JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 47, Number 4, July/August 2003

Properties of Photoreceptor Devices Consisting of Metal Free Phthalocyanine and Polymer

Sohji Tsuchiya
Fine Rubber Research Laboratory, Inc., Fukushima, Japan

Atsushi Omote
Matsushita Electric Industrial Co., Ltd., Advanced Technology Research Laboratories, Kanagawa, Japan

The dispersion effect in solution making a positively charged monolayer photoreceptor consisting of x-type metal-free phthalocyanine (x-H_2Pc) and a binder resin is studied. The photoreceptor is characterized by a high photosensitivity due to a new specific interaction between x-H_2Pc and the binder resin.[1] It is suggested that the characteristics of the solution structure and the chemical actions significantly affect the behavior of x-H_2Pc. To clarify more this behavior, the solution state is examined by viscometry, and the solid state is examined by X-ray diffraction, transmission and scanning electron microscope, and ion potential and xerographic measurements. From these results, it was found that the dispersion process of the x-H_2Pc pigment, depending on the composition and the dispersion time of the solution, significantly influences the physical properties and the electrophotographic characteristics of the monolayer photoreceptor.

Journal of Imaging Science and Technology 47: 366–371 (2003)

Introduction

In recent years, various kinds of organic photoreceptors (OPC) have been used for laser beam printers and digital copy machines employing laser diodes as the light source for electrophotography.[2] Most of them are constructed as a layered device in which a charge-generation layer is separated from a charge-transport layer. The photoreceptors of this type have been known to have some drawbacks, such as a failure upon exposure due to ozone from a negative charger, inhomogeneous distribution of negative charging and higher cost ascribable to the coating of multiple layers. In order to overcome these shortcomings, various monolayer photoreceptors are used as the pigments of titanyl phthalocyanine,[3,4] copper phthalocyanine[5] and perylene pigments[6] have also been examined. Phthalocyanines have been found to be interesting organic photoconductors which have a photoconductive sensitivity in the near-infrared region at about 780 nm suitable for laser diode light. Recently, it has been reported that the morphology of particles and crystallites in the pigments like the phthalocyanines has a great influence on the photoelectronic properties of the photoreceptors using the pigments dispersed in a polymer matrix.[7–9] However the influence of morphology differences on the properties have not yet been clarified in detail. The morphology properties of the photoreceptor films have been investigated by X-ray diffraction and scanning electron microscopy.[10] The monolayer photoreceptors basically function with positive charge during charging, consistent with the hole-conducting nature of the organic conductors.

We have studied the positively charged monolayer photoreceptor consisting of an x-type metal-free phthalocyanine (x-H_2Pc) and a binder resin, which is characterized by high photosensitivity due to a specific interaction between x-H_2Pc and the binder resin.[10] We are interested in the effects of the dispersion process in solution, composed of x-H_2Pc and the binder resin, on the photoreceptor morphology and physical properties in the solid state. However, the relationship between the pigment dispersion process and the characteristics of the OPC has not yet been defined. Otherwise, for the dual-layer OPC with the layer consisting of pigment and binder as the charge generation layer with a thickness of about 0.1 μm, has been postulated that the characteristics of the OPC are not significantly influenced by the dispersion process.[11]

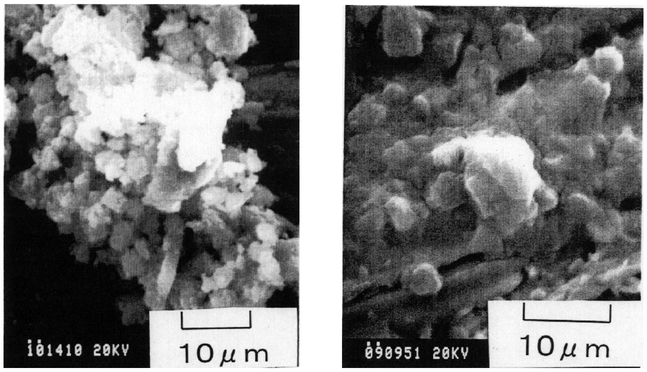
In this study, the state of the x-H_2Pc dispersed in a binder polymer and the relationship between the characteristics of the OPC state and the dispersion process were investigated.

