Charging Transients of Organic Electrophotographic Photoreceptors

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This work presents results of investigation of charge carrier injection-extraction phenomena in single layer and double layer organic photoreceptors (OPC), consisting of various hole (HTM) and electron (ETM) transport materials and two types of phthalocyanines, during their dosed charging, especially in its first stage (early stage of charging). In the first stage of charging of double layer OPC, there is evidence of hole extraction from phthalocyanine crystallites in the charge photogeneration layer (CGL). In the case of the X-form metal-free phthalocyanine and ~0.5 μm thick CGL, density of extracted holes reaches 1.0×10^{12} cm^{-2}, and in the OPC with Y-form TiOPc, the extracted charge is less by an order of magnitude. The charge carrier reservoir in phthalocyanine crystallites is restored by exposure to red light or by keeping the OPC in uncharged state in the dark for several hours. Preliminary charging of double layer photoreceptors to a non-work potential (positive for normal construction and negative for IDL OPC) causes a decrease of work potential (negative for normal and positive for IDL OPC) in cyclic mode. During charging to non-work potential, electrons are injected from the CGL into the transport layer (CTL) and are trapped in deep levels at the CGL-CTL interface. Consequently, the critical electric field in the CGL, corresponding to onset of intense hole thermal-field generation, is reached at progressively lower work potentials. Nonlinear of charge-voltage characteristic for dosed charging of single layer OPC with the barrier sublayer or/and overcoat layer is strongly dependent on polarity of preliminary charging and photodischarge. During positive charging and photodischarge, holes accumulate on the barrier sublayer, and their density (5×10^{12} cm^{-2}) can become several times larger than the density required for OPC charging to the maximum potential. During photoreceptor recharge by the opposite (negative) charge, holes drift from the barrier sublayer towards the OPC surface and partially accumulate on the inner surface of the protection layer. The same phenomena are observed in the case of OPC with overcoat barrier layer charge carriers accumulate at the barrier. Depending on the nature of hole and electron transport materials, holes partially accumulate near the OPC surface in the absence of the protection layer, too.

Journal of imaging Science and Technology 49: 326–335 (2005)

Introduction

Photoreceptors of modern electrophotographic copying devices and laser printers are mainly manufactured from organic semiconductors.[1–4] Organic semiconductor photoreceptors (OPC), which determine the quality and efficiency of optical information recording, are either single layer photoreceptors, where the charge carrier photogeneration and their transport take place in the same layer, or double layer photoreceptors, consisting of a separate charge carrier photogeneration layer (CGL), that is positioned either below or above the charge carrier transport layer (CTL). The term “single layer” or “double layer”, when applied to a photoreceptor, is relative because photoreceptors of both types frequently include the active layers (CGL and CTL), and may also include a barrier-adhesion layer, top protection layer, and possibly other layers. Those additional layers influence various properties of the OPC and its performance in an electrophotographic device. Both single layer and double layer photoreceptors are complex semiconductor structures, consisting of several components. At the very least, their composition includes carrier photogeneration materials (CGM), hole and electron transport materials, and polymeric binding materials. The CGM is required to ensure a sufficiently high photosensitivity in the desired spectral exposure region, whereas the carrier transport materials (CTM) are characterized by good hole or electron transfer and the necessary dielectric properties of the layer composition so that the photoreceptor can be charged to high potential and the discharge rate in the absence of image expo-

Original manuscript received January 12, 2004

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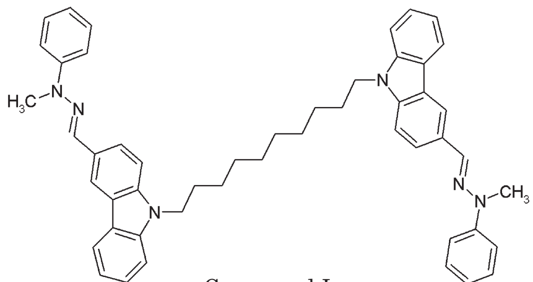
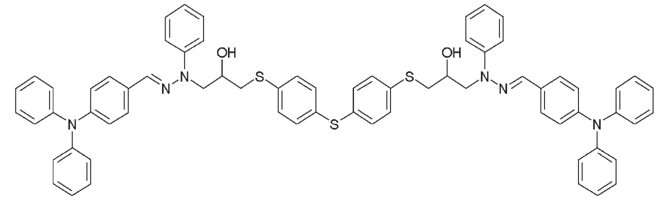
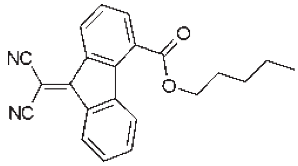


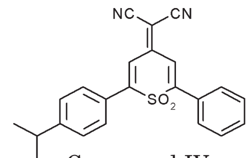
Compound I



Compound II



Compound III



Compound IV

Figure 1. Chemical structures of hole (I,II) and electron (III, IV) transporting materials

sure (dark decay rate) is small. Those properties should remain stable during the entire exploitation time of the OPC. Because of a complex structure of the OPC and because of properties of its components, various charge carrier injection-extraction processes and charge carrier generation in electric field can take place in the photoreceptor during its charging[3,5] process. Those physical phenomena, even when they are not directly observable in the equipment, can have a significant effect on the efficiency of the photoreceptor charging process and limit the charging potential and other parameters of the photoreceptor. In modern electrophotographic devices, charging is very intense and occurs over a very short time duration. Therefore, the process of carrier extraction, injection, generation, and space charge formation and their transients can govern the quality of device operation and its stability. Direct observation of the carrier extraction-injection phenomena, the process of carrier generation in an electric field and the other properties of a photoreceptor or its constituent parts becomes possible during incremental charging of the photoreceptor, i.e., by charging in small doses in the dark and measuring the resulting potential. During the deposition of small charge doses on the photoreceptor surface, the electric field strength in the photoreceptor gradually increases until the photoreceptor is completed charged to the desired operating potential. Under the influence of this field, free and quasi-free charge carriers can be extracted from the photoreceptor, injected from the photoreceptor surface into its bulk, or injected from one constituent layer of the photoreceptor into another layer. Consequently, a space charge can form in the photoreceptor. This space charge changes the electric field distribution in the photoreceptor and influences its electrophotographic parameters. The method of dosed charging makes it possible to investigate the carrier extraction and injection processes and their generation in the electric field. A relatively small number of publications has been devoted to study of those processes in photoreceptors but this phenomena has not been thoroughly investigated.[2,5] Therefore, this article studies the physical phenomena that occurs during photoreceptor charging.

