JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 43, Number 3, May/June 1999

Photoconduction Mechanism in Single-Layer Photoconductor with Metal-Free Phthalocyanine

K. Kubo, T. Kobayashi, S. Nagae, and T. Fujimoto
Advanced Technology R&D Center, Mitsubishi Electric Corporation, Hyogo, Japan

The photoconduction mechanism in a metal-free phthalocyanine pigment dispersed in a polymer matrix was investigated. The charging potential started to decay remarkably after a threshold light exposure. The threshold exposure increased as the initial potential increased and as the thickness of the photoconductive layer decreased. This result may indicate that the threshold exposure depends on the quantity of charge. The temperature dependence of the threshold exposure was also investigated. The threshold exposure decreases with increasing temperature. The activation energy was estimated to be 0.049eV at an electric field of 4.5×10^5V/cm. This value is almost equal to that of the photogeneration process in phthalocyanine. The photoinduced decay rate after the induction period increased and the activation energy decreased with increasing field intensity. The anticipated field dependent phenomenon was not found in these results. Therefore, we think there is a possibility that the mechanism is different from the prevalent trap theory.

Journal of Imaging Science and Technology 43: 248–253 (1999)

Introduction

Organic photoconductors are useful as electrophotographic photoreceptors in copy machines and laser printers. The electrophotographic process comprises charging, exposing, developing, transfer and fixing steps. The photoreceptor forms electrostatic latent images in the charging and exposing processes, then electrically adsorbs toners in the developing process, and puts them on paper in the transfer and fixing process. Most photoreceptors are negatively charged in an electrophotographic system. In general, corona discharge devices are available to charge photoreceptors. These devices generate ozone as by-product and the amount of ozone is greater with negatively charged photoreceptors than with positively charged photoreceptors.[1]

The single-layer photoconductor consisting of a phthalocyanine pigment dispersed in a polymer matrix[2] is a positively charged photoreceptor. This photoconductor is more eco-friendly than negatively charged ones. It comprises a single layer that has two functions: photocarrier generation and carrier transport. Its structure is so simple that it can be easily manufactured. Furthermore, the single-layer photoconductor is a high gamma photoreceptor.[3] It can sharpen the edge of electrostatic latent images in a laser printer and create hardcopies printed with high resolution and high quality. Therefore, such a photoconductor is a very promising electrophotographic photoreceptor.

The unique high gamma property occurs because the charging potential starts to decay remarkably after a certain threshold level of light exposure that we call the "induction effect".[2,4] Several mechanisms have been proposed to explain this phenomenon, for example, the simple trap model[5,6] and the structural trap model.[7,8] However, the induction mechanism is not completely clear at this time.

In this study, we investigated the photoconduction in the single-layer photoconductor with a metal-free phthalocyanine pigment to clarify the properties and mechanism of the induction. The exposure in the induction period was measured at various initial charging potentials for photoconductor samples of various thicknesses and at various temperatures. Then the results were analyzed to estimate the activation energy in the induction process. Subsequently, the decay rates after the induction period were measured at various temperatures, and we estimated the activation energy in the charge transport process. The mechanisms of the photoconduction and the induction effect are discussed on the basis of these results.

Experimental

Sample Preparation. The photoconductor consisted of an x-type metal-free phthalocyanine pigment dispersed in a resin matrix, which was a mixture of polyester and melamine polymers. The composition of the phthalocyanine and resin was 23 and 77 wt%, respectively. The samples were prepared as follows. First, a phthalocyanine pigment was deflocculated and dispersed in the resin with an organic solvent in a paint shaker. Then, a photoconductive layer was formed on a conductive substrate by dip coating, and the sample was air-dried and cured. The samples for the photoinduced decay measurements were formed on aluminum plates with oxide coating. A sandwich-type cell, in which the photoconductive layer was sandwiched between indium tin oxide (ITO)

