Thickness Influence on the Single Layer Organic Photoreceptor Properties

Edmundas Montrimas[1], Jonas Sidaravicius[1], Tadeusz Lozovski[1], Robertas Maldzius[1], Nusrallah Jubran[2], and Zbig Tokarski[2]
[1]Vilnius University, Department of Solid State Electronics, Vilnius, Lithuania
[2]Samsung Information Systems America; Digital Printing Solutions Laboratory Woodbury, Minnesota, USA

Abstract

The principle electrostatic parameters and the continuous performance of single-layer organic photoreceptors (SL OPR) in imaging cycle mode, such as in repeated usage in digital laser printers, are strongly dependent on the thickness of the photoreceptor. In addition to the electrostatic parameters, the charging conditions and the inertness of the photo-discharge are important during cycling. The role of OPR thickness was investigated for SL OPR containing TiOPc charge generation material, poly(vinyl butyral) binder, hydrazone based hole transport material and an electron transport material. The dependence of the charge-voltage characteristic, maximum achievable charging acceptance, photosensitivity, potential dark decay, and residual potential on SL OPR thickness was determined for positive and negative biased OPR via a novel dosed charging diagnostic method. The influence of SL OPR thickness on the discharge potentials, as evaluated 50 ms and 300 ms after a short light pulse, and on the residual potential was determined in cycling mode. The observed regularities were explained by characteristics of light absorption, charge carrier generation, and carrier drift and trapping within the SL OPR.

Introduction

The thickness of the photoactive layer determines many of the main parameters, such as charge and discharge potentials, dark decay rates, etc, of an electrophotographic photoreceptor (PR). The PR thickness primarily limits the charging potential and affects the deposited surface charge density creating that potential. These parameters are important for various regimes in an electrophotographic process – charging unit parameters, time duration required to completely charge the OPR, image development, etc. For example, at a given surface potential voltage, the required surface charge density to achieve this potential increases as the OPR layer thickness decreases and the extra surface charge density requires an increase in the amount of laser exposure to discharge the photoreceptors. The photoreceptor thickness also influences the formation of the latent electrostatic images and its parameters. The two most important factors that are influenced by OPR thickness are light absorption and electric field strength within the layer. The latter determines charge carrier photogeneration quantum yield, as well as the photosensitivity of organic photoreceptors. In addition, the charge transporting materials used in organic photoreceptors are characterized by a relatively low charge carrier mobility (3-4 orders of magnitude lower in comparison with amorphous Se) that is dependent on electric field strength. For thick OPR layers, the photogenerated charge carriers may not have sufficient time to reach the photoreceptor substrate or its surface to completely discharge the exposed OPR regions. These factors can become an obstacle for designing new electrophotographic equipment, especially when increased printing speeds are desired and the time period between exposure and development is decreased to fully discharge the OPR.

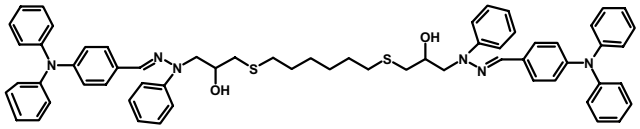
The OPR thickness has a strong influence on the residual potential magnitude and, during repetitive image cycling, on OPR electrophotographic parameter values, such as the discharge potential voltages and the potential dark decay rates. The OPR thickness is important for other reasons. A relatively thin active layer is desirable because the high degree of purity required and the specific crystalline structures for these semiconductor materials make these OPR materials expensive. On the other hand, it is desirable to have a sufficiently thick active layer to minimize the change of OPR parameters due to mechanical abrasion of the layer during normal equipment operation.

The influence of electrophotographic photoreceptor thickness on photoreceptor parameters has not been sufficiently investigated and a majority of such investigations have focused on inorganic photoreceptors.[1–3] This paper deals with the influence of the active layer thickness for an organic single layer photoreceptor on the following parameters: charge-voltage characteristics, maximum charging potential, photosensitivity, spectral distribution, residual potential, photodischarge inertness (illumination by an intense short light pulse whose duration is much shorter that the potential decay time), and the behavior in cyclic mode using a dosed charging diagnostic technique.