Experimental

Sample Preparation

The x-type metal-free phthalocyanine (x-H_2Pc) was used as the photoconductive pigment in the monolayer photoreceptor and purchased from Dainippon Ink and Chemicals, Inc. (Tokyo, Japan). The polymer binders used were polystyrene (PSt) (MW:280,000) purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) and polyvinylbutyral (PVB) (trade name BM-S; mol. wt. = 80,000) from Sekisui Chemicals, Inc. (Kyoto, Japan).

Original manuscript received November 20, 2002



(a) (b)

Figure 1. (a) SEM micrograph of x-H_2Pc particles; (b) SEM micrograph of x-H_2Pc particles after dispersion in solvent (THF) for 2 hours at room temperature.

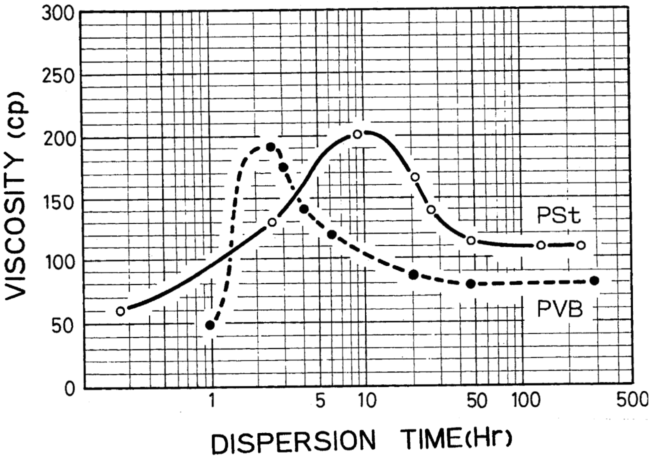


Figure 2. The viscosity of the THF solution consisting of x-H_2Pc and PSt or PVB; dependence on the dispersion time. ○ :PSt, ●:PVB.

The x-H_2Pc was mixed with the binder polymer, PVB or PSt, in a ratio from 15% to 80 wt% by weight in tetrahydrofuran (THF). The coating solution was then prepared by ball-milling or magnetic stirring of a mixture containing a 20 wt% binder resin in THF solution. The photoreceptor devices were made on an Al substrate by a spinner or a dipping technique and dried at 150°C for 2 hours in air. The thicknesses of the layers were in the range from about 10 to 20 μm as the photoreceptor device.

Measurements of Properties and Structures

The measurement of the solution viscosity was made by a viscometer (Viscomate-1: Yamaichi Kogyo, Ltd., Japan). X-ray diffraction patterns were measured with an RD-rB diffractometer (Rigaku Electric Ltd., Japan). The xerographic properties were evaluated from the photoinduced discharge measurements using a systematic xerographic analyzer (EPA-8100: Kawaguchi Electric Works, Ltd., Japan), where the light source was a halogen lamp. The ionization potential was measured by atmospheric photoelectron emission analysis (AC-1: Riken Keiki, Ltd., Japan). The SEM and TEM observations were made using S-4100 and H-7100 microscope respectively from Hitachi Ltd., Japan.

Results and Discussion

Solution Behavior

As is already known, phthalocyanine pigments are insoluble in common solvents, so the dispersion consisting of only H_2-phthalocyanine pigments and a solvent cannot become uniform even using an intense dispersion treatment. If the dispersion is stopped, the solution easily becomes separated into phthalocyanine particles and solvent. Finally, the crystallographic structure of the x-H_2Pc may change to β-H_2Pc in solution, which is the most stable crystal form, insofar as it is generally known that the forms and the morphology of some phthalocyanine particles are changed by exposure to a solvent.[11] The time needed to change crystal forms is dependent on the solvent species. The process of changing crystal forms during dispersion has not been clarified as yet. Therefore, the change in the x-H_2Pc particles before and after dispersion in the solvent THF for 2 hours at room temperature is followed by SEM as shown in Figs. 1(a) and 1(b). As shown in these figures, by dispersion in the solvent, the particles seem to become larger by aggregation, and have a slightly smoother surface due to some solubility of H_2Pc in THF. In solution consisting of only x-H_2Pc and the solvent THF, the form of x-H_2Pc changes to the β form within a few days. The β form can be judged from the separation of H_2Pc particles in the solution and the needle-shaped morphology change. The solution consisting of x-H_2Pc, THF and a binder such as PSt or PVB is, however, homogeneous and is stable for more than a month even under steady dispersion treatment using a ball-mill. Here, the dispersion is accomplished using a magnetic stirrer. The crystalline form of H_2Pc is fundamentally maintained in the x form.

