Procedures

Y-type titanium oxide phthalocyanine was blended with x-type

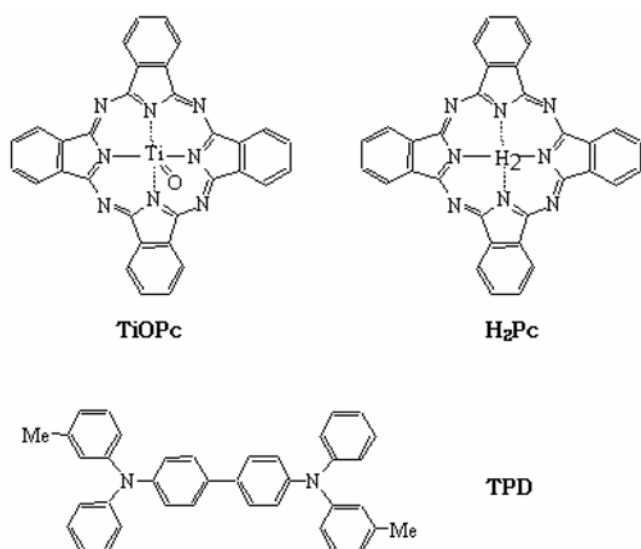†To whom correspondence should be addressed.
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Fig. 1. The Chemical structures of TiOPc, H₂Pc, and TPD.

Fig. 2. The configuration of an organic double layered photore-ceptor.

phthalocyanine in weight ratios of 1 : 0, 7 : 3, 4 : 6, and 0 : 1. The resulting charge generation material was mixed with the matrix mate-rial of polyvinylbutyral in a weight ratio of 6:4, in a solution of cy-clohexanone and acetate. The dispersion of the charge generation material was carried out with a high-speed mixer (Ultra T-basic 25, IKA) at a speed of 24,000 rpm/min for 1 h at 60 ℃. After the for-mation of the undercoating layer (UCL) on the aluminum tube, the
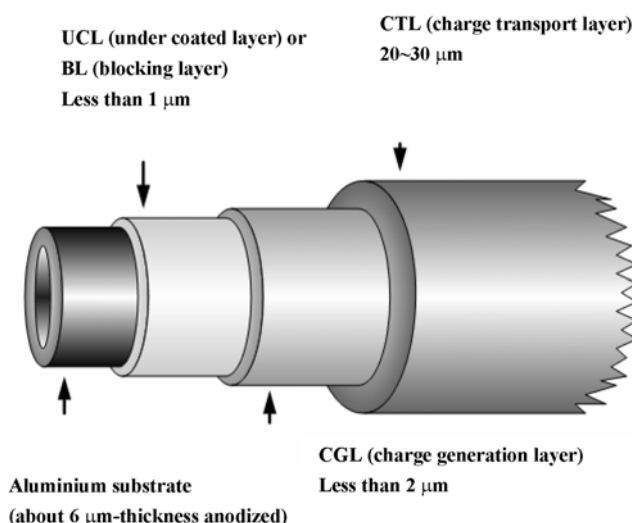
tube was cooled and the charge generation layer was coated onto the UCL by dip coating. The coated tube was then dried for 30 min at 100 ℃. The thickness of the charge generation layer was 0.5 μm.