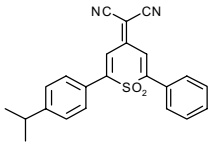
Experimental

Organic photoreceptors (OPR) of various thicknesses (5 μm to 30 μm) have been investigated. Titanyl phthalocyanine (TiOPc) dispersed in polyvinylbutyral (PVB) was used as the charge photogeneration material for this investigation. The hole transport material (HTM) was hydrazone based (Fig. 1, Compound I) and electron transport material (ETM) was phenylthiopyran based (Fig. 1, Compound II). The TiOPc: PVB: HTM: ETM components were used in a mass ratio of 1: 4.5: 16: 4. The layers were prepared from the dispersion of the mentioned materials in tetrahydrofuran (THF) by coating the solutions on an Al conductive polyester film that contained a barrier methyl cellulose (MC) sublayer. In addition, other single-layer OPR with different HTM and ETM have been investigated, but their investigation results were very similar to each other; hence their results were not presented in this paper.

Dosed charging of the layers has been investigated using the technique described in Ref. [4]. The electrophotographic parameters were investigated using the conventional techniques. The OPR sensitivity was determined (in static mode) from the exposure level required to decrease the charging potential by one-half of its initial value and the residual potential was recorded at 10-fold this time period.



I



II

Figure 1. Charge transporting materials used in single layer OPR: I – hole transporting compound. II – electron transporting compound.

In the dynamic image cycling mode, the residual potentials were measured after the image (exposure energy was 3-fold bigger than energy requiring a one-half drop in potential) and erase exposures. The inertness of potential decay under illumination has been evaluated based on discharge level at 50 ms and 300 ms after exposure to a 20 ms-long pulse of light with a wavelength of 780 nm. Figure 2 presents the a schematic of the cyclic measurement device. The charge acceptance (initial potential) U_0 has been measured at 130 ms from the end of charging, U_1 has been measured 175 ms after the U_0 measurement, U_{50} – 50 ms after the exposure (light pulse with intensity 11 erg/cm^2 and wavelength 780 nm), U_{300} –300 ms after the pulse exposure, and residual potential U_R was measured 100 ms after exposure to a 22 erg/cm^2 intense erase light pulse.

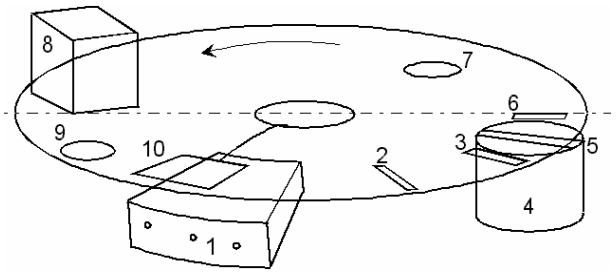


Figure 2. Scheme of cycling performance testing: 1 – charging unit, 2, 3, 6, 7, 9 – electrostatic voltmeter probes U_2, U_2, U_3, U_4,U_5 respectively, 4 – exposure module (780 nm), 5 - exposure slit, 8 – erasure module (720 nm), 10 - rotating disc with test samples. Time of events: synchronization pulse – 0, charging (+) – 210 ms, charge acceptance measurement 340 ms, potential dark decay – 510 ms, exposure (20 ms) – 565 ms, discharge potential 50 ms after exposure – 615 ms, discharge potential 300 ms after exposure – 855 ms, erasure – 1140 ms, residual potential measurement – 1440 ms

Results and Data Analysis

Figure 3 presents the charge-voltage characteristics of dosed positive charging of various thickness single layer photoreceptors. We can see that the nonlinearity of charge-voltage characteristic in the initial stage of dosed charging increased with increasing thickness of the photoreceptor (Fig. 3, inserts a and c). The charge-voltage characteristic was linear at the very start of dosed charging (up to 30 – 50 V). This indicates that the photoreceptor was being charged according to its geometric capacitance. However, with additional dosed charging of the OPR, the degree in which the surface potential increased with additional surface charges had decreased and it was not until the potential reached 100 – 200 V that the shape of the charge-voltage characteristic becomes linear with a slightly smaller slope relative to the previous charging segment.