Figure 2 shows that the viscosity of the solution consisting of x-H_2Pc, THF and PSt or PVB is dependent on the dispersion time. The viscosity increases with time from the initial value and then gradually decreases to a constant value. The viscosity is then maintained at a almost constant value for about one+month. It is thought that the viscosity change is consistent with the morphlogy change of phthalocyanine particles in solution and an interaction with phthalocyanine particles and a binder by dispersion.

The morphlogy change and the new interaction are also observed by transmission and scanning electron microscope as shown below. The small size of the phthalocyanine particles and a interaction between phthalocyanine particles and binder are also investigated by visible photoabsorption properties.[10] For the case of the solution with PVB as the binder, the change in viscosity is observed over a shorter dispersion time. It is thought that the result is dependent on strong interaction between PVB molecules and phthalocyanine particles in the THF solution.

Characteristics of the Solid State

X-ray Measurement. The solid structure of the photoreceptor is studied by measurements of X-ray diffraction pattern. Figure 3 shows the X-ray diffraction patterns of x-H_2Pc powders and a photoreceptor composed of x-H_2Pc and PSt after dispersion for 48 hours. A comparison of the two X-ray diffraction patterns reveals that there is a change such that diffraction lines at degrees higher than 2θ = 21.4° disappear, along with an increase in the peak at 16.5° and a decrease in the peak

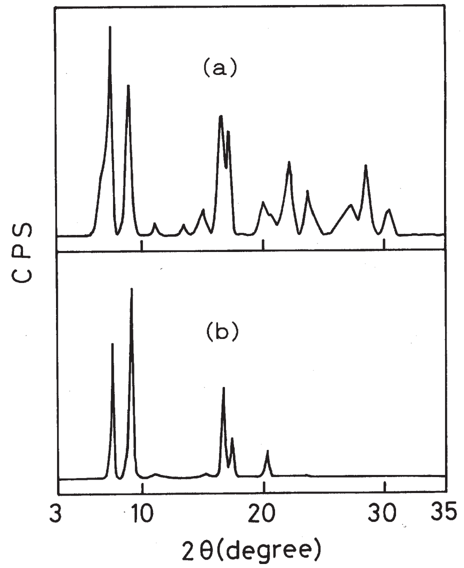
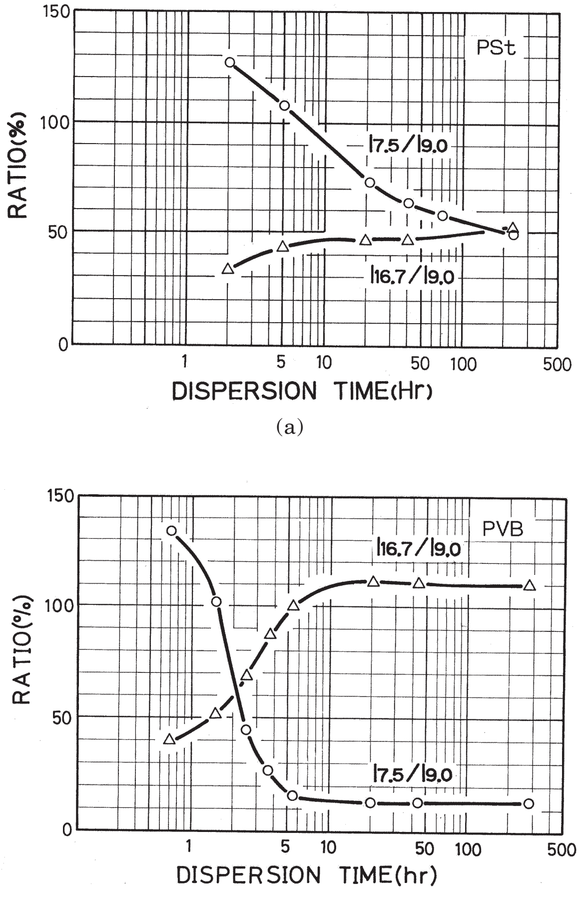