Materials

In this work, various multi-component single layer and double layer organic photoreceptors have been investigated by the method of dosed charging. A photoreceptor has to be characterized, on the one hand, by high photoconductivity and efficient carrier transfer during photoreceptor photodischarge, and on the other hand, by good dielectric properties. This was achieved by approximately choosing the type and composition of the carrier photogeneration and transport materials. The CGL of double layer (multi-layer) organic photoreceptors investigated in this work consists of Y-form titanyl phthalocyanine (TiOPc) or metal-free phthalocyanine (H_2Pc), dispersed in the polybutyral binding material (PVB) at a 1:1 w/w ratio. Charge transport layers were made using two different hydrazone compounds (Fig. 1, Compounds I and II). Transport materials were dissolved in the Z-type polycarbonate binding material (PC-Z) at a 1:1 w/w ratio. Since hydrazone structures are hole transport materials, only holes are mobile in the CTL. Therefore, when the CGL is coated on the CTL (normal dual layer OPC), the photoreceptor work potential is positive and, when the CGL is at the bottom (IDL - inverse dual layer OPC), the photoreceptor work potential is negative. All of the layers were dip coated from solution. Double layer OPC structures and compositions were as follows:

CTL -1: Al + (PC-Z + compound I, 1:1)
OPC - 1: Al+ (PC-Z + compound II, 1:1) + (H_2Pc + PVB, 1:1)
OPC - 2: Al+ (H_2Pc + PVB, 1:1)+ (PC-Z + compound II, 1:1)
OPC - 3: Al + (TiOPc + PVB, 1:1) +(PC-Z + compound II, 1:1)
OPC - 4: Al +(PC-Z + compound I, 1:1)+ (H_2Pc + PVB, 1:1).

The CGL and CTL thickness was approximately 0.5 μm and 10 μm, respectively.

When the photogeneration material is the Y form TiOPc, the photosensitivity of those layers in the wavelength region 700–800 nm was 200–250 m^2/J (reciprocal of the potential half decay exposure). At electric field strength 5×10^5 V/cm, hole mobility in the CTL is $\mu_h = 10^{-4} - 10^{-5}$ cm^2/Vs.

Single layer OPC were prepared from Y-form TiOPc or H_2Pc, hole transport material (Fig. 1, compound II), electron transport material (Fig. 1, compounds III and IV), and polyvinylbutyral. The dispersion was coated on the Al substrate, which was pre-coated with a 1 μm thick methylcellulose (MC) barrier-adhesion layer. Some OPC were covered with a 2–3 μm thick overcoat barrier-pro-

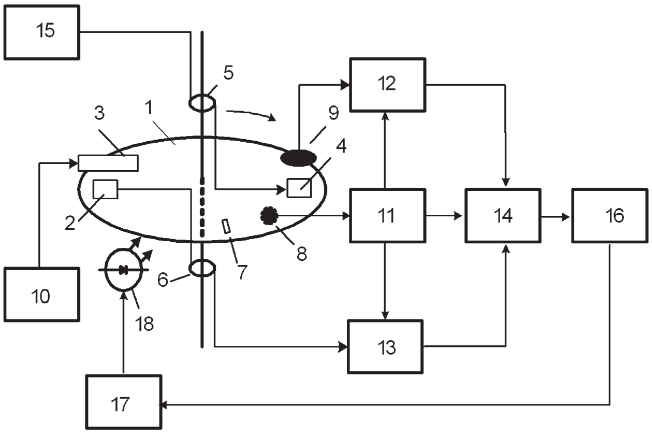


Figure 2. The device for dosed charging of a photoreceptor. 1 – OPC holder; 2 – OPC sample; 3 – corona charger; 4 – calibration plate; 5 – calibration current collector; 6 – current collector; 7 – synchronizer transducer; 8 – synchronizer sensor; 9 – signal electrode of the electrometer; 10 – high voltage source; 11 – synchronizing device; 12 – electrometer; 13 – charge integrator; 14 – analog-digital converter; 15 – calibration voltage source; 16 – computer; 17 – controlled exposure source; and 18 – light emitting diode.

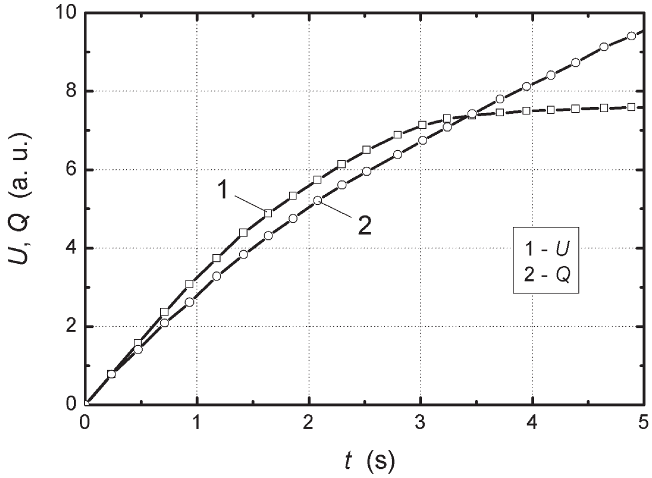


Figure 3. Time dependence of negative charge Q deposited on the CTL 1 surface and of potential U.

tection layer (OCL), formed using a dielectric polymer. The composition and component ratios of the OPC were chosen such as to ensure a sufficiently high hole and electron drift mobility, high spectral sensitivity in the wavelength range 700–800 nm (reciprocal of potential half-decay exposure is 300–350 m^2/J), low residual potential ($U_R < 100$ V), and low photodischarge inertness. The structure and composition of investigated single layer OPC were as follows:

OPC - 5: Al+MC+(PVB+ TiOPC+comp.II+comp.III,1:4: 16:8)+OCL
OPC - 6: Al+ MC+(PVB+ TiOPC+comp.II+comp.IV,1:4: 16:8)
OPC - 7: Al+[PVB+ TiOPC+comp.II+(comps.III+IV),1:4: 16:8] + OCL.

The single layer OPC thickness was 15 – 18 μm.

Techniques and Equipment

It was possible to determine the dependence of photoreceptor potential on the deposited charge density by the gradual deposition of small charge doses on the photoreceptor surface. The shape of this dependence provided information about carrier extraction and injection phenomena that took place during the initial charging stage.

Dosed charging of a photoreceptor prepared on a polyester sheet substrate was done using the rotating disk device designed in our laboratory (Fig. 2). The sheet photoreceptor was attached to the disk which rotated at a constant angular velocity relative to the corona charger and the potential measurement probe (Fig. 2). During one revolution of the disk (5 revolutions per sec), a charge dose ΔQ was deposited on the surface of the charged layer every time it passed under the corona charger. Charge dose ΔQ could be changed over the range from 10^{-10} C to 10^{-4} C by changing the corona wire voltage. The charged layer was connected in series with the charge integrator and ΔQ was measured every cycle. This dose of charge created a potential ΔU. OPC potential was measured using an electrometer with non-vibrating electrode. Electrometer was calibrated every cycle and potential measurement accuracy was ± 0.55 V in the range from 5 V to 100 V and ± 7 V in the range from 100 V to 3500 V. The charge-voltage characteristic $U = f(Q)$ and capacitance-voltage characteristic $C = f(U)$ were derived from the time dependence of the charge deposited on the photoreceptor surface $Q(t)$ and potential $U(t)$ (Fig. 3). Here C is the effective capacitance, because it was evaluated assuming that all the deposited charge ended up on the OPC surface. In reality, a portion of the charge can leak through the photoreceptor. The shape of characteristics $U = f(t)$ and $C = f(t)$ provides information about processes of hole extraction-injection and their accumulation in the barrier regions.