This nonlinearity of charge-voltage characteristics is caused by extraction of quasi-free charge carriers and of carriers localized in shallow trapping levels from the titanyl phthalocyanine crystallites, which caused the charge carrier to flow through the photoreceptor.

When the photoreceptor after the first positive dosed charging (Fig. 3, curve 1 for the case A) was at first discharged to zero potential by the deposition of negative charge and then immediately recharged by positive dosed charging, the charge-voltage characteristic become near linear (Fig. 3, curve 2), i.e., dosed charging characteristics nearly resembled the photoreceptor geometric capacitive charging characteristic (Fig.3, 0.12 nF/cm^2). In this case the charge carrier reservoir was emptied partly during the first dosed positive charging cycle.

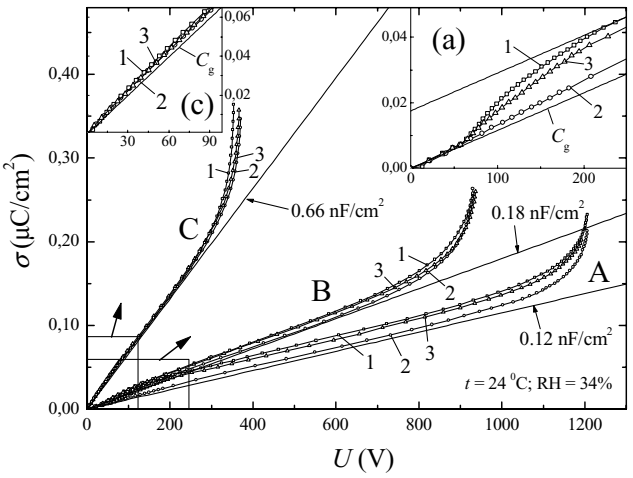


Figure 3. Dosed charging charge-voltage characteristic. OPR thickness: A – 27 μm, B – 11.5 μm, C – 5 μm. 1 – the first positive charging, 2 – positive charging after discharge to zero by deposition of negative charge, 3 – positive charging after discharge to zero by exposing to red light. Inserts: enlarged parts of initial stage of A OPR (a) and C OPR (c) dosed charging.

If the photoreceptor was kept in the dark for a sufficiently long time or was exposed to light, then the reservoir (phthalocyanine crystallites) became enriched with charge carriers and the charge-voltage characteristic of dosed charging become more nonlinear (Fig. 3, curve 3). From the nonlinearity in the initial charge-voltage characteristic stage, the density of extracted carriers in relatively thick (20 – 30 μm) photoreceptors was determined to reach 10^{11} cm^{-2}, whereas in relatively thin photoreceptors density of extracted charge carriers was much lower. Therefore, the initial charge-voltage characteristic stage for thinner photoreceptors is nearly linear and approaches the geometric capacitance (Fig. 3, B and C). It should be noted that the charge-voltage characteristics of dosed charging are significantly nonlinear for photoreceptors containing X-form metal-free phthalocyanine. The extracted charge density in such photoreceptors reached 10^{12} cm^{-2}.[4]

As the charging potential approached the limiting surface potential, the charge-voltage characteristic deviated more and more from the linear shape, i.e., the surface potential grew at a slower rate than the charge deposition rate. This illustrated that the charge carriers were being injected and moved through the OPR layer. The limiting charging potential is reached when the additional deposited charge did not change the surface potential. The linear portion of the charge-voltage characteristic can be used to calculate the OPR effective capacitance ($C_{eff} = Q / U$). This value was then used to reaffirm the thickness of the layer. If the OPR dielectric constant is known then the thickness is given by $l = \varepsilon_0 \varepsilon / C_g$, or if the thickness is known then the dielectric constant for the photoreceptor is given as $\varepsilon = l \cdot C_g / \varepsilon_0$. Using this relationship, the dielectric constant of the investigated photoreceptors was determined to be $\varepsilon = 3.34$.