Original manuscript received July 30, 1998

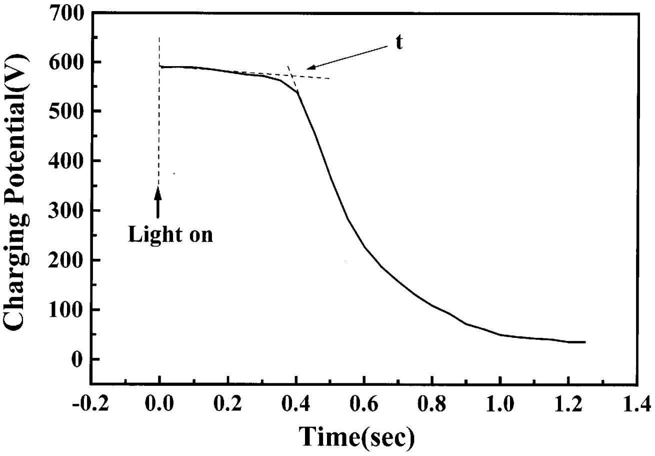

Figure 1. Photoinduced decay curve of single-layer photoconductor with metal-free phthalocyanine; λ = 780 nm, I =1.9 μw/cm^2. Sample thickness = 16.8 μm.

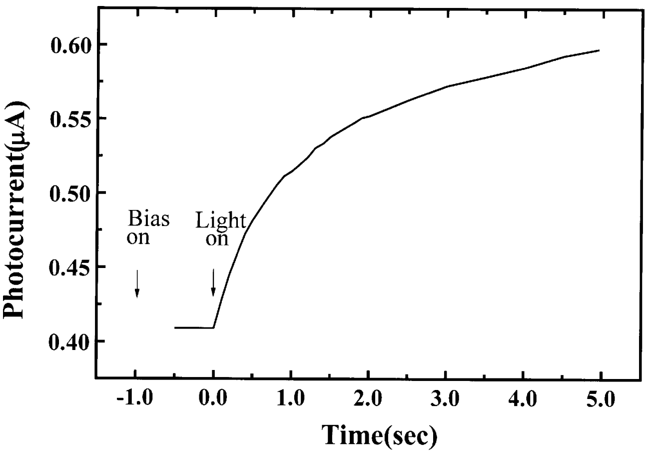

Figure 2. Photocurrent curve of photoconductor with metal-free phthalocyanine; λ = 780 nm, I = 1.5 μw/cm^2. Sample thickness = 18.0 μm, bias = 400v.

on a glass substrate and vacuum-deposited gold (Au), was used for the photocurrent measurements.

Measurements. The photoinduced decay was measured by evaluating the electrophotographic properties of the photoconductors (GENTEC Cynthia59). The samples were positively charged with a corona discharge device and irradiated by monochromatic light (λ = 780 nm). The photocurrent was measured with a picoammeter and a voltage power supply, and a cryostat controlled the sample's temperature. The thickness of the photoconductive layer was evaluated with a thickness meter and determined as an average value at several points.

Results

Induction Effect. Figure 1 shows a photoinduced decay curve (PIDC), where the charging potential is plotted against the exposure time. The charging potential is nearly constant at the beginning of exposure, but decays remarkably when the total light exposure reached a certain threshold. This phenomenon is the induction effect.

The threshold exposure necessary to start decay was estimated from the product of time t in Fig. 1 and the light intensity. Time t is designated as the intersection of two dotted lines extrapolated from the line before and after the start of significant decay. The threshold exposure was found to be almost independent of light intensity.

Figure 2 shows the photocurrent as a function of exposure time, measured in the sandwich-type cell with constant applied voltage. Light intensity, sample thickness and voltage were similar to those of the PIDC in Fig. 1. The induction effect in the photocurrent was not found on the same time scale as in the PIDC. This indicates that the induction effect is a unique phenomenon in the PIDC, perhaps because constant voltage is applied to the photoconductor during the photocurrent measurement or because a strong charge could be momentarily injected into the photoconductor in the sandwich-cell configuration.

Potential Dependence of the Threshold Exposure

Figure 3 shows the threshold exposure against the initial charging potential in 7.0, 11.6 and 16.8 μm thick samples. The threshold exposure increases almost linearly with increasing potential. The number of photons estimated from the threshold exposure was approximately 10^{11}–10^{12}/cm^2. It was the same order as that of the charge carriers for charging up to the initial potential.