Figure 3. X-ray diffraction patterns of (a) x-H_2Pc powders; and (b) the photoreceptor composed of x-H_2Pc and PSt.

at 7.5°. Pronounced variation is seen in the two diffraction pattern peaks at 7.5° and 9.0°, which are inherent to x-H_2Pc; only the former peak decreases. These variations, depending on the dispersion times, are also different between the PSt and PVB binders. Figure 4(a) shows the dependencies of the ratios of the peak intensities at 7.5° and 16.5° to that at 9.0° on the dispersion times with the PSt binder. Figure 4(b) also shows a similar dependence for the PVB binder. However, the variations observed with PVB are much larger than with PSt. The crystalline forms of H_2Pc in both polymers are fundamentally maintained as the x form. The variation of X-ray diffraction peaks appears consistent with an anisotropic morphology change in the x-H_2Pc particles as shown in the TEM observations and the change is greater and varies more quickly for PVB than for PSt. X-H_2Pc is easily transformed into β-H_2Pc within a week at room temperature during the dispersion in an organic solvent alone. In solution containing the binder, it is found that x-H_2Pc is stabilized and the crystallographic x form but with new morphology, which is preserved for over one month.

Ionization Potential. In order to elucidate the difference in the ionization potential (I_p) in various samples, measurements by atmospheric photoelectron emission analysis were made. Figure 5 shows the photoelectron emission spectra of the photoreceptors composed of x-H_2Pc and a PSt at a ratio of 1:4 by weight prepared with different dispersion times of 12, 36, 72 and 136 hours. Figure 6 shows the spectra of the photoreceptor using x-H_2Pc and PVB at a ratio of 1:4 by weight with different dispersion times of 18, 66 and 136 hours. We found that the values of Ip are not significantly changed depending on dispersion time and binder. The values of I_p are in the range from 5.2 to 5.3 eV. The slopes of the straight line portions of the curves indicate emission efficiencies that change significantly with both dispersion time and binder. Both samples have higher emission efficiencies with dispersion time, and in the PVB case there is a larger dependency than for PSt. I_p does not change with the morphology change as shown by



(a)

(b)

Figure 4. The dependence of the ratios of the peak intensities at 7.5°and 16.5° to that at 9.1° on the dispersion time of the photoreceptors composed of (a) PSt and (b) PVB, mixed with x-H_2Pc at a ratio of 1:4 by weight in THF solution.

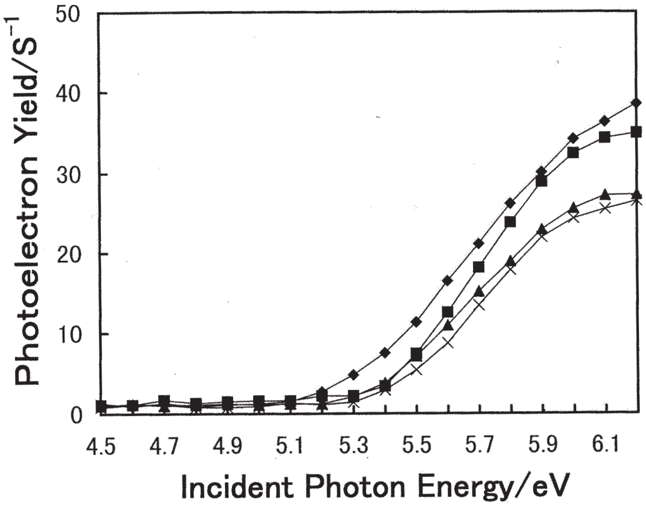


Figure 5. The photoelectron emission spectra of the photoreceptors composed of PSt mixed with x-H_2Pc at a ratio of 1:4 by weight under the different dispersion times in THF solution for 12(+), 36(▲), 72(■) and 136(♦) hours

