Electrophotographic and Hole Transport Properties of Polycarbonates Doped by Organic Photoconductors and Their Light- and Corona Discharge Stabilization

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Abstract

Electrophotographic and hole transport properties of organic photoconductor layers on the base of a phenyltolyl-(β-naphtylamine) (PTNA) doped polycarbonate (PC) and pure (binderless) PTNA were investigated. PTNA was doped into different PCs of types PC-A and PC-Z. Hole drift mobility measured by conventional time-of-flight techniques in the PTNA+PC films was lower than that in the binderless PTNA films. Electrophotographic properties of OPC drums on the base of the PTNA and DEH doped PC layers were studied. An influence of light- , corona- and light + corona intensities on the electrophotographic characteristics of the OPC drums with stabilized or non stabilized charge transporting and generating layers was investigated as well. A stabilization of the electrophotographic layer compounds by various additives such as an antioxidant, an ultraviolet absorber, and an agent for preventing light- and corona induced deterioration was performed.

Introduction

Organic Photoconductors (OPC) are widely used for production of drums for laser printers, diode printers and copiers. Properties of OPC's including 4-diethylamino-benzaldehyde-diphenylhydrozone (DEH) and N, N'-diphenyl-N, N'-bis (3-methylphenyl)-[1,1'-biphenyl] -4,4'-diamine (TPD) are under study[1]. The similar properties are observed for a new OPC - phenyltolyl-β-naphtylamine (PTNA) which may be promise for electrophotographic devices[2-4]. PTNA like TPD forms reasonably stable amorphous glasses without polymer binder. This paper describes the results of the investigation of hole transport in OPC (PTNA, DEH) doped bisphenol-A-polycarbonate (PC-A) and bisphenol-Z-polycarbonate (PC-Z) systems. It was interesting to study an effect of polymer characteristics (in particular, molecular weight) on hole transport in OPC doped PC systems.

To be useful for electrophotographic devices a new OPC requires an investigation of its light-, ozone- and corona discharge stabilities. As it is known various types of light-, ozone- and corona discharge stabilizers and other additives in a charge transporting layer (CTL) and/or a charge generating layer (CGL) may be used. It is useful to study effects of corona discharge and light intensities on electrophotographic characteristic PTNA and DEH doped PC systems.

Experimental

Samples studied by xerographic method consisted of an Al substrate, a barrier-adhesion layer of 0.8 - 1.5 microns thick, a generation layer of 0.3 - 0.8 microns thick, and a transport layer of 25 - 35 microns thick. Barrier-adhesion layer was cast from a solution of a polyamide (PA 6/66/610). The CGL was composed of a titanil phthalocyanine pigment (TiOPc, ST10.10/2 of SynTec GmbH) or bis-azo pigment (RT-557 of Reproton Co. Ltd.) dispersed in polyvinylethylale PVE (2:1). The CTL were PTNA or DEH doped PC. The layers were prepared by a dip coating method. PTNA was produced from N-phenyl-β-naphtylamine and iodo-benzene and then recrystallized with ethanol[2,3].

PC-1 and PC-3 (PC-A, PO "Zarya", Russia) were with molecular weights equal to ca 45000 and 30000 respectively and melting indexes (168 ^{0}C/1.2kg) equal to ca 3.0-3.5 g/10min and 7.1-7.6 g/10min respectively. The specific viscosity of 0.5 g/dl solutions PC-1, PC-3, PC-Z (E-2000, Mitsubishi Chemical Co.) and PC-A (PC-A, Australia) in dichloromethane were 0.96, 0.78, 0.78 and 0.62 dl/g respectively.

Sensitivity $S_{1/2}$ $(lx \cdot s)^{-1}$ for halogen lamp (T_{color} = 2850 K) was given by exposure required to reduce the corona charged surface potential to halfvalue. Dark decay was determined by a decrease of the initial surface potential after left in the dark for 5 seconds (DD_5,%). Residual potential V_R was determined by a surface potential after exposure 10 $E_{1/2}$.

Hole drift mobility in CTL was studied by a conventional time-of-flight (TOF) method[1], according to techniques described in the previous paper[4]. Both xerographic and TOF measurements were carried out at room temperature.

The corona-, light- and corona+light stability of samples were investigated by using a special rotate machine. Initial electrophotographic characteristics of OPC drum samples (sensitivity $S_{1/2}$ for halogen lamp, residual potential V_R, dark decay $DD_{5\%}$) were determined. The rotating drum was treated by light (halogen lamp with intensity 450 or 2200 Lx) or corona discharge (with different intensity) or light + corona discharge. After 1000 - 200000 revolutions (cycles) the electrophotographic characteristics were determined immediately. Finally, the drum was dark-rested for 12 hours and measurements were repeated.