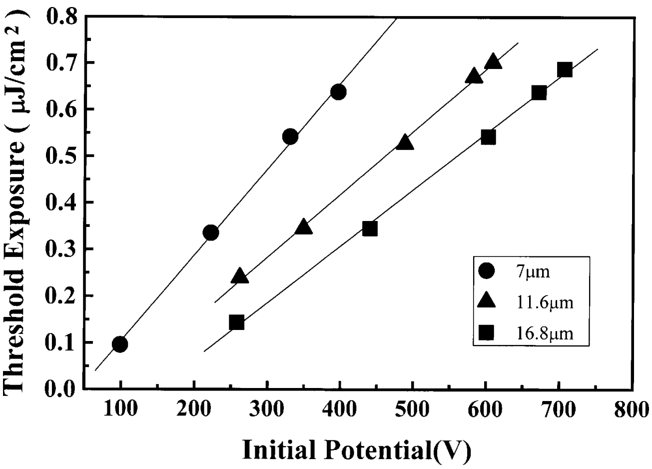

Figure 3. Plots of threshold exposure of photoconductor with metal-free phthalocyanine against initial charging potential.

If we compare this result for samples of different thickness, it is clear that the thinner sample needs a greater threshold exposure at the same potential. These results are consistent with the relationship between the potential and the quantity of charge.

Figure 4 shows plots of the threshold exposure in Fig. 3 against the electric field intensity. The threshold exposure is larger in the thicker sample at the identical electric field and at the identical charge density. However, the threshold exposure is not directly proportional to the thickness. This may indicate that charge traps in a portion of the photoconductive layer have an influence on the threshold exposure.

Temperature Dependence of the Threshold Exposure

Figure 5 shows the threshold exposure in the PIDC as a function of temperature. The dependence on the tem-

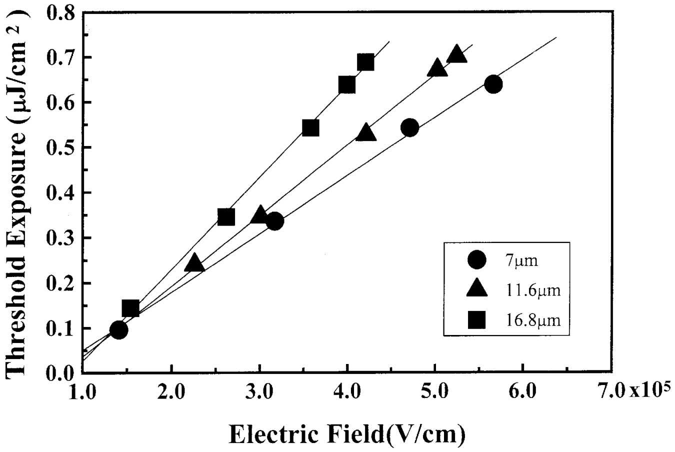

Figure 4. Plots of threshold exposure against electric field intensity of photoconductor with metal-free phthalocyanine.

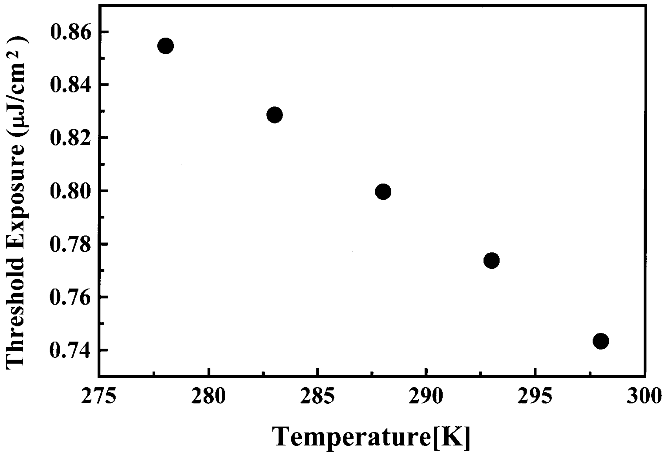

Figure 5. Temperature dependence of threshold exposure of photoconductor with metal-free phthalocyanine. Initial potential = 522v; sample thickness = 11.6 μm.

perature suggests that the induction effect has a relationship with a thermally activated process, such as charge generation, charge transport or carrier trapping. The dependence, however, is negative, so that it is difficult to get information about the induction process from the plots.