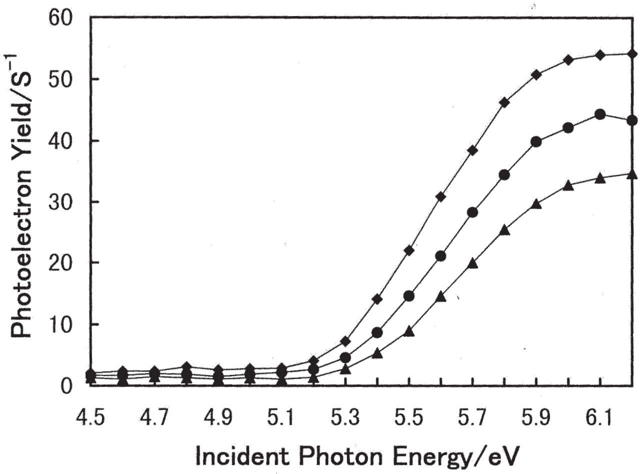


Figure 6. The photoelectron emission spectra of the photoreceptors composed of PVB mixed with x-H_2Pc at a ratio of 1:4 by weight under the different dispersion times in THF solution for 18(▲), 66(●) and 136(◆) hours.

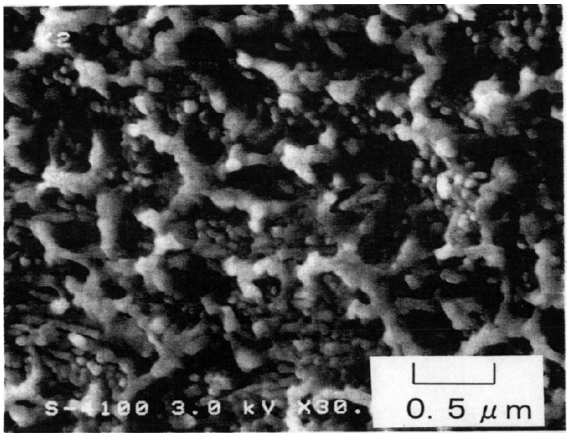
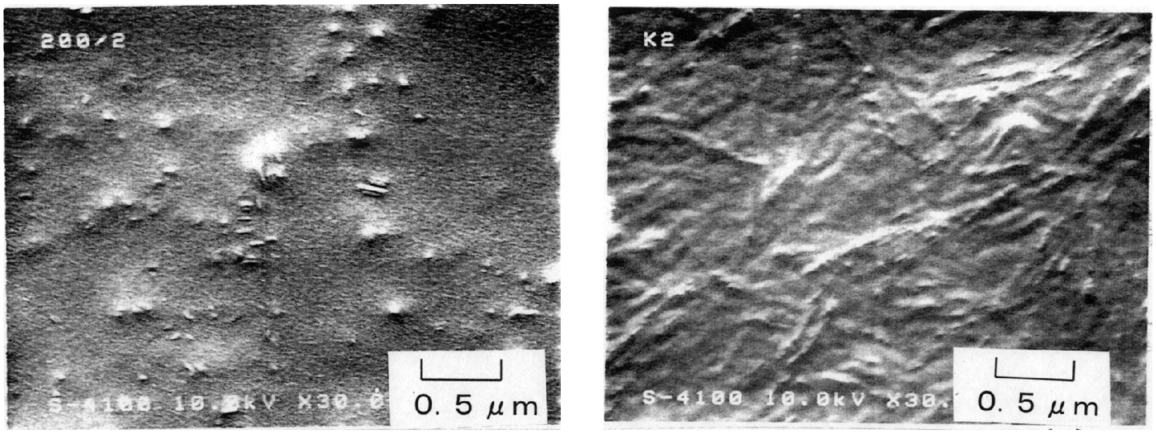


Figure 7. A SEM cross-sectional view of the photoreceptors of x-H_2Pc and PVB.