For fabricating the charge transport layer, TPD was blended with the charge transport binder in a weight ratio of 4 : 6, in tetrahydro-furan at 60 ℃. PC and PE were used as the charge transport binders. The viscosity of the solution for the fabrication of charge transport
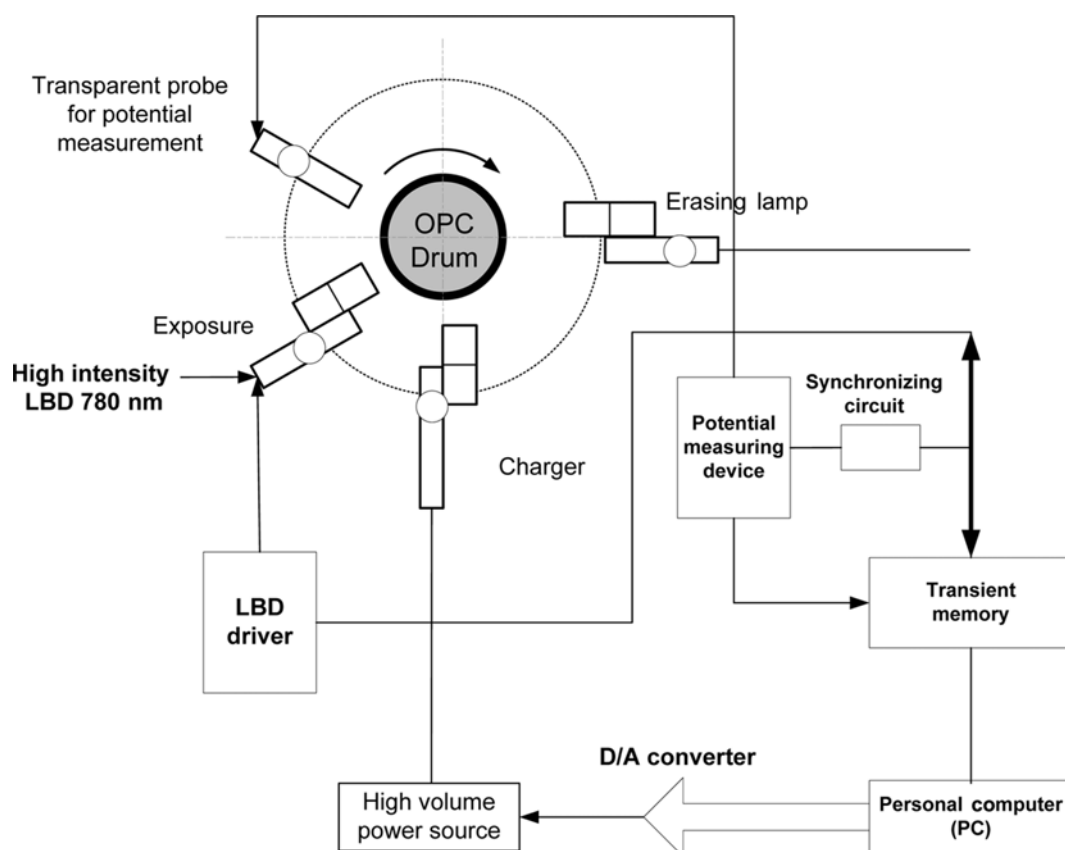

Fig. 3. Schematic diagram of electronic characteristics analyzer for the photoinduced discharge curve.

layer was 300 cP. The charge transport layer (having a final thickness of 20 μm) was coated over the CGL by dip coating, and then dried.

Absorption spectra of the charge generation layer solutions were obtained by using an FTIR spectrometer (Bomen MB100, Hartman & Braun). Surface images of the charge generation layer were obtained by SEM (S-2500C, Hitachi). X-ray diffraction patterns of the charge generation material composites were determined with an X-ray diffractometer (D5000, Siemens). To obtain the XRD patterns, the solutions of the charge generation material were filtered and then dried at 100 °C.

The electronic characteristics of the double-layered photoreceptor were analyzed by using the photo-induced discharge curve. A schematic diagram of the electronic characteristics analyzer (Cynthia91, Gentec Co.) for the organic photoconductor is shown in Fig. 3.

The light source (780 nm) from Xe emission was applied through a neutral density filter. Several parameters can be obtained from the measurement: the surface charge potential (V_o), the residual potential (V_r), the percentage of the potential discharge after 1 s of exposure (V_1), the time of half discharge ($t_{1/2}$), and the half discharge exposure energy ($E_{1/2}$).

The surface of the photoconductor becomes positively or negatively charged when it passes through the charged area of the corona. The electrical potential of the charged photoconductor was recorded with a measuring probe. When the surface electrical potential reaches to some range of electrical potential, a light source of 780 nm from Xe emission irradiates the surface of the organic photoconductor passing through the neutral density filter. Electron-hole pairs created by the light irradiation are separated by the electrical field applied. The charge carrier evolved moves through the charge transport layer and then reduces the surface electrical potential of the photoconductor. This variation was obtained by a non-contact discharging probe and the data was then saved in a computer through an AD converter. The diminution behavior of the surface electrical potential upon the irradiation of light onto the double-layered photoconductor represents the function of the photoelectrical transformation efficiency [9]. The initial charge generating property, diminishing speed of surface electrical potential, dark decay speed, photosensitivity, and surface and residual potentials are all major factors when evaluating photoelectric processes.