Drum No. 1 has only RT-557 + PVE (2:1) in a CGL, and DEH + PC-3 (1:1) in a CTL, and has not any stabilizers. Drum No.2 has RT-557 + PVE (2:1) + hindered phenol phenozane-28 (5 wt.%) in a CGL, and DEH + PC-3 (1:1) in a CTL. Drums of type No. 3.X have RT-557 + PVE (2:1) + phenozane-28 (5 wt.%) in a CGL, and DEH + PC-3 (1:1) + stabilizer in a CTL. Drums of type No. 4.X have RT-557 + PVE (2:1) + chloranil (5 wt.%) in a CGL, and DEH + PC-3 (1:1) + stabilizer in a CTL. Drums of type No. 5.X have RT-557 + PVE (2:1) + stabilizers in a CGL, and DEH + PC-3 (1:1) + stabilizer Irganox-565 (Ciba-Geigy, 1 wt. %) in a CTL ("standard" CTL). Drums of type No. 6.X have RT-557 + PVE (2:1) + chloranil (5 wt.%) in a CGL, and PTNA + PC-3 (1:1) + stabilizer in a CTL. Drums of type No. 7.X have TiOPc + PVE (2:1) + chloranil (5 wt.%) in a CGL, and DEH + PC-3 (1:1) + stabilizer in a CTL.

Results and Discussion

Figure 1 shows the hole mobility as a function of electric field strength for PTNA doped polycarbonates (1:1) of different types. As follows from Fig.1 the mobility strongly depend on the kind of PC and its molecular weight. This fact is very useful for development of novel OPC layers.

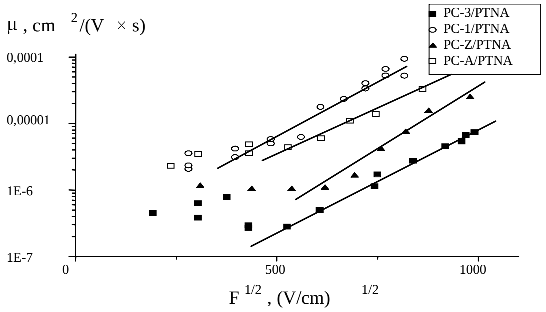

Figure 1. The hole mobility as a function of electric field strength for PTNA doped polycarbonates (1:1).

Figure 2 shows the hole mobility as a function of electric field strength for PTNA doped polycarbonate PC-3 and for pure PTNA. As is seen, the mobility in PTNA+PC films is lower than that in the binderless PTNA films evidently due to a larger distance between adjacent transporting molecules.

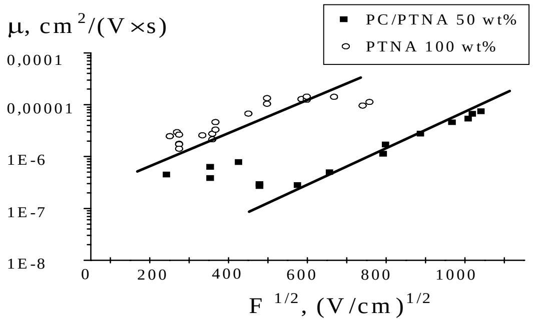

Figure 2. The hole mobility μ as a function of electric field strength F $^{1/2}$ of PTNA doped PC-3 and pure PTNA.

As follows from Fig.1 the hole drift mobility in the limit of zero field strength for the PTNA+PC-1 (50 wt.%) system is equal 1.0 $\times 10^{-7}$ cm^2 /V×s. The dipole moment for PTNA calculated by PM3 method is equal 1.28 Debye. For tritolylamine (TTA) in PC (45 wt.%) these values are equal 2.5 10^{-5} cm^2 /V×s and 0.90 Debye accordingly[1]. Molar concentrations of TTA and PTNA in PC are close in magnitude. As is seen, the larger dipole moment of triarylamine molecule the lower drift mobility. Such a correlation was observed in a series of studies[8-11].

During the electrophotographic process, the OPC is subjected to a series of charge and illumination which often produce changes in the electric and optical properties of the OPC. These changes are usually called fatique. In order to overcome such disadvantages and to maintain the electrophotographic characteristics, an antioxidant of a hindered phenol type, a phosphite type, a sulphide type, electron acceptors and so on was used in CTL or CGL or into both CTL and CGL.

CTL and CGL without Stabilizers

For OPC's of type drum No 1 (without stabilizers in both CTL and CGL) a rise of initial values of V_R (to - 270 V, after dark-resting - to -100 V) and a drop of initial values of S/S_0 (to 83 %, after dark-resting - to 100 %) after 25000 cycles are observed. The light intensity was 450 Lx, the initial surface potential was - 1100 V.

It was interesting to study factors that influence on these characteristics of OPC drum.

Figures 3- 8 show the residual potential V_R and relative sensitivity S/S_0 for Drum No 1. vs. light- , corona- and light+corona intensities (initial values V_R and S_0 , values V_R and S were measured after 25000 cycles immediately and after dark-resting for 12 hours). As follows from the Figures, light, corona and light+corona influence on electrophotographic characteristics - V_R values are increased and values of S/S_0 are decreased.