Charging of the photoreceptor can take a relatively long time when the charge doses are very small. Therefore, the photoreceptor discharge in the dark may be significant and cause a decrease of the measured limiting potential value. In order to determine the true limiting potential value, the photoreceptor should be charged rapidly, in relatively large charge doses. However, in this situation the carrier injection-extraction processes which takes place in the initial stage of photoreceptor charging are hidden. Therefore, small doses of charge were used in the initial stage of charging and the subsequent charging was done using relatively large doses of charge. This type of photoreceptor charging method was achieved by adjusting the magnitude of the electrifier voltage and by changing angular rotation velocity of the disk.

Results and Discussion

Double Layer OPC

Charge-voltage and capacitance-voltage characteristics of positive and negative dosed charging were investigated separately for full construction double layer photoreceptors and for just the CTL (Fig. 4). We can see that the CTL charge-voltage characteristics are linear over a wide range of positive and negative potential values (Fig. 4, curves 1, 2). This means that the charge extraction-injection phenomena do not occur in the initial stage of dosed charging of the CTL or in the medium potential regions. Thus, the entire deposited positive or negative charge accumulates on the CTL surface, charging the capacitance of the CTL.

The charge-voltage characteristics of dosed charging are linear over a wide range of potential values in the case of full construction, double layer photoreceptors:

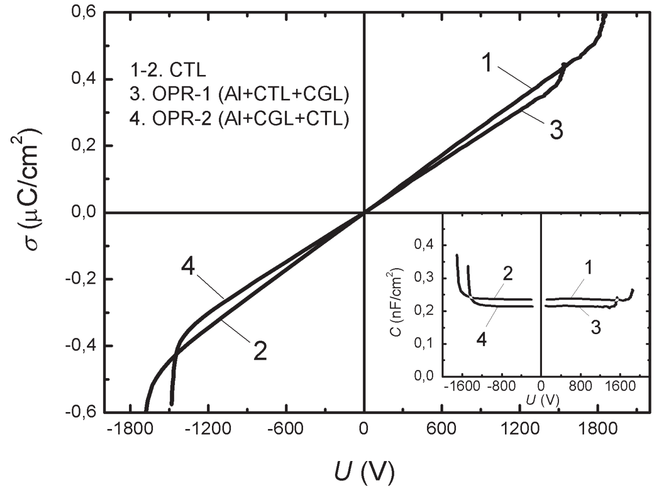


Figure 4. Charge-voltage and capacitance-voltage (insert) characteristics of dosed charging of CTL 1 (curves 1,2), OPC 1 with the CGL at the top (curve 3) and OPC 2 with the CGL at the bottom (curve 4)

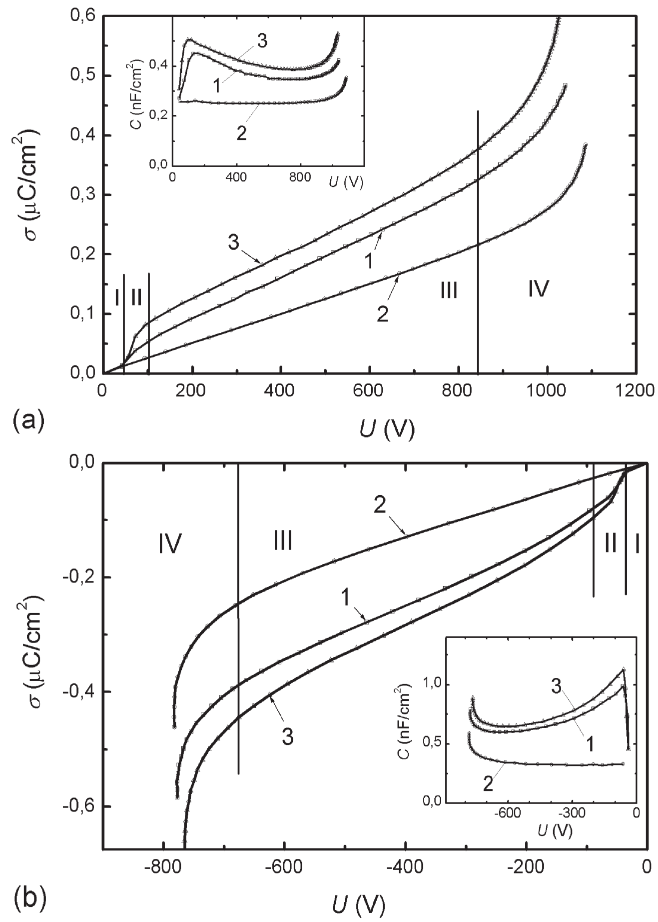


Figure 5. Charge-voltage and capacitance-voltage (insert) characteristics of dosed charging of double layer OPC 1 with the H_2Pc CGL at the top (a) and OPC 2 with the H_2Pc CGL at the bottom (b). 1 – first charging after adaptation in the dark; 2 – charging after discharge by deposition of opposite charge; and 3 – charging after discharge by exposure to red light.

when the CGL is formed on the top of the photoreceptor and charging is negative (IDL, work potential positive) or when the CGL is formed beneath the CTL (normal OPC) and charging is positive (Fig. 4, curves 3 and 4). This indicates that there is no conductivity current through the OPC, and that charge carriers inside it are either immobile or that their contribution is insignificant. Electrons generated in the thin CGL are localized after reaching the CTL because electrons are immobile in the CTL. On the other hand, the hole and electron displacement in the thin CGL is insignificant and has no marked influence on linearity of the charge-voltage characteristic. The bend in the curve of the charge-voltage characteristic indicates that thermal field generation of carriers becomes significant at high potentials and OPC potential reaches its maximum value.