(a) (b)

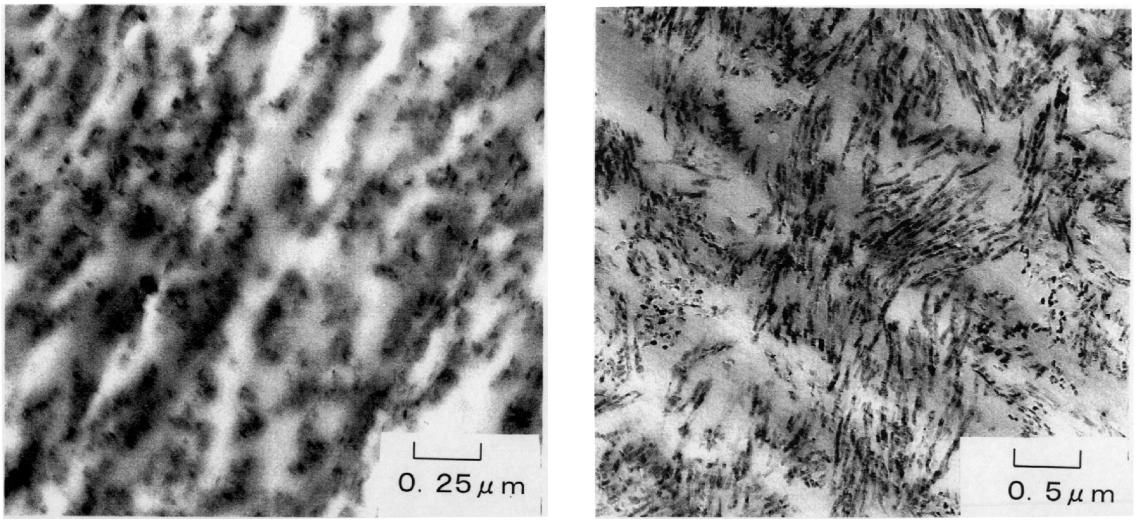
Figure 8. The micrographs of the surfaces of the photoreceptors with (a) PSt and (b) PVB mixed with x-H_2Pc at a ratio of 1:4 by weight dispersed in THF solution for 5 days.

the X-ray diffraction measurements of the x-H_2Pc particles, with or without binder. The difference in the emission efficiency is presumed to be caused by the effects of the morphology change and the change in coverage of the x-H_2Pc particles with the binder on dispersion in THF solution.

Scanning and Transmission Electron Microscopy Results. Observations using scanning and transmission electron microscopes were made to investigate the dispersion state of the x-H_2Pc pigments in the photoreceptor. Cross-sectional views of the photoreceptor films using various binders, and reacted for different dispersion times, are taken by scanning electron microscopy (SEM). It is observed that there are no differences in the dispersion state of x-H_2Pc depending on binder or dispersion time, as typically shown in Fig. 7, which is a cross-sectional view of a photoreceptor consisting of x-H_2Pc and PVB. From this SEM photograph, it seems that the dispersion of the particles is fairly uniform with no holes in the photoreceptor.

The surfaces of the photoreceptors using the PVB and PSt binders are observed as shown in Fig. 8. Both surfaces are relatively smooth, but there are some differences. Figure 8(a) shows that the surface using PSt is partially pitted with x-H_2Pc particles; Figure 8(b) shows linear situations when using PVB. Furthermore, the dispersing states of x-H_2Pc in the photoreceptors are observed in good detail by transmission electron microscopy (TEM) as shown in Fig. 9. The size of the x-H_2Pc particles in both photoreceptors using PSt and PVB is 0.1 ~ 0.2 µm in both Figs. 9(a) and 9(b). The shape of the x-H_2Pc particle in PVB is observed more clearly is and more tile-like than that in PSt. Another characteristically different point is that some darkish domains in the spots are observed in the photoreceptor using PVB. We presume that the smallest pigment particles of the x-H_2Pc dissolve slightly in THF during the dispersing treatment, and might exist in these domains within the binder and the particles of x-H_2Pc in a new crystalline form.[10]

Xerographic Characteristics. The photosensitivity (xerographic characteristics) is influenced by the preparation conditions of the photoreceptor. We observed the dependence on both the binder and the dispersion time in THF solution. Typically photoinduced decay curves for the photoreceptors composed of x-H_2Pc and PVB, or PSt are shown in Fig. 10. The dispersion time in this



(a) (b)

Figure 9. The TEM images of the photoreceptors with (a) PSt and (b) PVB mixed with x-H_2Pc at a ratio of 1:4 by weight dispersed in THF solution for 5 days.