Photoreceptor charging and dark discharge potentials were investigated in two modes. Figure 4 illustrates the static mode method where the dependence of charging potential and its decrease in the dark are characterized by the half-life $t_{1/2}$ potential decrease. Both positive and negative limiting charging potentials increased with increasing OPR thickness, but this dependence was nonlinear. The initial growth of the positive and negative charging potentials with increasing thickness was the fastest but this growth rate decrease and there was a tendency for saturation. The slight difference of positive and negative limiting potentials at various values of photoreceptor thickness indicates that the charge carrier generation in the bulk of a photoreceptor plays an important role limiting the potential magnitude. The half-life dependence for dark discharge with increasing thickness (Fig. 4, curves 3 and 4) confirms this conclusion.

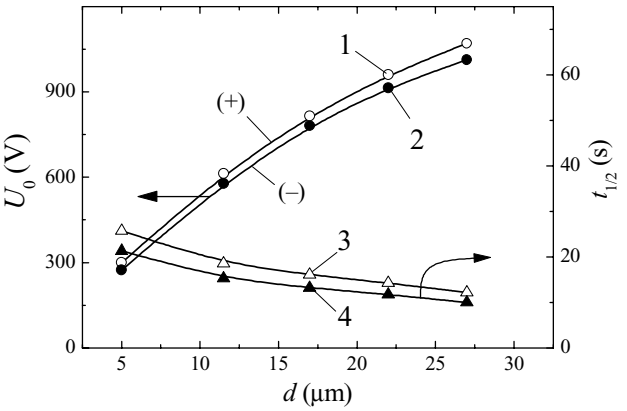


Figure 4. Dependence of initial charging potential (1, 2) and its dark decay half-life $t_{u/2}$ (3, 4) on OPR thickness at positive (1, 3) and negative (2, 4) charging

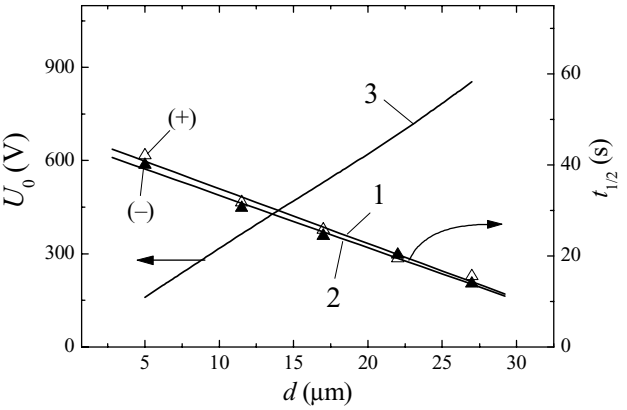


Figure 5. Dependence of potential dark decay halftime $t_{u/2}$ on OPR thickness at positive (1) and negative (2) charging and at equal initial intrinsic electric field strength $3 \cdot 10^5$ V/cm. Line 3 - OPR potential at which electric field strength is equal for all thickness

A small difference between the dark discharge half-life of the various thickness, positively and negatively charged photoreceptors indicates that dark discharge mainly occurs due to charge carrier generation in the bulk of the photoreceptor. This small difference in dark decay values may be caused by the difference in charge injection from the electrode.

The charge carrier thermal generation in the bulk of the photoreceptor and the charge injection from the electrodes can be controlled by the internal electric fields. The photoreceptor charging potential values with respect to thickness were chosen so as to ensure the same electric field strength ($3 \cdot 10^5$ V/cm), regardless of photoreceptor thickness (Fig. 5, line 1). Our investigation of potential decrease half-times in the dark ($t_{1/2}$) has shown that the $t_{1/2}$ decreased with increasing layer thickness (Fig. 5, curves 1 and 2) but at a rate level that is 70% of the increase in thickness. It follows that the dark discharge of the investigated photoreceptors is caused by field-stimulated thermal generation in the bulk of the layer and also by charge carrier injection from the electrode.