The shape of charge-voltage and capacitance-voltage characteristics of dosed charging becomes much more complicated in the case when the photoreceptor with the CGL on the CTL (IDL) surface was charged positively (work potential) or when the CGL is below the CTL (normal DL) and the photoreceptor was charged negatively (Figs. 5(a) and 5(b), curves 1). Such charge-voltage characteristics of the first dosed charging have several characteristic regions with a different dependence on voltage. Thus, in the initial stage of dosed charging, i.e., up to 20 – 50 V, the increase of potential with increasing density of charge deposited on the photoreceptor is linear (I region). As the deposited charge density further increases, the potential increase slows down significantly (II region) and it increases again after reaching 100 – 150 V (III region). In the IV region, the increase in potential slows down again and reaches the limiting value because the entire charge deposited on the OPC surface leaks through the layer. The slow growth of potential with deposited charge density in the II region indicated that a significant current flows through the photoreceptor during dosed charging. This current is caused by the CGL phthalocyanine crystallites because the CTL charge-voltage characteristic is linear.

After the positive charged OPC with the top CGL ((IDL, Fig. 5(a), curve 1) is discharged to zero by the deposition of a negative charge and it is again positively re-charged, the charge-voltage characteristic (Fig. 5(a), curve 2) is linear over a wide range of potential values, whereas effective capacitance does not change (Fig. 5(a) insert, curve 2). It follows that the charge-voltage characteristic of dosed charging, whose slope is equal to the slope of the region I of the first dosed charging charge-voltage characteristic corresponding to the initial charging (Fig. 5(a), curve 2), reflects a change in the OPC geometric capacitance. Hence, the hole reservoir that is localized in the CGL was partly at least depleted during the initial dosed charging. The shallow energy levels are completely emptied, whereas the deep states are only partially emptied. The fact that hole liberation starts after charging potential reaches a certain magnitude (region I of the charge-voltage characteristic) indicates that holes in the reservoir are not free. However, when the photoreceptor is charged to a positive work potential (Fig. 5(a), curve 1) and discharged by exposure to red light, the charge-voltage characteristic becomes nonlinear again (Fig. 5, curve 3), i.e., the hole reservoir in the CGL is filled again during exposure to red light. This does not occur when the OPC was discharged by depositing opposite polarity charges because in this case no free carriers are generated in OPC. Very similar results (Fig. 5(b)) were obtained for "normal" OPC with CTL coated on CGL (work potential negative).

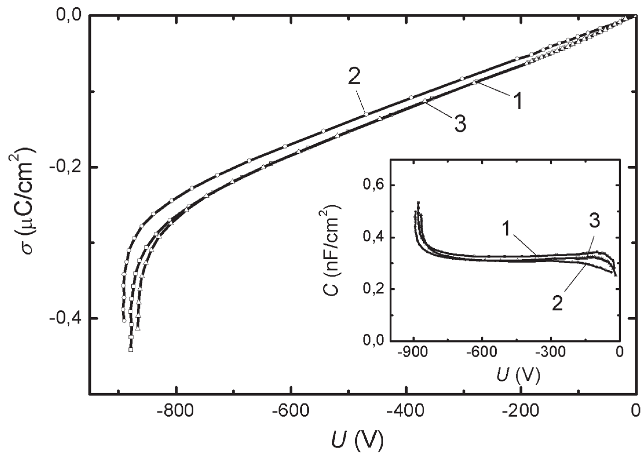


Figure 6. Charge-voltage and capacitance-voltage (inset) characteristics of negative dosed charging of the double layer OPC 3 with the TiOPc CGL. 1 – first charging after adaptation in the dark; 2 – charging after discharge by deposition of positive charge; and 3 – charging after discharge by exposure to red light.

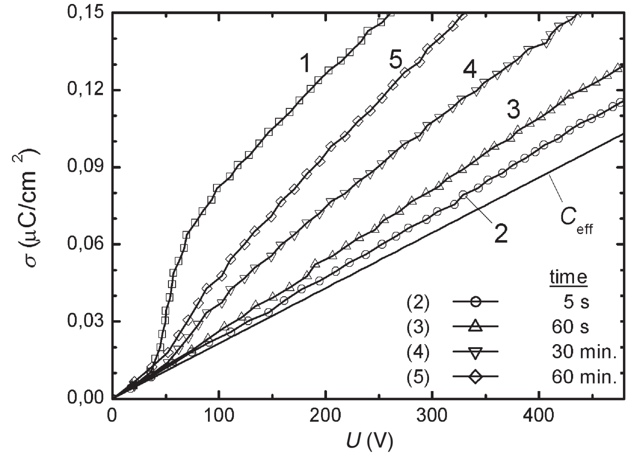


Figure 7. Charge-voltage characteristics of dosed charging of the double layer OPC 1 with the H_2Pc CGL at the top. First charging after adaptation in the dark (curve 1); charging at 5 s (curve 2); 1 min (curve 3); 30 min (curve 4); 60 min (curve 5) since the discharge by deposition of negative charge, C_{eff} – charging of geometrical capacitance

By comparing double layer OPC prepared with the two different types of CGL, it was found that an especially significant hole reservoir was formed in the metal-free phthalocyanine crystallites. In the case of the double layer OPC with Y-form TiOPc in the CGL, the nonlinearity of charge-voltage and capacitance-voltage characteristics of dosed charging were much smaller (Fig. 6) in comparison with corresponding characteristics of the OPC with metal-free phthalocyanine. This indicates that during the first dosed charging, the density of holes extracted from the photoreceptor with metal-free phthalocyanine is much larger than in the case of TiOPc.

The nonlinear charge-voltage characteristics of the II region can be used to evaluate the amount of quasi-free charge carriers in CGL. The concentration of quasi-free holes and holes localized in shallow states that are liberated in the initial stage of dosed charging, reached $(0.5 – 1.0) \times 10^{12}$ cm^{-2} at a CGL thickness 0.5 μm in the case of metal-free phthalocyanine and $(0.5 – 1.5) \times 10^{11}$ cm^{-2} in the case of Y-form TiOPc. It must be noted that the slope of charge-voltage characteristic in the III region (Figs. 5(a) and 5(b), curves 1 and 3) is larger in comparison with the slope of the geometric capacitance charge-voltage characteristic. The nonlinearity of charge-voltage characteristic of dosed charging and its larger slope as well as the larger effective capacitance in the III region in comparison with the geometric capacitance charge-voltage characteristic (Figs. 5(a) and 5(b), insert, curves 1 and 3) indicate that hole current flows through the OPC at higher potentials. This means that the current is caused by holes localized in deep levels of phthalocyanine crystallites. The emptying of these deeper levels requires stronger electric fields.

The depleted hole reservoir can be filled again by exposing the OPC in the photosensitivity region as seen on Figs. 5(a) and 5(b). However, it should also be filled in the dark with time due to thermal generation of charge carriers. This is shown by the following experiments. In the case when the hole reservoir in the CGL with metal-free phthalocyanine was partly depleted during the first dosed charging and filling the hole reservior at zero electric field in the dark is a relatively slow process. By delaying the discharge of the OPC by several seconds and then depositing opposite polarity charges onto the OPC, the charge-voltage characteristic (Fig. 7, curve 2) corresponded to the charging of the OPC geometric capacitance (Fig. 7, curve Ceff). At longer delay between discharging and charging the charge-voltage characteristic ramps up slowly. Even after a 60 min delay, a partial restoration of the hole reservoir was observed in curve 5 of Fig. 7.

