Effect of Ambient Gases on the Charge Acceptance of Cu-phthalocyanine/polymer Single Layer Photoreceptors

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Abstract

The charge acceptance of single layer organic photo-receptors consisting of α-type Cu-phthalocyanine pigments and hydrazone charge transport materials dispersed in thermo-setting acrylic polymer is found to decrease when the surface is exposed to ambient NO_x gas. The electronic surface properties of the photoreceptors are investigated by treating the surface with HNO_3 aqueous solutions and by measuring the applied voltage-current characteristics. Internal photo-emission experiments determine the energy-level relationship between metal electrodes and the photoreceptors. The hole injection from the treated surface can be attributed to the adsorption of acceptor ions at the surface. The improvement of charge acceptance based on this conclusion is suggested.

Introduction

The electrophotographic applications of single layer organic photoreceptors (SLP) have recently been investigated extensively.[1] Ueda and Noda reported on the photoinduced discharge of one such photoreceptor consisting of α-type Cu-phthalocyanine pigments and hydrazone charge transport materials dispersed in thermo-setting acrylic polymer (CuPc/polymer SLP).[2] In the present paper, we report the observation of reduction in the charge acceptance of CuPc/polymer SLP, when the positively charged SLP is exposed to ambient NO_x gas. In order to identify the mechanism of this effect, the electronic surface properties are investigated by treating the surface with HNO_3 aqueous solutions and by measuring the applied voltage-current characteristics. Based on our findings, a practical way for improving the charge acceptance is suggested.

Experimental and Results

The photoconductive layer (PCL) consisting of α-type Cu-phthalocyanine pigments and hydrazone charge transport materials (CTM) dispersed in thermo-setting acrylic polymer (CuPc/polymer SLP)[2] is coated on an Al substrate, the surface of which is anodized as an effective blocking layer to charge injection. The photoinduced discharge curves with positive charging show the J-shape, and not the S-shape, because the PCL contains CTM.
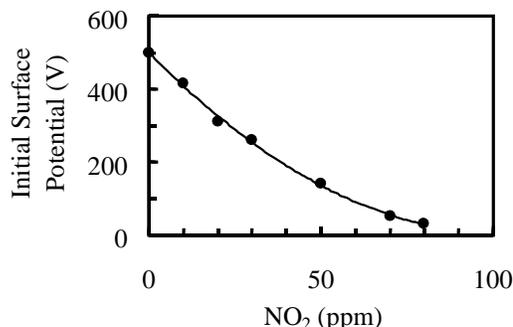

Figure 1. Initial surface potential measured after being placed in NO_2 gas for 2 hours, as a function of the gas density for Cu-phthalocyanine/polymer single layer photoreceptors.

After exposing the PCL to ambient NO_2 gas for 2 hours, the initial surface potential (i.e. the charge acceptance) is measured as a function of the gas density. The results are shown in Fig. 1. The reduced charge acceptance recovers when the PCL is placed in normal ambient air for several min. Therefore, the initial surface potential once reduced increases during repeated charging and exposure cycles in the normal ambient air. This indicates that the reduction in charge acceptance is due to physical adsorption of NO_2 gas. On the other hand, the non-recovery of charge acceptance for the case of extended exposure to NO_2 gas suggests that the physical adsorption has changed into chemical adsorption. It is observed that the charge acceptance is not reduced when the PCL is exposed to O_2, CO_2, or CO ambient gas up to 2,500 ppm.

The free surface of CuPc/polymer SLP is treated with HNO_3 aqueous solution for 30 min and dried for more than 30 min at room temperature. The relation between the initial surface potential of the treated PCL and the normality N of HNO_3 aqueous solution is shown in Fig. 2. Once reduced after the treatment, the charge acceptance recovers during repeated charging and discharge cycles, as in the case of NO_2 exposure (Fig. 1). However, such

recovery is not observed when the treatment in HNO_3 aqueous solution lasts several hrs. We believe the same mechanism operates in the nitration by HNO_3 aqueous solution and in the adsorption of NO_2 gas on the free surface.
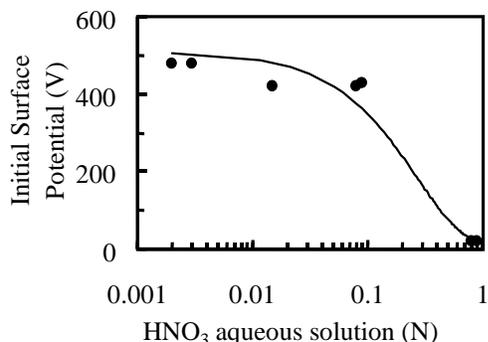