OPR thickness has a strong influence on the photosensitivity and residual potential of positively and negatively charged OPR (Fig. 6). The initial part of photodischarge kinetics curve is S-shaped for all OPR thickness values. In the case of positive charging, the OPR photosensitivity increased with thickness and reached a maximum at 15 μm – 20 μm. The photosensitivity of a negatively charged thin (5 μm) photoreceptor is only little different from the photosensitivity of a positively charged OPR. As OPR thickness increased, the photosensitivity of the negatively charged OPR dramatically decreased and at 30 μm it was 10 – 12 times lower than photosensitivity of a positively charged layer. This was expected because the electron drift mobility in the investigated OPRs does not exceed 10^{-8} cm^2/V·s, which is 2 or 3 orders of magnitude lower than the hole drift mobility and can be illustrated by the following example. At intermediate initial potential values (500 V) and at an exposure intensity of 10^{17} quants/s·m^2, the electron transit time in photoreceptors with thickness d 20 μm exceeds the photodischarge time by an order of magnitude. This means that electron contribution to OPR photosensitivity is very insignificant.

Another factor is light absorption in the OPR. Absorption of light with wavelength 700 – 800 nm in a thin OPR is almost homogeneous. However, absorption of the same light intensity in a thick OPR is strongly inhomogeneous – the major part of incident energy is absorbed near the surface of the photoreceptor. In the case of positive potential, holes drift from the photogeneration region through the entire photoreceptor. When the OPR is charged negatively, the photogenerated holes drift from the photogeneration region towards the surface and their contribution to photodischarge is small.

In order to achieve complete discharge of the OPR, the exposure should be increased so that a sufficient number of holes are generated in the bulk of the layer. This effect becomes more prominent when the OPR thickness is increased. This model is confirmed by spectral distribution of photosensitivity (Fig. 7).

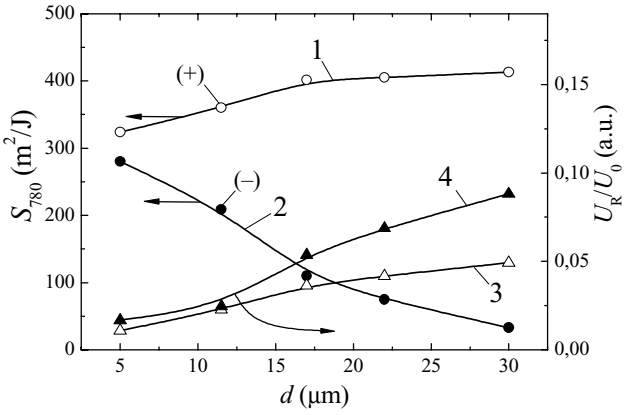


Figure 6. Dependence of OPR photosensitivity (1, 2) and of residual potential (3, 4) on OPR thickness at positive (1, 3) and negative (2, 4) charging

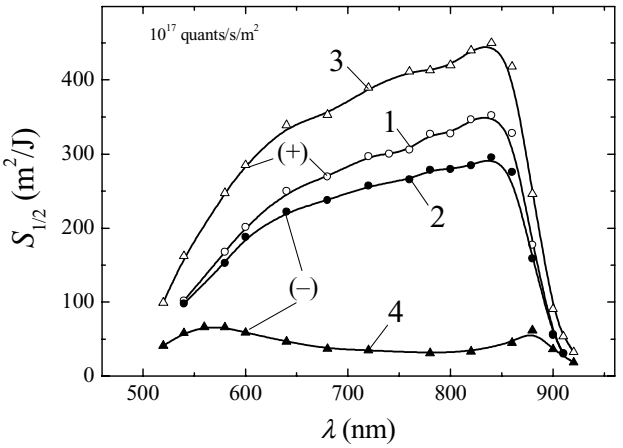


Figure 7. Photosensitivity spectral distribution of thin (1, 3) and thick (3, 4) OPR at positive (1, 2) and negative charging (2, 4). Illumination - semi-infinite pulse, intensity – 10^{17} quanta/m^{2}s