Until now, we have discussed the OPC characteristics in the case of only positive charging or only negative charging. One might expect that a change of charging polarity (which may happen in real equipment during the transfer of the image developed in electric field) would cause a change in the OPC behavior. Indeed, when the photoreceptor with CGL on top of CTL (IDL) prior to the positive charging has been charged negatively, or when photoreceptor with CTL on top of CGL (normal dual layer OPC) prior to the negative charging has been charged positively, a new phenomena was observed. At first changes in the limiting potential were found. For example, in the case when the IDL OPC (CGL on top of CTL) with positive work potential was charged negatively prior to positive charging (Fig. 8, curve 2), the limiting (positive) work potential decreased significantly (Fig. 8, curve 3) in comparison with the first positive charging (Fig. 8, curve 1). This result can be explained as follows. During the preliminary negative charging, electrons are injected from the CGL into the CTL and are trapped in deep states at the CGL-CTL interface, because electrons in the CTL are immobile. An increase of the density of electrons trapped in those states increases the electric field strength in CGL. Consequently the critical electric field strength in CGL, when intense hole generation starts, is formed at lower OPC potentials. As a result, the negative charge acceptance (limiting potential) is lower. The same can be said about the decrease of the OPC positive limiting potential in the case of preliminary positive charging of the normal OPC (CGL below CTL, Fig. 9, curves 3 and 4). The maximum potential is restored with OPC adaptation in the dark time. The restoration of the limiting work potential can be restored by light (Fig. 8, curve 4). Holes photogenerated in the CGL drift

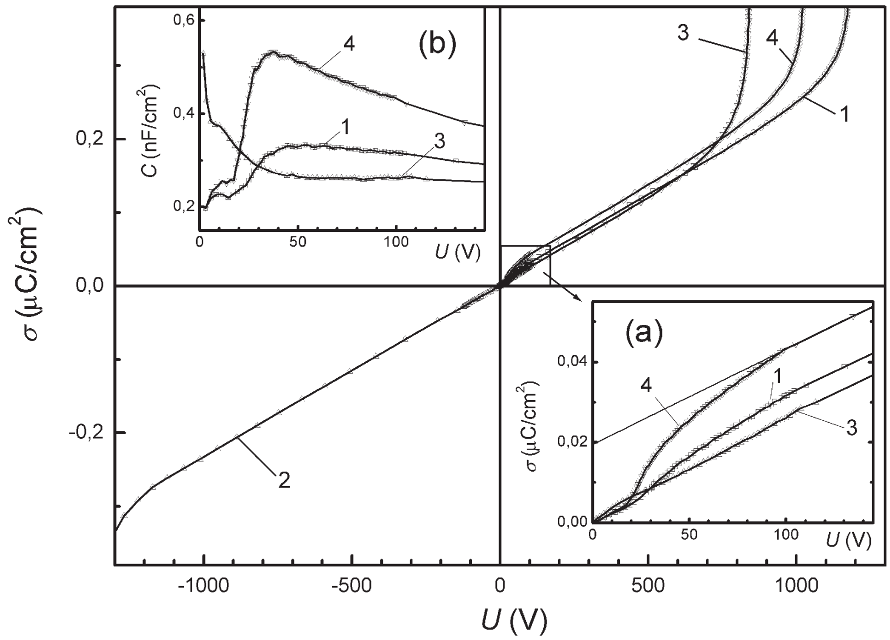


Figure 8. Charge-voltage (insert a – enlarged initial part) and capacitance-voltage; (insert b) characteristics of dosed charging of the double layer OPC 4 with the H_2Pc CGL at the top. 1 – first positive charging after adaptation in the dark; 2 – negative charging after discharge by exposure to red light; 3 – positive charging after discharge by deposition of positive charge; and 4 – positive charging after discharge by exposure to red light.

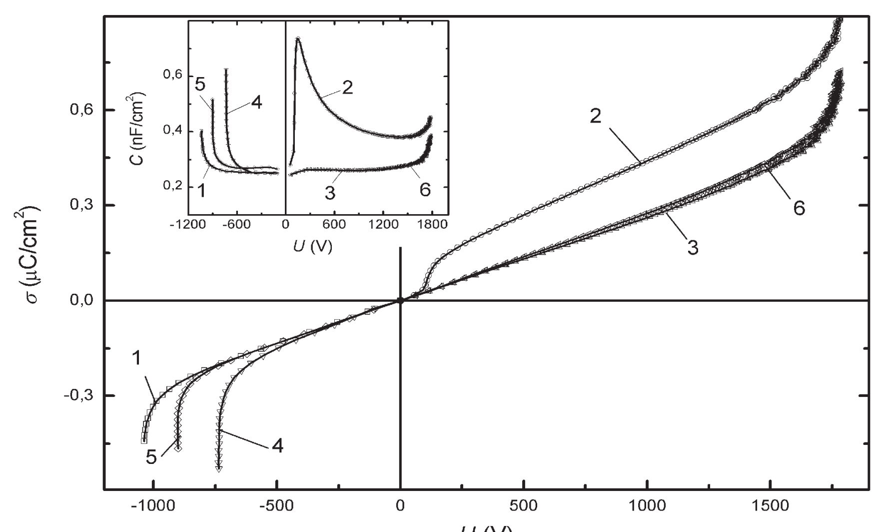


Figure 9. Charge-voltage and capacitance-voltage (insert) characteristics of dosed charging of the double layer OPC 3 with the TiOPc CGL at the bottom. 1 – first negative charging after adaptation in the dark; 2 – positive charging after discharge by exposure to red light; 3 – positive charging after discharge by deposition of negative charge; 4 – negative charging after discharge by deposition of negative charge; 5 – negative charging after discharge by exposure to red light; and 6 – positive charging after adaptation in the dark.

through the region of negative space charge, where a part of the drifting holes recombine with, and thus decrease density of, electrons trapped in deep states.