RESULTS AND DISCUSSION

1. Light Absorbance and Particle Structure Analyses

Generally, charge generation materials are classified into two classes: the azo pigments, and the metal and non-metal phthalocyanines. The absorption bands of the y-type metal/x-type metal-free phthalocyanine composites dissolved in the solution of cyclohexanone and acetate, and dispersed in polyvinylbutyral, were measured by IR-reflective spectroscopy. The absorption spectra of the charge generation layer having different compositions are shown in Fig. 4. The absorption band of metal phthalocyanine was observed in the region of 760-780 nm. However, the absorption peak of the non-metal phthalocyanine appeared around 780 nm. A small absorption peak at 780 nm was observed for y-type TiOPc. By contrast, a big absorbance peak was observed for x-type H_2Pc. The absorbance at 760 nm increased with increasing amounts of metal phthalocyanine.
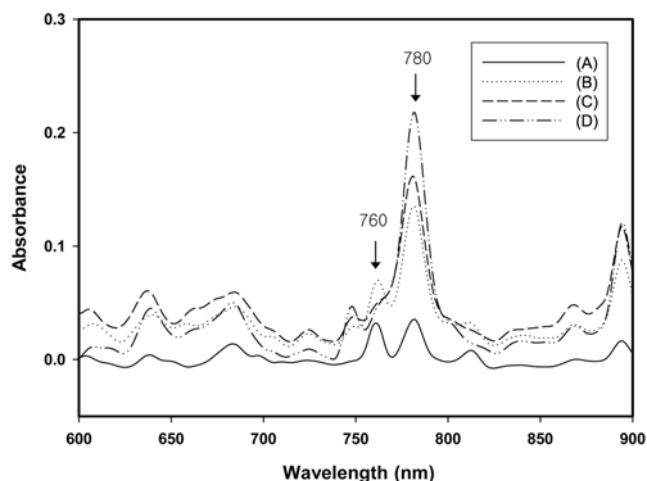

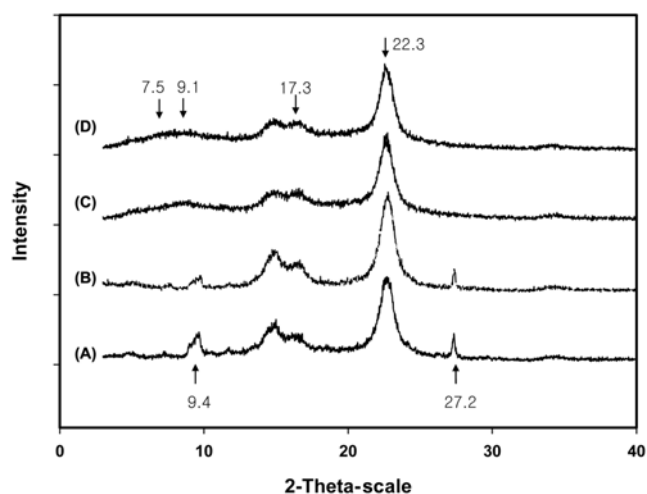Fig. 4. Absorption spectra of TiOPc=100 (A), TiOPc/H_2Pc=70/30 (B), TiOPc/H_2Pc=40/60 (C), and H_2Pc=100 (D).

Fig. 5. X-Ray diffraction patterns of TiOPc=100 (A), TiOPc/H_2Pc= 70/30 (B), TiOPc/H_2Pc=40/60 (C), and H_2Pc=100 (D).

XRD patterns of the charge generating mixtures of metal/non-metal phthalocyanine and polyvinylbutyral, that had been filtered and dried to produce powders, are shown in Fig. 5. The y-type TiOPc has diffraction peaks at $2\theta=9.4°$, 27.2°. However, the XRD pattern of the y-type TiOPc dispersed in polyvinylbutyral shows absorption peaks at $2\theta=9.4°$, 15.0°, 22.3°, and 27.2°. This means that the crystal structure of TiOPc is not changed by its dispersion in polyvinylbutyral. It also shows that some new peaks appear due to the interaction between the TiOPc and polyvinylbutyral. The diffraction peaks of the x-type H_2Pc appear at $2\theta=7.5°$, 9.1°, 17.3°, and 22.3°. However, when the x-type H_2Pc was dispersed in polyvinylbutyral, some peaks appeared at the same positions, while some peaks disappeared [10]. Although it is known that phthalocyanine resin is not soluble in organic solvents, we confirmed that some portion of the non-metal phthalocyanine can be dissolved in the solvents tetrahydrofuran and cyclohexanone [11].