Figure 2. Initial surface potential for Cu-phthalocyanine/polymer single layer photoreceptor after treated for 30 min, as a function of a normality N of HNO_3 aqueous solution.
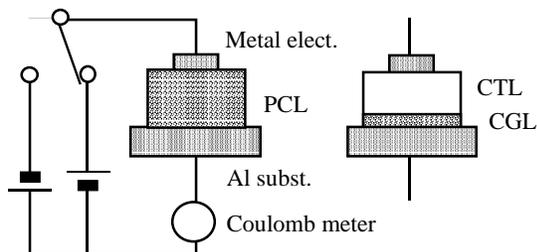

Figure 3. Experimental arrangement for measuring the applied voltage-current characteristics
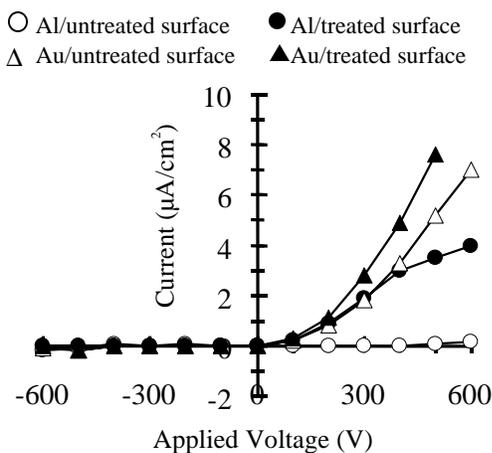

Figure 4. Applied voltage-current characteristics for the Cu-phthalocyanine/polymer single layer photoreceptors.
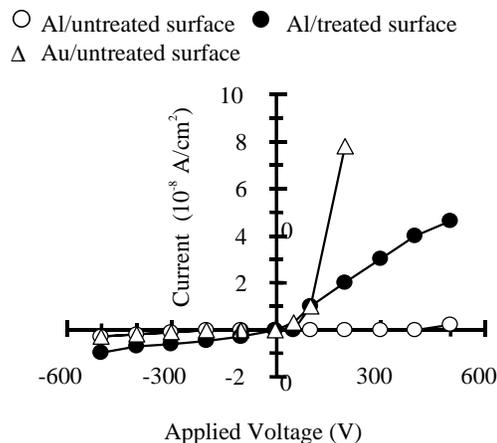

Figure 5. Applied voltage-current characteristics for the Cu-phthalocyanine dual layer photoreceptors.

Applied Voltage-Current Characteristics

The experimental arrangement of the applied voltage-current (V-I) characteristics is illustrated schematically in Fig. 3. The metal electrodes on the surface of PCL are prepared by vacuum deposition.

The V-I characteristics are shown in Fig. 4. With an Al electrode on untreated surface (Al/untreated surface), the current is negligible for both positive and negative applied voltages. On the other hand, a large current is observed for positive applied voltage with an Au electrode (Au/untreated surface). This means that holes can be injected from the Au electrode into the PCL. The current is approximately proportional to the square of the applied voltage, indicating that it is space-charge limited. The rectifying characteristics are similar to that of metal-semiconductor interfaces. However, the rectifying direction appears reversed.

Also shown in Fig. 4 are the V-I characteristics for PCL's treated with HNO_3 aqueous solution, 1N and 30 min. With an Al electrode (Al/treated surface), a large current is observed for positive applied voltage, indicating that the hole injection from the Al electrode into the treated PCL becomes possible.