Therefore, we attempted to analyze the temperature dependence of the threshold exposure. The existence of the threshold exposure suggests that a certain constant amount of photogenerated carriers is necessary before the potential begins to decay. The certain constant amount of photogenerated carriers F is proportional to the product of threshold exposure L and carrier generation efficiency η. L and η are functions of temperature T and are designated as $L(T)$ and $\eta(T)$. Then, F is expressed as

$$F = A \cdot L(T) \cdot \eta(T), \tag{1}$$

where A is a coefficient. The coefficient A is constant if the thermally activated process in induction is the only photocarrier generation process. If the induction process includes another thermally activated process, the expression may include an exponential term. The carrier generation efficiency $\eta(T)$ is generally expressed as

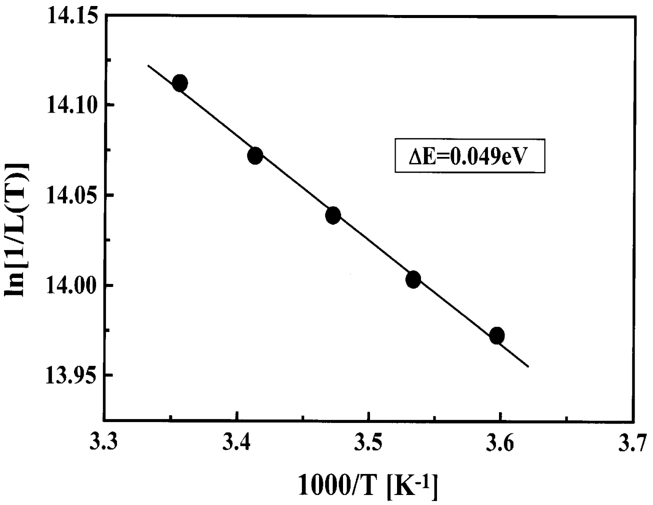

Figure 6. Arrhenius plot of reciprocal of threshold exposure of photoconductor with metal-free phthalocyanine; initial potential = 522v; sample thickness = 11.6 μm.

$$\eta(T) = \eta 0 \cdot \exp(-E0/\mathrm{k}T), \tag{2}$$

where $\eta 0$ is constant, $E0$ is the activation energy, k the Boltzmann constant and T the temperature.[9]

The combination of Eqs. 1 and 2 leads to

$$1/L(T) = C \exp(-E/\mathrm{k}T). \tag{3}$$

Here C is a constant coefficient, and E is the activation energy for the induction process ($E = E0$ or maybe $E0 + E^{\mathrm{other}}$).

Figure 6 is the Arrhenius plot of the reciprocal of the threshold exposure shown in Fig. 5. The activation energy E is estimated to be 0.049eV, where the initial potential is 522V and the electric field is 4.5×10^5V/cm. As to the photocarrier generation in x-type metal-free phthalocyanine, Popovic[9] obtained approximately 0.045eV as the activation energy at 4.5×10^5V/cm. The good agreement between these two values may indicate that the thermally activated process in the induction period is simply the photocarrier generation process.

Figure 7 shows the values of the activation energy in Eq. 3 at several initial potentials. The values were 0.067-0.049eV at a potential range of 290-522V and at a field range of 2.5–4.5×10^5V/cm. As the initial potential increases, the activation energy decreases. The decrease in the activation energy should accelerate the induction process and decrease the threshold exposure; however, the threshold exposure increases with an increase in the initial potential, as shown in Fig. 3. Therefore, we think that the thermally excited process is not the only factor causing the induction effect.

Photoinduced Decay Rates After the Induction

The potential in the PIDC decays after the induction period. We examined the temperature dependence of the photoinduced decay rate at various initial potentials and obtained information about the charge transport process. Figure 8 shows the Arrhenius plots of the decay rates. Each decay rate was the largest decay rate measured in each PIDC and was estimated from the maximum in the first derivative of the PIDC. The decay rates

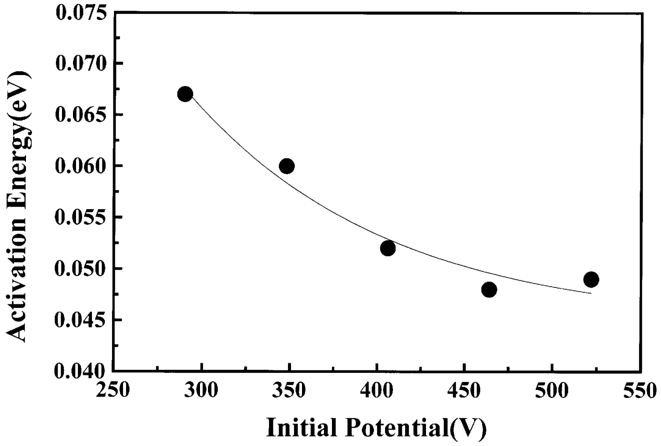

Figure 7. Activation energy of induction effect as a function of initial charging potential in photoconductor with metal-free phthalocyanine; sample thickness = 11.6 µm.