The polarity of the preliminary charging strongly influenced the nonlinearity of charge-voltage characteristics of double layer OPC in the initial stage of dosed charging. In the case when the normal double layer OPC (CTL upon the CGL) with negative work potential is first charged negatively (Fig. 9, curve 1), then discharged by exposure to red light, and subsequently re-charged positively, the charge-voltage characteristic of the latter, dosed charging is strongly nonlinear (Fig. 9, curve 2). This nonlinear charge-voltage characteristic indicates that during positive charging a significant hole current flows through the OPC, again because electrons in the CTL are immobile. These holes cannot originate from phthalocyanine crystallites, because the CGL is below the CTL. The positive ions deposited on the OPC surface cannot act as a source of holes, too, because in such a case the nonlinearity of the charge-voltage characteristic would also be observed when the OPC undergoes positive dosed charging for the first time after long adaptation in the dark (Fig. 9, curve 6). Such nonlinearity of the charge-voltage characteristic of positive dosed

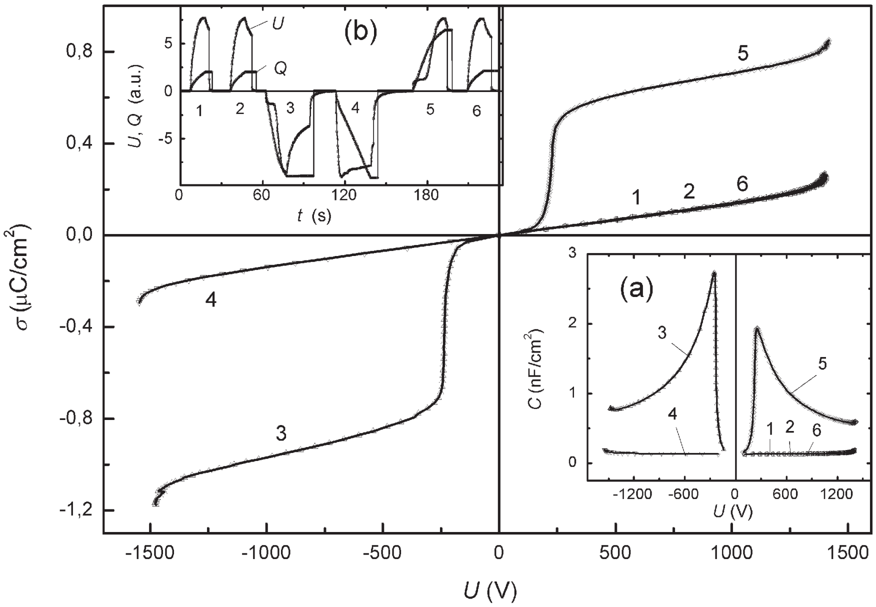


Figure 10. Charge-voltage and capacitance-voltage (insert a) characteristics and measurement sequence (insert b) in the case of dosed charging of the single layer OPC 5 with the barrier sublayer and the OCL. 1 – first positive charging after adaptation in the dark; 2 – positive charging after discharge by exposure to red light; 3 – negative charging after discharge by exposure to red light; 4 – negative charging after discharge by exposure to red light; 5 – positive charging after discharge by exposure to red light; and 6 – positive charging after discharge by exposure to red light.

charging can be caused by holes accumulated near the CTL surface during the preliminary negative charging and photodischarge. However, for this to occur, there must be a blocking barrier for holes in the surface region of the CTL, which interferes with hole recombination with the surface negative charge. Because there is no intentional barrier over the CTL it is proposed that such barrier layer may form adventatiously due to the interaction of ambient air with the OPC components, specifically with the hole TM.

Single Layer OPC

The charge carrier extraction and the shape of charge-voltage characteristics of dosed charging of single layer OPC with hole and electron transport materials and homogeneously distributed crystallites of Y-form TiOPc (or metal-free Pc) resembled those observed in double layer OPC with the same phthalocyanines in the CGL (Figs. 5(a), 5(b), and Fig. 6).

Strong nonlinearity of charge-voltage and capacitance-voltage characteristics in the initial stage of charging was observed in the case of single layer OPC after a preliminary charging to potential of opposite polarity and discharge by exposure to red light (Fig. 10, curves 3 and 5). If an OPC with the barrier sublayer formed on the Al substrate and with the top protection barrier layer (OCL) was at first charged positively (Fig. 10, curves 1,2) and photodischarged by exposure to red light and then dose charged negatively, then the charge-voltage and capacitance-voltage characteristics of this dosed charging are strongly nonlinear (Fig. 10, curve 3). This shows that a significant hole current flows through the OPC during negative dosed charging. The origin of this current is not TiOPc, because such a big current was not observed during the first charging (Fig. 10, curve 1). Therefore, it is supposed that the reservoir of those holes consists of holes accumulated at the interface between the photoreceptor and its barrier sublayer during photodischarge of the positively charged OPC: photogenerated electrons discharge the surface and holes drift towards electrons on Al substrate but are trapped at the barrier. During negative dosed charging, those holes drift from the barrier sublayer surface towards the OPC surface. Holes accumulate at the interface between the photoreceptor and its sublayer only when the sublayer acts as a blocking barrier for holes and prevents their recombination with electrons of the substrate electrode. The density of holes that accumulate at the barrier sublayer reached $(2 - 4) \times 10^{12}$ cm^{-2}, and it can exceed the hole density required for charging of the OPC to the maximum potential. Similar phenomena were observed at the barrier on the surface (Fig. 10, curves 4 and 5).

Hole density on the barriers depends on magnitude of the potential of the preliminary opposite polarity charging. This is well seen on Fig. 11, where the charge-voltage characteristic for OPC with OCL and without sublayer barrier are presented. The nonlinearity of positive charging increased considerably when negative potential was raised from 86 V to the maximum value 660 V.

The amount of charge trapped at the barrier depended on the charging and discharging regimes (Fig. 12). The OPC with sublayer barrier was charged positively to the maximum potential (Fig. 12, curve 1), discharged by exposure to red light and then charged negatively. Charge-voltage characteristic of negative charging was nonlinear (Fig. 12, curve 2). When the OPC was discharged by light, charged positively (Fig. 12, curve 3), discharged by light (repeated) and negatively charged again, then the nonlinearity of negative charge-voltage characteristic (Fig. 12, curve 5) increased. Such charge-discharge cycles were performed by increasing the number of positive charging doses before negative charging, and a further increase of nonlinearity of charge-voltage characteristic was observed (Fig. 12, curves 6 –10). This shows that accumulation of holes at the barrier in-