The CuPc/polymer SLP's with untreated surface have a good charge acceptance for both positive and negative corona charging. On the other hand, the SLP's with pre-treated surface show no charge acceptance for positive corona charging, but a high charge acceptance for negative corona charging. These results are consistent with the V-I characteristics shown in Fig. 4.

The V-I characteristics for CuPc dual layer photoreceptors (CuPc DLP) shown in Fig. 5 are similar to that of CuPc/polymer SLP shown in Fig. 4. This is not unexpected because the charge transport layer (CTL) of the CuPc DLP consists of the hydrazone CTM and the thermo-setting acrylic polymer used for the CuPc/polymer SLP.

The work functions of Al, Au, and the SLP are determined by the Kelvin method to be 3.9, 4.9 and 4.6 eV, respectively. The ionization potentials of both the PCL of

the SLP and the CTL of the DLP are 5.2 eV, determined from external photoemission experiments. The absorption edge ("band gap") of the PCL is 2.0 eV by fluorometry.

Internal Photoemission Experiment

Internal photoemission (photo-injection) of holes from a metal into an insulator can be used to determine the energy level relationships at the interface between the metal electrode and the photoreceptor.[3] The usual experimental setup (Water cell) is illustrated in Fig. 6. The CTL is prepared on Al substrates directly.
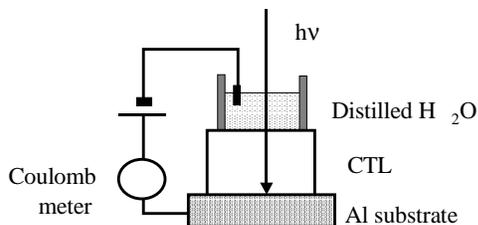

Figure 6. Experimental arrangement for observing the internal photoemission (Water cell). Distilled water was held in a plastic box sealed to the CTL.
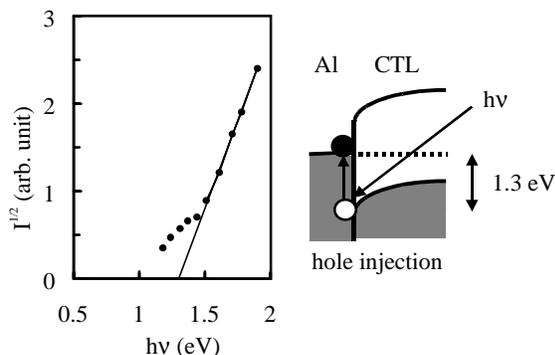

Figure 7. The threshold energy of 1.3 eV was determined for the interface between the Al electrode and the CTL.
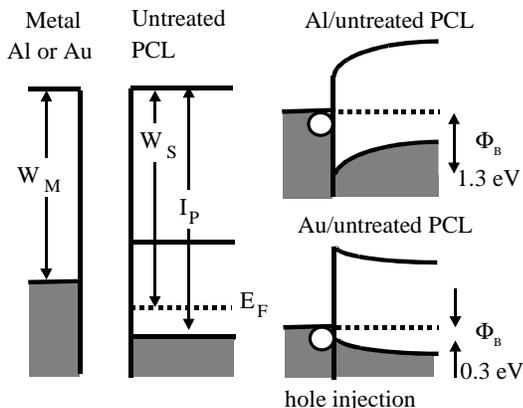

Figure 8. Energy level relationship at the interface between the metal electrode and the CuPc/polymer SLP.

An electron in Al receives the photon energy and undergoes a transition to an excited state, leaving a hole in the valence band as illustrated in Fig. 7. The holes may then enter the transport levels in the CTL. For the interface between Al and CTL, the threshold energy value of 1.3 eV is determined.

Discussion

Consider the contact between a metal electrode with a work function W_M and a photoreceptor with a work function W_S and an ionization potential I_P, as illustrated in Fig. 8. The Schottky barrier is given by,[4,5]

$$\Phi_B = W_M - I_P \tag{1}$$

Using the WM of Al and the I_P of PCL given in the previous section, the Schottky barrier of $\Phi_B = 1.3$ eV is obtained from Eq. 1. This value is in agreement with the result on the threshold energy in the internal photoemission experiment (Fig. 7). The high barrier prevents hole injection from Al to untreated PCL (Al/untreated surface), as schematically illustrated in Fig. 8. Similarly, a Schottky barrier of $\Phi_B = 0.3$ eV is obtained for Au/untreated surface, and is also shown schematically in Fig. 8. A nearly Ohmic contact allows the hole injection from Au to the untreated PCL. We will apply this hole injection mechanism to the discussion of Al/treated surface.