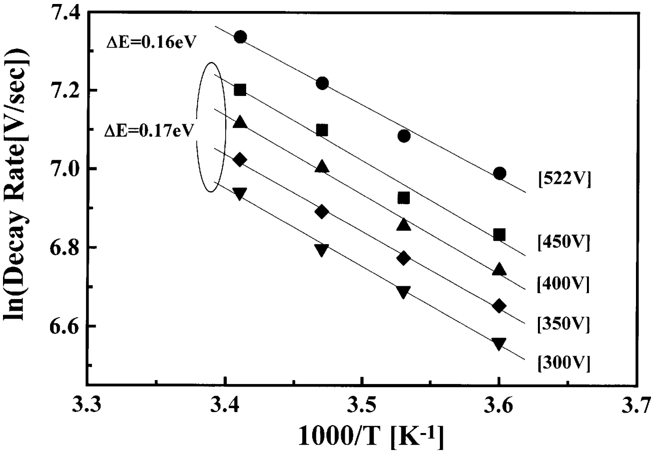

Figure 8. Temperature dependence of photoinduced decay rates of photoconductor with metal-free phthalocyanine; sample thickness = 11.6 µm.

increase as the temperature rises. This result indicates that the charge transport process is positively dependent on the temperature. The activation energy of the decay is 0.17 – 0.16eV at a potential range of 300– 522V, with an electric field range of 2.6 × 10^5 – 4.5 × 10^5V/cm.

Next, we obtained the activation energy of the charge transport process from the measurements of the photocurrent. The charge transport process in the photocurrent measurement is presumed to be same as the process in the photoinduced decay. The activation energy estimated from the photocurrent was 0.29 – 0.18eV at an electric field range of 0.11 to 0.82 × 10^5V/cm. Figure 9 shows the activation energy values obtained from the photocurrent and the photoinduced decay as a function of field intensity. The activation energy of the charge transport process is dependent on the electric field at a low field range of 10^4 V/cm and only slightly dependent at a high field range greater than 10^5 V/cm. As a whole, the value decreases with increasing field intensity.

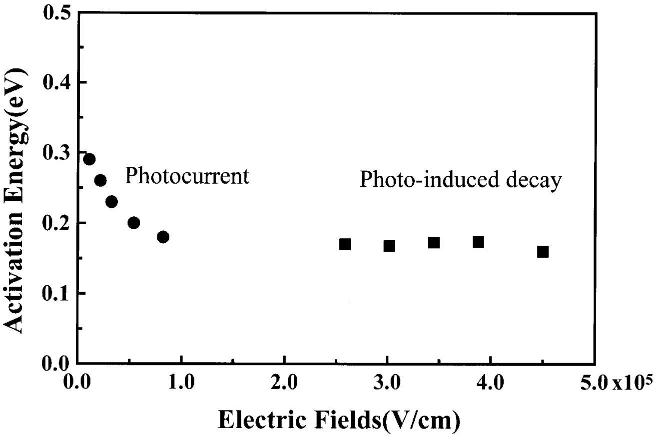

Figure 9. Activation energies for photoinduced decay and photocurrent of photoconductor with metal-free phthalocyanine.

Discussion

Thus far, induction effect has been described as the phenomenon that causes an S-shaped PIDC for the negatively charged photoreceptors.[5–8] The photoreceptor with phthalocyanine is positively charged and the PIDC seems to fall monotonically rather than be S-shaped (Fig. 1). The threshold exposure is almost independent of light intensity and the photoconductor has a high gamma property. The mechanism of the induction effect in the photoconductor with phthalocyanine may not always be the same as the mechanism that has been suggested for negatively charged photoconductors.

The difference between the photoinduced decay and the photocurrent results indicate that both charging carriers and photoinduced carriers play important roles in the induction effect (Figs. 1 and 2). Moreover, the distribution and the quantity of charge seem to be important factors as well.