The shape of this spectral distribution in the case of thin (5 μm) OPR is minimally affected by the charging polarity and is similar to the light absorption spectrum (Fig.7, curves 1 and 2). In the case of a thick (30 μm) positively charged OPR, the shape of photosensitivity spectral distribution remains the same (Fig. 7, curve 3), but photosensitivity of the negatively charged thick OPR is almost independent of light wavelength (Fig. 7, curve 4). This result can be explained, having in mind that light is absorbed near the surface and that photodischarge is caused only by hole i.e., unipolar drift. This explanation is in accord with small photosensitivity maximums of the negatively charged OPR

in regions of weak absorption – at 570 nm and 850 nm (Fig. 7, curve 4).

In dynamic investigative mode, additional information about photoreceptor electric, photoelectric properties, and their suitability for practical applications was attained by investigating multiple charging, exposure, and erasure cycles of photoreceptors. The repeated charging-photodischarge imaging cycles of a photoreceptor made it possible to determine the relationship between the number of cycles and the initial charging potential (U_0), initial discharge rate in the dark, discharge potential (U_{50}) 50 ms after pulse exposure, discharge potential (U_{300}) 300 ms after pulse exposure, and residual potential U_R, which is measured after the erasure exposure. Figure 8 presents a typical charging-photodischarge imaging cyclogram of the investigated photoreceptors. After 2,000 imaging cycles, the initial charging potential of photoreceptors with various thickness decreases by (5–7) % of its initial value. After the same number of cycles, the change in the residual potential and discharge potentials, U_{50} and U_{300}, was insignificant. Figure 9 presents the dependence of these electrophotographic parameters on OPR thickness.

As the photoreceptor thickness was increased from 5 μm to 30 μm, the positive charging potential U_0 monotonously increased from 400 V to 1400 V with a tendency toward saturation. The initial potential magnitude measured in dynamic cyclical mode for photoreceptors with different thickness was noticeably larger in comparison with those measured in static mode (Fig. 4). This results from the fact that the cycling equipment (Fig. 2) enables measurement of U_0 130 ms after the end of charging, whereas in static mode the potential was measured 0.5 s after the end of charging.

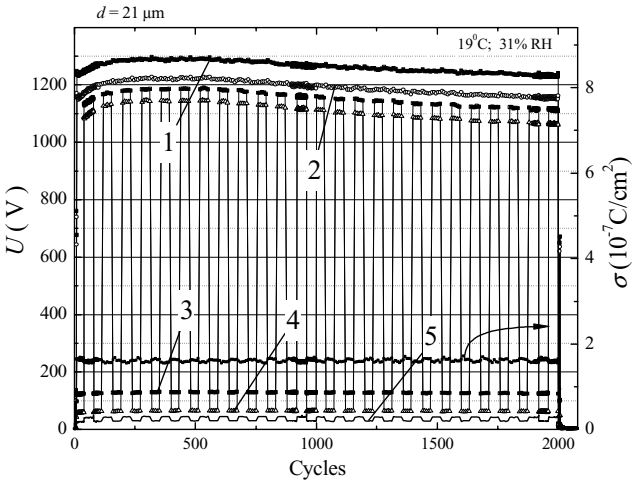


Figure 8. OPR cycling performance: 1 – charge acceptance, 2 – potential after 130 ms after charging (dark decay), 3 – discharge potential 50ms after exposure, 4 – discharge potential 300 ms after exposure, 5 – potential after erasure exposure