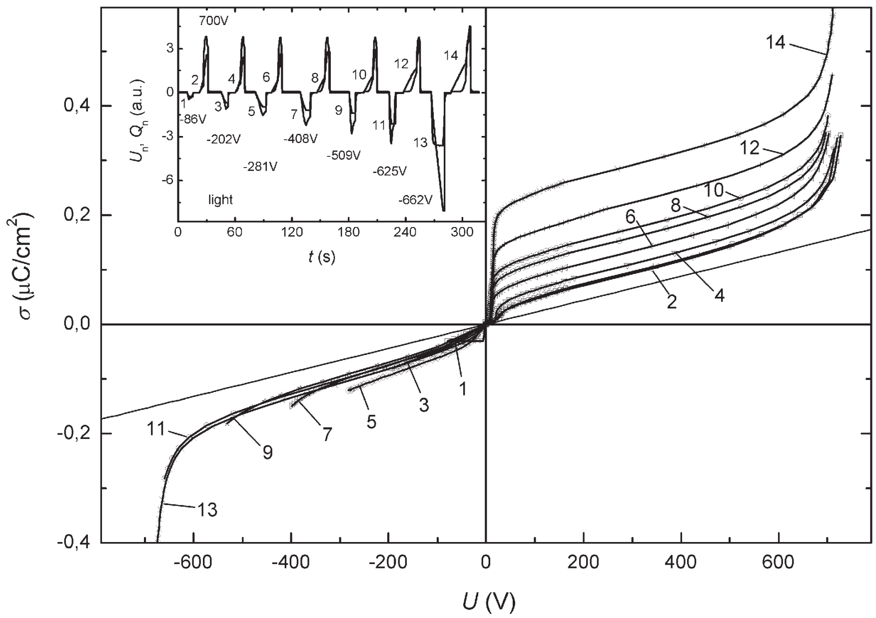


Figure 11. Charge-voltage and capacitance-voltage (insert a) characteristics of positive - negative dosed charging of OPC-7 at different levels of negative charging. Negative charging level and charging sequence – insert b. Curves 1,3,5,7,9,10,13 – negative charging, curves 2,4,6,8,10,12,14 – positive charging after discharge with red light.

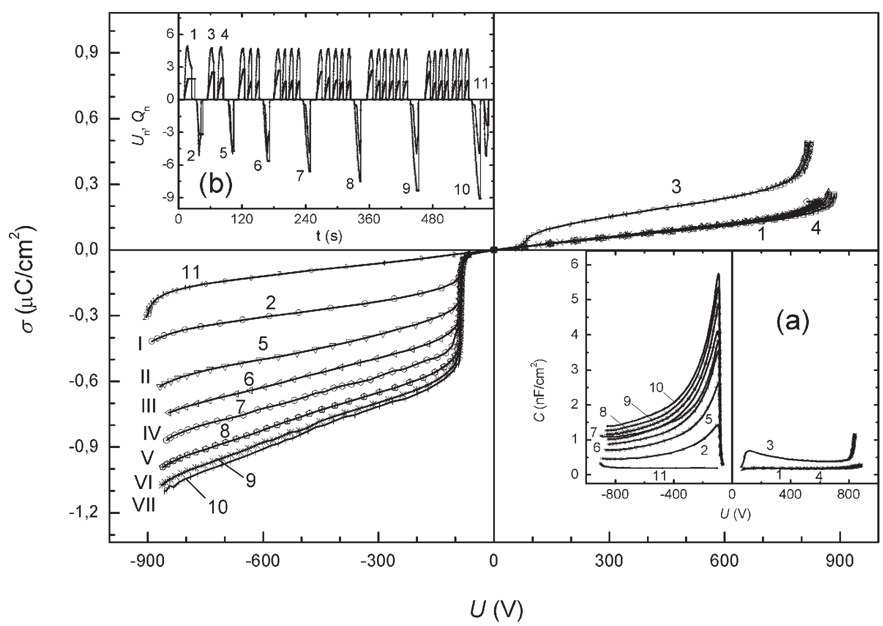


Figure 12. Charge-voltage, capacitance-voltage (insert a) characteristics and measurement sequence (insert b) in the case of dosed charging of the single layer OPC 6 with the barrier sublayer and without the OCL. 1 – positive charging to limiting potential (U_{max}) after adaptation in the dark; 2 – negative charging after discharge by exposure to red light; 3 – positive charging after discharge by exposure to red light; 4 – same as 3; 5 – negative charging after two sequences of positive charging and discharge by red light; 6 – negative charging after three sequences of charging to U_{max} and discharge by red light; 7 – same as 6, but positive charging after discharge by red light was repeated 4 times; 8 – same as 6, but positive charging was repeated 5 times; 9 – same as 6, but positive charging was repeated 6 times; 10 – same as 6, but positive charging was repeated 7 times; and 11 – negative charging after discharge by exposure to red light.

creases, and at subsequent negative charging hole current increases.

The sublayers of aluminum oxide and methylcellulose act as efficient blocking barriers for holes. However, when the barrier sublayer is not created intentionally and the photoreceptor was deposited upon polished aluminum, charge-voltage characteristic of dosed negative charging becomes linear (Fig. 13, curves 3 and 4), because in the absence of the barrier photogenerated holes recombine after reaching the OPC cathode.

In the case when a negatively charged OPC was discharged to zero by exposure to red light, the charge-voltage characteristic of the repeated negative dosed charging became linear (Fig. 10, curve 4). This observa-

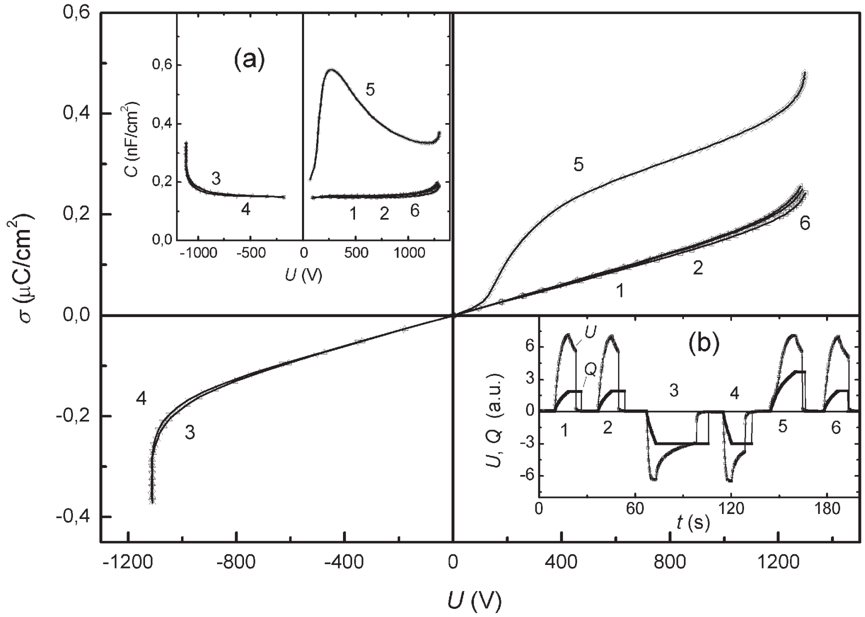


Figure 13. Charge-voltage and capacitance-voltage (insert a) characteristics and measurement sequence (insert b) of dosed charging of the single layer OPC 7 without the barrier sublayer, but with the OCL. 1 – first positive charging after adaptation in the dark; 2 – positive charging after discharge by exposure to red light; 3 – negative charging after discharge by exposure to red light; 4 – the same as 3; 5 – positive charging after discharge by exposure to red light; and 6 – the same as 5.