The increase in threshold exposure with increasing potential indicates that the induction period increases as the electric field intensity and the quantity of charge increases (Fig. 3). The thickness dependence of the threshold exposure approximately supports this result. Figure 4 shows the existence of a factor such as charge trapping that occurs during the induction period. However, a simple trap cannot be considered to cause the induction effect because field intensity should reduce the depth of the simple trap according to the Pool-Frenkel effect,[10] whereas the threshold exposure only increases with increasing field intensity. As such, the induction process occurs a little below the surface of the photoconductor because the threshold exposure was not found to be proportional to thickness. The existence of a trap seems to complicate the explanation of the induction effect.

The induction process apparently includes a temperature-dependent process (Fig. 5), including the carrier generation process. It is important to determine whether or not there is any other temperature-dependent process. The comparison of the estimated activation energy in the induction process with the value reported in the photogeneration process indicates that there is little possibility of including any other temperature-dependent process in the induction process (Fig. 6). Moreover, a decrease in the activation energy with increasing field intensity is ordinarily a field-dependent change (Fig. 7).

The potential decay process after the induction period should reflect the charge transport process in the photoconductor. The decay rates increase with increasing field intensity (Fig. 8), and the activation energy in the transport process decreases with increasing field intensity (Fig. 9). Compared with the activation energy of the induction process, that of the transport process is larger and the basis of each process is thought to be different.

Several theories have been suggested to explain the mechanism of the induction effect.[5–8] One theory is based on the simple trap model such that carrier traps are filled with photogenerated carriers during the induction period, then the charging potential decays.[5] The number of traps is related to the length of the induction period in the PIDC.[5,6] The theory, however, cannot explain all of the properties of the induction effect as described above.

Another theory is based on structural traps.[7,8] The structural traps are traps or dead ends in a random network formed by the disordered dispersion of photoconductive particles or aggregates. Borsenberger and coworkers explain the S-shaped PIDC of their aggregate organic photoconductor in terms of field-dependent trapping by structural traps, but their explanation is restricted to the electron-dominated photoinduced discharge.[8] This idea is similar to the disorder model suggested by Bässler to explain the conductivity in molecularly doped polymers.[11] That model is based on negative differential resistance against the field intensity of the charge transport and has been experimentally demonstrated in molecularly doped polymers and evaporated organic compounds.[12,13] The negative differential resistance against the electric field is caused by field-induced localization of charge in traps or dead ends. According to the structural trap model, the induction effect can be explained as the phenomenon occurring when the charge is captured in traps or in dead ends in a random network and moves to the substrate with a gradual reduction in the local field intensity. The potential dependence of the threshold exposure can be explained by the field-induced localization in traps or dead ends. However, the negative resistance of the drift mobility against the field intensity has not been demonstrated in the photoconductor with phthalocyanine at a practical field range.[5] In addition, the photoconductor is a positively charged photoreceptor and the induction effect in a positively charged photoreceptor has never been explained with structural traps.

S-shaped dark decay was measured in the photoconductor with phthalocyanine. S-shaped dark decay did not appear in the photoconductor that was not charged or light-exposed, but after a repetition of charging and dark decay or after a repetition of charging and photoinduced decay, the S-shaped dark decay eventually appeared. Moreover, we found that the dark decay rate increased with increasing field intensity with a maximum at a low field range. This means the dark decay rate also decreases with increasing field intensity at some higher field range. These phenomena are believed to be caused by traps and trapped carriers in the photoconductor. We think the traps may be structural traps. The property of dark decay is still under investigation.

We infer that the induction effect in PIDC of the photoconductor with phthalocyanine is caused by another mechanism. Traps exist in the whole region of the photoconductive layer. If photogenerated carriers fill all traps in the induction period, the potential would then decay. The potential did not decay much during this period, so the induction phenomenon seems to take place specifically in the upper, sub-surface region of the layer. This is supported by the report that the induction effect is also measured in a double-layer photoconductor that has an upper charge generation layer including phthalocyanine.[14]

Let us suppose that the origin of the induction effect begins in the structural traps. In the induction period, enough photogenerated carriers would be generated to neutralize field-dependent structural traps, and charge carriers would start to move to the substrate. Because the quantity of the charge would not change, the electric field intensity from the part where the carriers exist to the substrate would not change and the structural traps would exist throughout the period. Therefore, the structural traps should be related to both the induction process and the charge transport process.