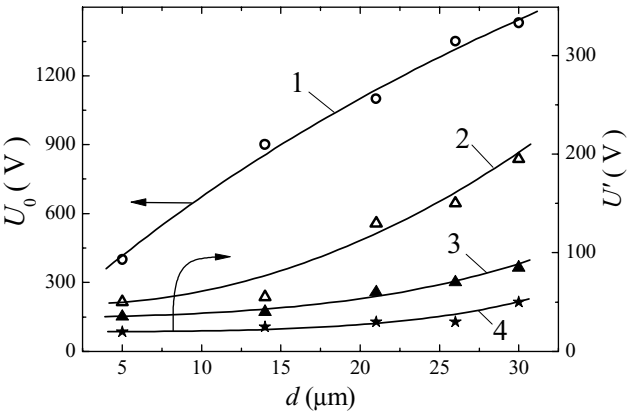


Figure 9. OPR charge acceptance (1), discharge potential after 50 ms (2) and 300 ms (3) after exposure and potential after erasure dependence (4) on OPR thickness in cycling regime

In the case of thin (5 μm) OPR, the dark discharge rate during the first 175 ms of a cycle did not exceed 150 V/s, and it reached 500 V/s in the case of a 30 μm-thick photoreceptor. As the photoreceptor thickness increased from 5 μm to 30 μm, the discharge potential U_{50} (50 ms after the exposure pulse) increases from 60 V to 200 V (Fig. 8, curve 2) and the discharge potential U_{300} (300 ms after the exposure pulse) increased from 40 V to 90 V , a change that was proportionally smaller than for U_{50}. This indicated that not all of the photogenerated holes passed through the entire thickness of the OPR during 50 ms. This observation indicates that hole drift mobility is an important factor for photodischarge inertness. In our case it was determined that hole drift mobility in the investigated photoreceptors at electric field strength $2.5 \cdot 10^5$ V/cm was equal to 10^{-6} cm^2/V·s and that it decreases slightly with increasing OPR thickness.

The residual potential (U_R), obtained after pulse exposure to light with intensity 22 erg/cm^2, is also slightly dependent on photoreceptor thickness (Fig. 9, curve 4).

Conclusions

After measuring the main electrophotographic parameters of a photoreceptor – initial charging potential, potential decrease rate in the dark (especially during the initial stage of the decrease), photosensitivity and its spectral distribution, photoinertness, and residual potential at various values of photoreceptor thickness - the optimum thickness of an investigated OPR was determined to be approximately 15 – 20 μm.

References

1. M. Scharfe. Electrophotography Principles and optimization. Letchworth, England, Research Studies Press Ltd., New York, John Wiley & Sons Inc, 1984.

2. V. I. Gaidelis, N. N. Markevich, E. A. Montrimas. Physical processes in electrophotographic ZnO layers. Vilnius, Mintis, 1968 (in Russian).
3. D. C. Hoesterey. J. Appl. Phys., **33**(3), 992, 1962.
4. T. Lozowski, R. Maldzius, E. Montrimas. *Synthetic Metals,* 109 (2000) 195-198

Biographies

Zbig Tokarski received his Ph.D. in Chemical Engineering from the University of Connecticut, Storrs, CT in 1990. He has worked on optical organic material research at Wright Patterson Air Force Base for 9 years and on electro-photographic materials and physics for the last 8 years, first with Imation Corp and now with Samsung Electronics. Dr. Tokarski is currently a senior group leader with Samsung Information Systems America, Digital Printing Solutions Laboratory, Woodbury, Minnesota. His main research activities involve all areas of electrophotography.

Edmundas Montrimas received his PhD (1968) and Habil.Dr. (1973) in Physics from Vilnius University (Lithuania). From 1958 to 1964 he has worked on development of electrophotographic and electro-radiographic photoreceptors and processes at Institute of Electrography (Vilnius, Lithuania). He is currently a full professor at Vilnius University (1975). His main reseach activities focus on the investigation of physical processes in inorganic and organic electrophotographic photoreceptors.

Jonas Sidaravicius received his PhD in Chemical Physics from S. Vavilov Optical Institute (Saint Petersburg, Russia) in 1968. From 1959 to 1999, he had worked on the development of electrophotographic organic photore-ceptors and other materials related to electrography at Instutute of Electrography (Vilnius, Lithuania). He is currently a research fellow at Vilnius University and an Associate Prof. at Vilnius Gediminas Technical University. His main activities are the development of new organic electrophotographic photoreceptors and investigation of their properties. zbig.tokarski@samsung.com