tion indicated that the hole reservoir near the barrier sublayer was depleted during the first negative charging. The holes near the barrier reservoir, as well as the holes photogenerated during the discharge to zero, drifted towards the OPC surface and recombined there with negative surface charge or accumulated in the surface region of the OPC or at the interface between the OCL barrier and the OPC (Fig. 10, curve 5). A significant nonlinearity of the charge-voltage characteristic of dosed positive charging (Fig. 10, curve 5) showed that a large density of holes accumulated in the OPC surface region in contact with the OCL during the preliminary charging and exposure. It is interesting to note that significant nonlinearity of the charge-voltage characteristic of dosed positive charging was also sometimes observed in the case when the OPC was not covered by the OCL (Fig. 12, curve 3). This means that the holes accumulate in the near-to-surface region of the OPC during the preliminary negative charging and discharge. Understandably, such hole reservoir can form if the OPC surface region has a barrier for holes, which limits recombination of holes with the surface negative charge. Since in this case the layer was not covered with OCL, the most probable explanation of this barrier is interaction of OPC components with ambient molecules, similar to the case of the double layer OPC (Fig. 9). This conclusion is in accord with the fact that such a physical barrier is observed only occasionally and only for certain materials. For example, in the OPC with hole transport material hydrazone II (Fig. 1) and electron TM material IV (Fig. 1), there was evidence of the physical barrier, but after replacing the electron TM material with III, the physical barrier was not observed.

Density of holes accumulated on the barrier sublayer decreases decreased with time. This is was evident from the shape of charge-voltage characteristics, as shown in Fig. 14. In the case when, after the preliminary positive charging and photodischarge by exposure to red light, holes are accumulated on the barrier sublayer, and subsequent negative dosed charging is started after a certain time delay, then an increase in this time causes a decrease in the nonlinearity of the charge-voltage characteristic of negative dosed charging. This means that the number of holes drifting from the barrier sublayer towards the OPC surface decreased with time.

Conclusions

1. In the initial stage of charging of double layer OPC consisting of charge transport and charge photogeneration layers, carrier extraction from phthalocyanine crystallites occured. In the case of X-form metal-free Pc (H_2Pc), the extracted charge in the investigated layers was as high as $0.5 – 1.0 \times 10^{12}$ cm^{-2}, whereas in the case of Y-form TiOPc, the extracted charge was less by an order of magnitude. The charge carrier reservoir in phthalocyanine crystallites was completely restored by exposure to red light or by keeping the OPC for a long time in uncharged state in the dark.
2. Preliminary charging of double layer photoreceptors, consisting of the CTL and the CGL, to non-work potential causes a decrease of work potential, because the critical electric field was reached at a lower work potential; this decrease, in its turn, was caused by electron injection from the CGL and electron trapping in deep levels at the CGL-CTL interface.
3. Nonlinearity of the characteristic of dosed charging of the single layer OPC with a barrier sublayer was strongly dependent on polarity of the preliminary charging and photodischarge. During positive charging and photodischarge, holes accumulate on the barrier sublayer and their density (5×10^{12} cm^{-2}, when CGL thickness is ~0.5 μm) can be several times larger than the density required for charging the OPC to the maximum potential. During the recharge of

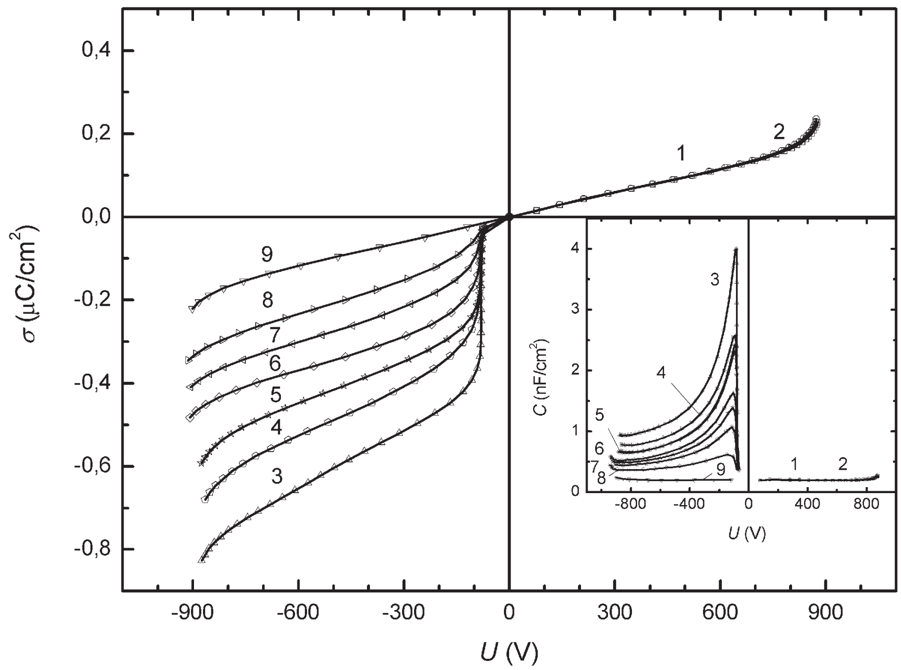


Figure 14. Charge-voltage and capacitance-voltage (insert) characteristics of dosed charging of the single layer OPC 6 with the barrier sublayer, but without the OCL, and their change with time between discharge by red light and after the subsequent multiple negative charging. 1 – first positive charging after adaptation in the dark; 2 – positive charging after discharge by red light; 3 – negative charging immediately after the discharge; 4 – negative charging 10 s after the discharge; 5 – after 30 s; 6 – after 60 s; 7 – after 10 min; 8 – after 30 min; and 9 – negative charging after adaptation in the dark.

the photoreceptor with the opposite (negative) charge, holes drift from the barrier sublayer towards the OPC surface and partially accumulate on the inner side of the protection layer. Depending on the nature of hole and electron transport materials, the holes partially accumulate in the near-to-surface region of the OPC in the case when the barrier OCL was absent, too. Such phenomena can be explained by supposing that some barrier was formed by interaction of ambient molecules with charge transporting materials.

References

1. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems*, Marcel Dekker, Inc.. New York, NY, 1998.
2. J. W. Weigl, J. Mammino, G. L. Whittaker, R. W. Radler, and J. F. Byrne, in *Current Problems in Electrophotography*. Walter de Gruinter, Berlin, 1972, pp. 287-300.
3. K. Kubo, T. Kobayashi, S. Nagae, and T. Fujimoto, *J. Imaging Sci. Technol.* **43,** 248 (1999).
4. P. M. Borsenberger and D. S. Weiss, Photoreceptors: Organic Photoconductors, in *Handbook of Imaging Materials*, Marcel Dekker, Inc., New York, NY, 1991, pp. 379 – 446.
5. T. Lozowski, R. Maldzius and E. Montrimas, *Synthetic Metals* **109,** 195-198 (2000).