The SEM images of the charge generation layer coated onto the aluminum film are shown in Fig. 6. TiOPc particles dispersed in polyvinylbutyral are shown in A of Fig. 6. The TiOPc particles are
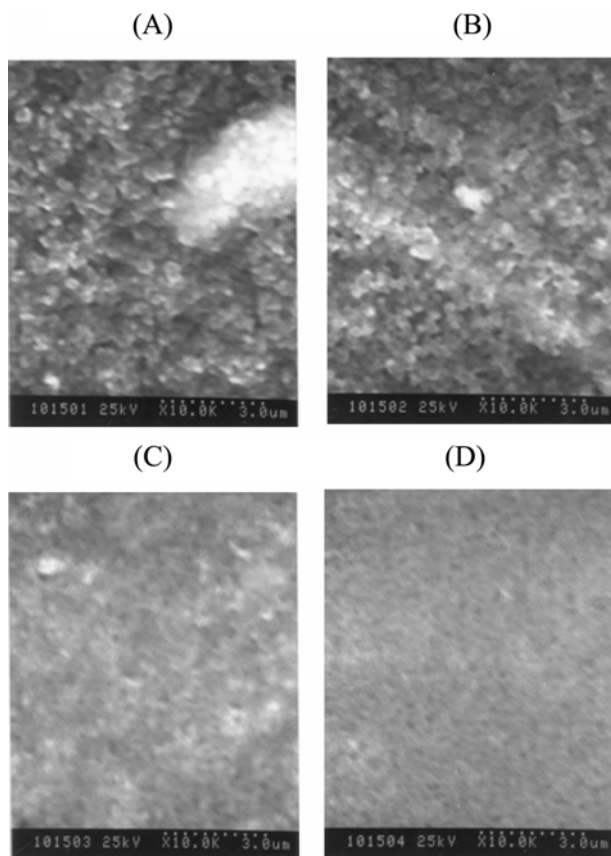
Fig. 6. SEM images of TiOPc=100 (A), TiOPc/H₂Pc=70/30 (B), TiOPc/H₂Pc=40/60 (C), and H₂Pc=100 (D).

about 0.3 nm in diameter. They become smaller and the dispersion state becomes more homogeneous with increasing amounts of non-metal phthalocyanine (H₂Pc). When the charge generation layer was fabricated with phthalocyanine (H₂Pc) and polyvinylbutyral, the dispersion state of the phthalocyanine (H₂Pc) was so good that no particles could be observed, as shown in D of Fig. 6.
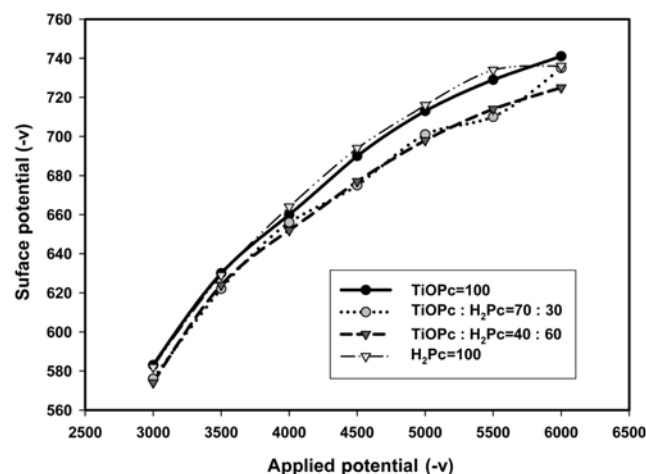
2. Electro-photographic Characteristics