However, the activation energy in the induction effect was almost equal to that of the carrier generation (Fig. 6) and does not show a field-dependent change as predicted by the structural trap model (Fig. 7). Furthermore, the difference of the activation energy estimated between the induction process and the charge transport process indicates that the origins of these processes are different from each other (Figs. 7 and 9). It seems unreasonable to conclude that the structural traps cause the induction effect.

The charge transport process after the induction period is also a thermally activated process, which may be an intermolecular or inter-particle hopping process. The activation energy in the photoconduction process was dependent on the field intensity in the low fields and somewhat dependent in the high fields.

From the experimental results, we think that the quantity and the distribution of the charge from corona charging and the photogenerated carriers are important in the induction process. The potential dependence of the threshold exposure may result from the change of the quantity of the charge due to corona charging. The charging carriers are slightly distributed inside the photoconductive layer and the carriers exist in the binder. This idea seems to be supported by a volume charge capacitor model, where charging carriers are distributed inside the photoconductive layer in the photoconductor with ZnO,[15] and by the report of the depth of charge injection in the metal/polymer contacts, where the depth can be up to several microns from the surface.[16] Accordingly, we consider the following explanation for the induction effect.

First, charging carriers are distributed slightly inside the photoconductive layer and the carriers exist in the binder polymer or at the interface between the binder and phthalocyanine particles. Then, at the beginning of the photoinduced decay, the charge needs to move from charge holders, such as the binder, to a conductive material, such as phthalocyanine, for the charge transport. At that time, the minus charge of the photogenerated carriers neutralizes the charging carriers around the phthalocyanine particles and a hole remains in the particle, so that it is a conductive material. Consequently, the positive charge from corona charging is taken into phthalocyanine as a hole. From this point, we present two different mechanisms as follows.

One mechanism is based on the change of the local electric field. At first, the space charge field formed by charging carriers interrupts hole transport through phthalocyanine particles. Then, as the charge is taken into phthalocyanines, the electric field toward the substrate becomes stronger and holes can move to the substrate. Otherwise, holes move by diffusing up to the edge of the charging region. Some photocarriers are necessary to change the local field intensity or to diffuse the carriers.

The other mechanism is based on a production of the charge transport paths. The photogenerated electrons in phthalocyanines are given to electron-accepting materials, such as oxygen, and the electron-accepting materials facilitate charge transport paths. When the photogenerated electron neutralizes the charging carriers around the phthalocyanine, the electron-accepting materials cannot accept electrons and do not facilitate or spread the charge transport paths, so that the charge does not move and the potential does not decay.

These mechanisms qualitatively explain the induction effect but are not well demonstrated. Therefore, to further clarify the mechanism of the induction effect, more information about the phenomenon is necessary. In addition, it is important to discuss how the charge is distributed in the photoconductor, how photogenerated carriers move and what material keeps charges, photogenerated holes and electrons.

Conclusion

The photoconduction mechanism in the photoconductor with a metal-free phthalocyanine pigment dispersed in a polymer matrix was investigated. We obtained the following results.

1. The threshold exposure in the induction effect increased with increasing initial potential and with decreasing thickness of the photoconductive layer.
2. The activation energy in the induction effect was estimated to be 0.049eV at the electric field 4.5×10^5 V/cm, which is nearly equal to that of the photocarrier generation.
3. The activation energy in the induction effect was estimated to be 0.067–0.049eV at a field range of $2.5 - 4.5 \times 10^5$V/cm. The values decreased with increasing field intensity.
4. The activation energy of the charge transport process was estimated to be 0.29 – 0.18eV at an electric field range of 0.11 to 0.82×10^5V/cm and 0.17 – 0.16eV at an electric field range of $2.6 \times 10^5 - 4.5 \times 10^5$V/cm. The activation energy of the charge transport process decreases with increasing field intensity.

From these results, we infer the possibility of a different mechanism from the prevailing trap theories. The suggested mechanisms pay attention to the quantity and the distribution of charging carriers and photogenerated carriers. We think it is necessary to study the movement of charge carriers in a microscopic area to more clearly elucidate the induction effect. △

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