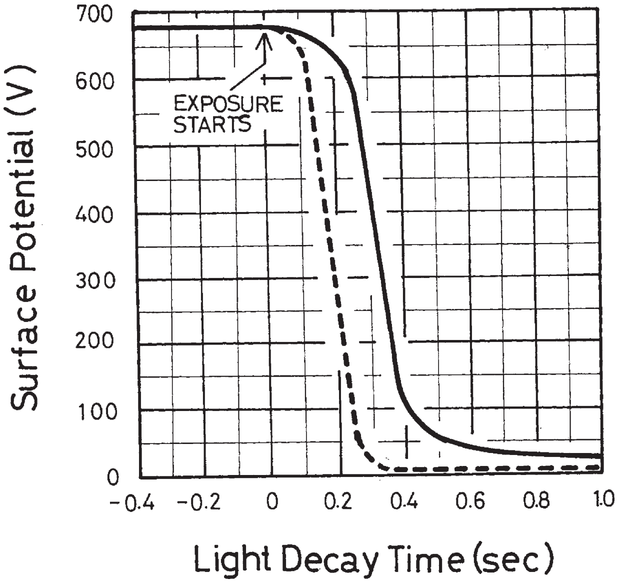


Figure 10. The photoinduced decay curves of the photoreceptors with PSt and PVB as binders mixed with x-H_2Pc at a ratio of 1:4 by weight. —:PSt, – – –:PVB.

case was 5 days during which the viscosity reached a saturation value. The light exposure was carried out with 10 lux white light in this experiment. From a comparison of these curves, it is found that the photoreceptor using PVB has a higher photosensitivity due to a smaller induction time before the surface voltage sharply decreased on the light exposure. $E_{1/2}$ of the photosensitivity of the photoreceptors using PSt, which is the energy necessary to decrease the surface potential to one-half of the initial value, is dependent on the dispersion time as is viscosity, shown in Fig. 11. The viscosity increases with dispersion time from its initial state and then gradually decreases to a constant value; the photoinduced decay curves meanwhile become sharper and the photosensitivity increases. Particularly, the photosensitivity change is large over the dispersion time during which the viscosity increases. The viscosity and the photosensitivity are then maintained at a almost constant value for about one month.

The xerographic characteristics of the photoreceptor consisting of x-H_2Pc and the matrix polymer have been related to the results of the measurements of Ip and the drift mobility.[12] It is thought that the photosensitivity reflects the conditions of making the photoreceptor which lead to morphology change in the x-H_2Pc particles, such as the crystalline form and the particle form, as well as the existence of domains brought about due to a new interaction of H_2Pc molecules or the extremely small pigment particles with the binder during the dispersion treatment. The morphology change of x-H_2Pc particles and the existence of such domains might be the cause of an increase in the number of change transporting species per unit volume. The domains also might make the distance between the trans-

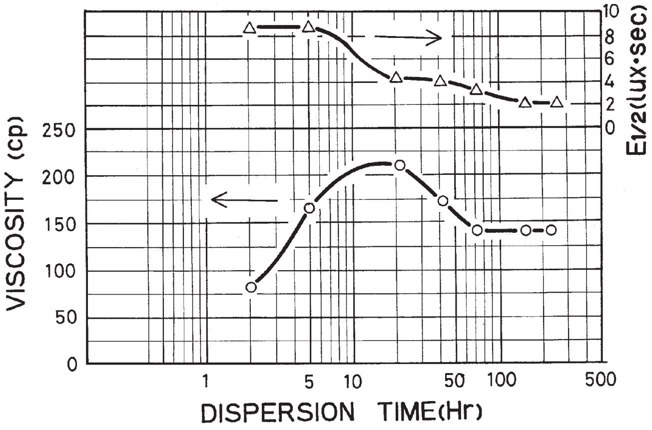


Figure 11. The photosensitivity as $E_{1/2}$ of the photoreceptor and the viscosity of the solution of x-H_2Pc and PSt at a ratio of 1:4 by weight vary with the dispersion time in 20 wt% binder resin in THF. (O, Δ indicate viscosity, photosensitivity of $E_{1/2}$ respectively.)