2-1. Charging

To get fine electro-photography through a double-layered organic photoconductor, the characteristics of the surface electric potentials obtained at the each of the photo imaging processes (*e.g.*, charging, exposure, development, and fixation) are very important [12,13]. Generally, the initial surface potential obtained through the corona electro discharge is needed to reach a higher electrical potential in a shorter period. The organic photoconductors (having different composition ratios of TiOPc and H₂Pc) were charged from −3,000 to −6,000 V at the revolution speed of 48 rpm by a DC charger. The resulting surface electrical potentials are shown in Fig. 7. The surface electrical potential was found to increase with increasing the applied potential. The obtained surface potential values were above the international standard value (±500 V). These results mean that the organic photoconductors fabricated are suitable to be used as photosensitive materials. The values of the surface electrical potential did not show big differences upon varying the composition of the charge generation materials. Generally, the charge generation materials composed of a pure component show better charging properties than the mixed ones.

2-2. Dark Decay

Generally, the dark decay value represents the charge storage or preservation feature. The smaller the dark decay value of a photoconductor the better; its value should be less than 20 V/sec. Dark decay values of the organic photoconductors having different compositions are shown in Fig. 8. When the initial surface electrical potential value was (−)5,000 V, the value in the dark decreased as time went by. The dark decaying rates were proportional to the content of TiOPc in the organic photoconductors.

2-3. Photosensitivity

Photosensitivity of photoconductive materials is dependent on the light absorbance efficiency, carrier generation rate, and drift mobility. Thus, the mobility of a charge carrier can be evaluated by measuring photosensitivity. When the surface of the photoconductors was exposed through the neutral density filter to the light of Xe lamp, after initially being charged with an electrical potential of 600(±10) V, the photoelectric and residual potentials were obtained. Also, the half-life exposure ($E_{1/2}$) needed to diminish the electrical poten-
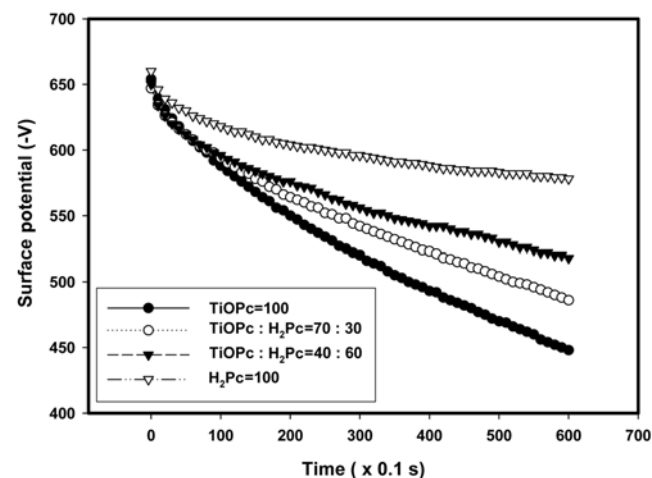

Fig. 7. Charging curves of organic photoconductors with different TiOPc/H₂Pc ratios.

Fig. 8. Dark decay curves of organic photoconductors with different TiOPc/H₂Pc ratios.
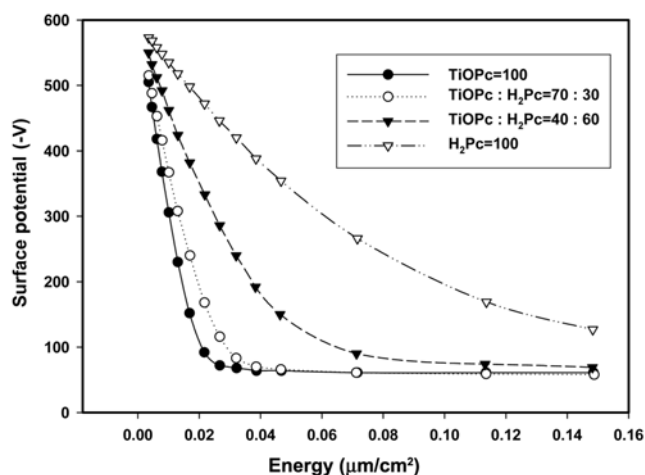
Fig. 9. Photosensitivity curves of organic photoconductors with different TiOPc/H₂Pc ratios.