The V-I characteristics of the Al/untreated surface and Al/treated surface in Fig. 4 correspond respectively to the high charge acceptance and the low charge acceptance, in positive corona charging. Therefore, the ionization potential of positive corona ions can be expected to be nearly equal to the work function of Al, that is about 4 eV.
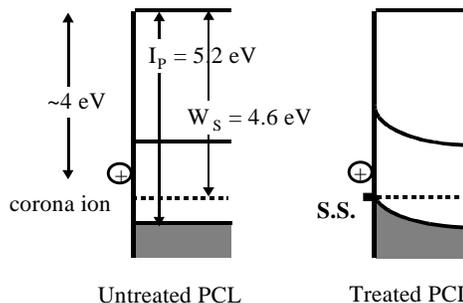

Figure 9. Energy level shifting by the surface states.

Surface States and Carrier Injection

The nitration of the free surface by HNO_3 aqueous solution and the adsorption of NO_2 gas on the free surface produce surface states at the free surface of PCL. The barrier model with the surface states is shown in Fig. 9. A measurement by external photoelecrtric effect gives the ionization potential of PCL as $I_P = 5.2$ eV. This leads to a large barrier of 1.3 eV for Al/untreated surface of CuPc SLP, based on Eq. 1 and a large energy gap of more than 1.0 eV between a positive corona ion and the energy level

of the PCL assuming that the ionization potential of positive corona ions is 4 eV as shown in Fig. 9.

Now suppose the nitration or exposure to ambient NO_2 introduces acceptor-like states at the surface. Then, the ionization potential for states near the surface reduces to a smaller value closer to that of the bulk state (upward shifting of the energy level). This reduces the barrier and facilitates hole injections from Al into the treated PCL and energy gap between the positive corona ion and the energy level of the treated PCL as shown in Fig. 9.

Improvement of the Charge Acceptance

We have prepared a useful protective layer of SiO on the surface of CuPc/polymer SLP drums to prevent the reduction in charge acceptance. The layer with a thickness of 0.3 μm is vacuum deposited on the surface of PCL on Al substrates, and aged at 55°C for 5 hrs. The thickness of 0.3 μm shows enough prevention and less residual potentials. However, neither Al_2O_3, SiC, SiO_2 nor Si_3N_4 has been found to be effective as a protective layer.

Conclusion

When a negative voltage is applied to the Al or Au electrode on CuPc/polymer SLP, no current is observed, as shown in Fig. 4. This means that no electron can inject from the metal substrate into the positively corona charged PCL, regardless of whether the substrate is Al or Au. Therefore, one would expect a high charge acceptance for CuPc/polymer SLP.

For CuPc DLP in practical use nowadays, it is not necessary to consider the NOx problem seriously because they are used with negative charging. However, when a reversal development process is applied to CuPc DLP, the corona discharge at the toner transfer station is positive and a special care may be necessary. If a DLP using positive charging were to be in practical use in the future, the discussion in this paper should be considered.

It is concluded that the charge acceptance of CuPc/polymer SLP depends significantly on the electronic surface properties of the photoreceptor, because of the adsorption of acceptor ions on the free surface. We are able to prepare a useful protective layer of SiO on the surface of CuPc/polymer SLP.

References

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Biography

Kuniki Seino received his M.S. degree in Physics in 1967 and a D.Sc. in Physics in 1972 from the Kwansei Gakuin University in Japan. He joined Minolta Co. Ltd., in 1967, where he has been engaged in research on photoreceptors and electrophotographic imaging processes. From 1991 to 1996, he managed the development of analog and digital copying machines including full color equipment. He is a member of the IS&T and the Imaging Society of Japan.