porting sites shorter than between crystalline H_2Pc particles. This interpretation is suggested by the TEM observation and the measurements of optical absorption and the drift mobility.[10,12]

Many studies of drift mobility have been performed to elcidate the influence of dipole moment in molecularly doped polymers.[13] The mobilities are dependent on the polymer host as well as the dopant molecules.[14] The mobility decreases with increasing dipole moment. In our results, the hole mobilities of both the monolayer photoreceptors using PSt and PVB with different dipole moments are comparable to those of the molecular doped polymers;[12] however the photosensitivity of the photoreceptor using PVB, which has a higher dipole moment, is higher than that using PSt, but reflects the characteristics of the x-H_2Pc, rather than those of the host polymer. The differences between the polymers are the length of the induction time in the photoinduced decay curves and the forms of the photocurrent wave.[12] From these results, we suggest that the photoreceptor using PSt is more trap dependent than that using PVB. It is presumed that the dispersive nature of the monolayer OPC is the origin of the induction effect in the photoinduced decay curves.

Conclusions

We found that there are differences between the monolayer photoreceptors using the PSt binder and PVB in the xerographic, microscopic characteristics and physical properties. We also found that the morphology of x-H_2Pc particles like the crystalline form and the particle form is changed with dispersion time and an interaction with H_2Pc pigments and a binder during the dispersion treatment causes the formation of domains. The photosensitivity of the photoreceptor and the viscosity of the coating solution are dependent on the dispersion time and finally reach an almost constant value. It is thought that the effects of the dispersion characteristics of the solution consisting of x-H_2Pc, a binder and a solvent are related to microscopic characteristics and physical properties, which yield a high photosensitive photoreceptor. We presume that the difference in the interactions between the particles or the extremely small pigment particles of x-H_2Pc and the binder molecules significantly influences the characteristics of the photoreceptors using different binders.

Acknowledgment. The authors wish to thank Dr. S. Yoshimura for the helpful discussions and Mr. T. Asano and Mr. H. Kusayanagi of Matsushita Research Institute Tokyo, Inc., for their technical assistance with the experiments.

References

1. A. Y. C. Chan, *Mater. Lett.* **4**(5/7), 239–243, (1986).
2. K. C. Nguyen and D. S. Weiss, *J. Imaging Technol.* **15**(4), 158–163 (1989).
3. T. Kitamura and H. Yoshimura, *Proc. IS&T's 8th International Congress on Advances in Non-Impact Printing Technologies*, IS&T, Springfield, VA, 1992, pp. 237–241.
4. T. Enokida, *Proc. Japan Hardcopy '92 Fall Meeting*, SEPJ, Tokyo, 1992, pp. 61–64.
5. J. Decker, K. Fukae, S. Johnson, S. Kaieda, and I. Yoshida, *Proc. IS&T's 7th International Congress on Advances in Non-Impact Printing Technologies*, IS&T, Springfield, VA, 1991, pp. 328–331.
6. T. Nakazawa, N. Muto and M. Tsutsui, *Proc. Japan Hardcopy '88*, SEPJ, Tokyo, 1988, pp. 70–73.
7. R. O. Loutfy, *Can. J. Chem.* **59,** 549–555 (1981).
8. T. Enokida, R. Hirohashi and S. Mizukami, *J. Imaging. Sci.* **35,** 235–239 (1991).
9. T. Enokida and R. Hirohashi, *J. Imaging Sci. Technol.* **35,** 135–139 (1992).
10. S. Tsuchiya, A. Omote, M. Murakami and S. Yoshimura, *J. Imaging Sci. Technol.* **39(**4), 294–298 (1995).
11. E. Miyamoto, Y. Yamaguchi and M. Yokoyama, *Electrophotography* **28(**4), 364–370 (1989).
12. A. Omote and S. Tsuchiya, *J. Imaging Sci. Technol.* **39,** 271 (1995).
13. P. M. Borsenberger, *J. Appl. Phys.* **68,** 5188 (1990).
14. A. Fujii, T. Shoda, S. Aramaki, and T. Murayama, *J. Imaging Sci. Technol.* **43,** 430 (1999).