Table 1. Photosensitivity of TiOPc/ H₂Pc composites

Composite system	TiOPc (%)	H₂Pc (%)	Light source	$E_{1/2}$	V_0	V_L	V_R
TiOPc/H₂Pc	100	0	780 nm	0.01031	612	61	17
	70	40		0.01346	597	58	14
	30	60		0.02372	590	69	16
	0	100		0.06108	596	127	16

Fig. 10. Photofatigue curves of organic photoconductors with different TiOPc/H₂Pc ratios.

tial to half of the initial value was obtained. The half-life exposures ($E_{1/2}$), photoelectrical potentials, and residual potentials of the organic photoconductors are shown in Fig. 9 and Table 1. With increasing TiOPc content, the photoelectrical potentials were found to decrease, while the photosensitivity increased. However, with increasing H₂Pc content, the photoelectrical potentials were found to increase, while the photosensitivity decreased. There was no significant difference in residual potential upon varying the composition.

2-4. Photofatigue

The photo-fatigue of organic photoconductors means irreversible changes due to repeated cycles of charging and discharging. These irreversible changes sometimes accompany a decrease in charge capacity, an increasing rate of dark decay, and an increased residual potential. These possible irreversible changes come from the IR irradiation from the corona charge [14], the irreversible oxidation and reduction in the photoconductors [15,16], the photonic oxidation of the charge transport material, any newly derived materials causing various traps, and curbing factors in the charge transport process. These factors diminish the lifetime of photoconductors. One hundred average values of the surface electrical potential, measured twice for each data, are shown in Fig. 10. The data was obtained after the samples were exposed to the light of the Xe lamp through the filter (its neutral density was fixed at 850) after being initially charged with an electrical potential of −5,000 V. Generally, irreversible changes occur by repeated charging and discharging cycles. As a result, the photoelectrical and dark decay potentials increase or decrease. However, these potentials were constant during the repeated cycles. The dark decay potential was shown constant, regardless of the change in composition of the charge gener-
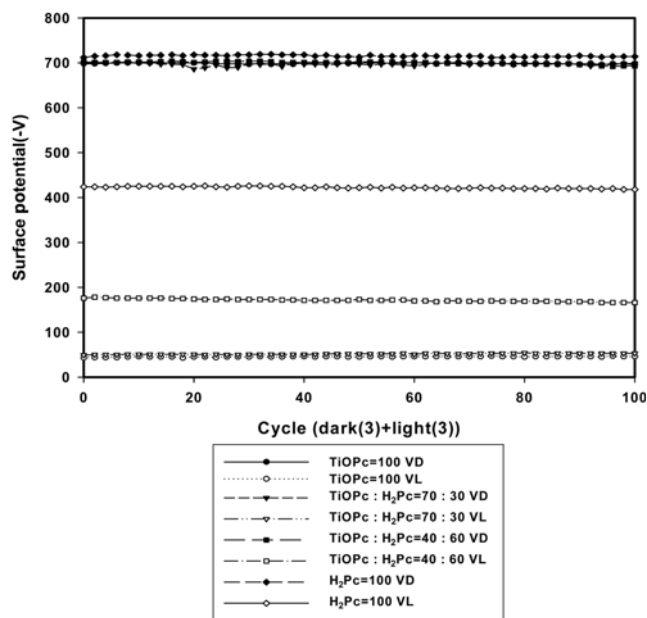
ating material. The photoelectric potential was found to be high when the composition of non-metal H₂Pc was high.

CONCLUSIONS

Photoconductive TiOPc/H₂Pc composites were prepared and investigated in double-layered photoreceptor devices. Results from IR spectroscopy, XRD, and SEM indicate that the dispersion state becomes more homogeneous with increasing amounts of non-metal phthalocyanine (H₂Pc). Also, the following results were obtained through xerographic measurements.

1. The initial charge potential was not dependent on the compositional ratio of the charge generating material.

2. The dark decaying rates were proportional to the amount of TiOPc in the organic photoconductors.

3. The photoelectrical potentials increased with increasing composition of non-metal phthalocyanine, while the photosensitivity decreased. The residual potential value did not vary greatly with compositional changes.

4. The dark electrical and photoelectrical potentials of the organic photoconductors were not changed by repeated cycles of charging and discharging.

ACKNOWLEDGMENT

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