The changes in the characteristics (cycle stability, Figures 3 and 8) are partially reversal, and can strongly influence on properties of the OPC drums. As is seen from Figures 6 and 7, the effect of corona or of light (separately) on values of residual potential and sensitivity considerably increases with increasing of both light, and corona intensities. The total effect a corona + light on these values greatly depends on intensity of a corona, and especially greatly - on light intensity (Figures 4, 5).

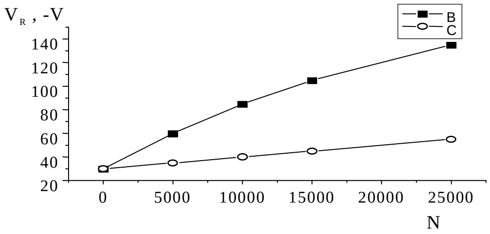

Figure 3. Cycle dependence of residual potential V_R for Drum No 1. Cycle "charging – exposition". The initial surface potential was -1100 V. B –after N cycles immediately, C – dark-rested for 12 hours after N cycles.

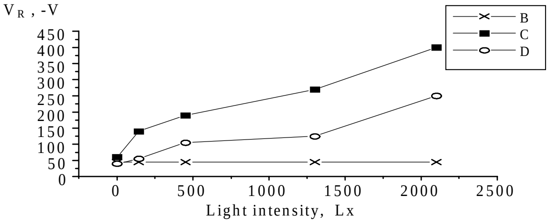

Figure 4. Light intensity dependence of residual potential V_R for Drum No 1. Cycle "charging – exposition". The initial surface potential was - 1200 V; C –after 25 000 cycles immediately, D – dark-rested for 12 hours after 25 000 cycles, B – without light and corona.

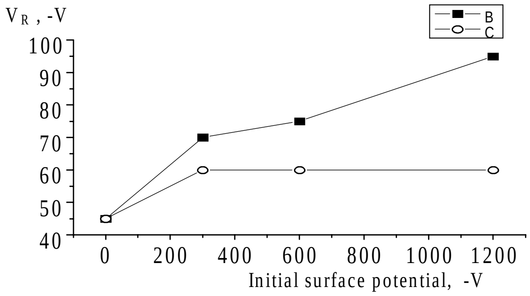

Figure 5. Corona intensity dependence (initial surface potential) of residual potential V_R for Drum No 1. Cycle "charging – exposition". C –after 25 000 cycles immediately, D – dark-rested for 12 hours after 25 000 cycles, B – without corona and light.

CGL with Stabilizers

Various types of additives such as hindered phenols, hindered amines, sulfides, etc., dyes, electron accepting compounds and their mixtures as stabilizers for CGL were investigated. The suitable results were obtained for the CGL with a phenozane-28 stabilizer (5 wt.%) a rise of initial values of V_R (to - 110 V, after dark-resting - to -65 V) and a drop of initial values of S/S_0 (to 73 %, after dark-resting - to 83 %) after 35000 cycles were found.

In the CGL with a chloranil stabilizer (5 wt.%) a rise of initial values of V_R (to - 90 V, after dark-resting - to -55 V) and a drop of initial values of S/S_0 (to 118 %, after dark-resting - to 104 %) after 35000 cycles are observed. In all cases the dark decay changed inconsiderably.

These compositions of CGL were accepted in a future as "standard".

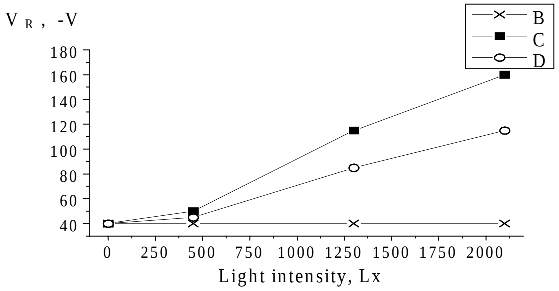

Figure 6. Light intensity dependence of residual potential V_R for Drum No 1. Cycle ''exposition''. The corona was absent; C –after 25 000 cycles immediately, D – dark-rested for 12 hours after 25 000 cycles, B – without light and corona.

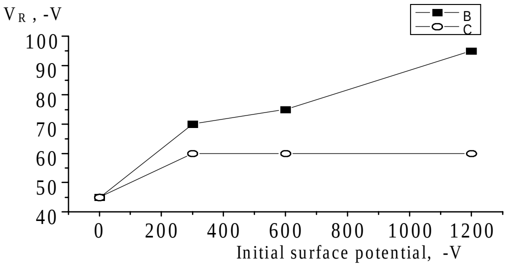

Figure 7. Corona intensity dependence (initial surface potential) of residual potential V_R for Drum No 1. Cycle "charging". The light was absent. B –after 25 000 cycles immediately, C – dark-rested for 12 hours after 25 000 cycles.

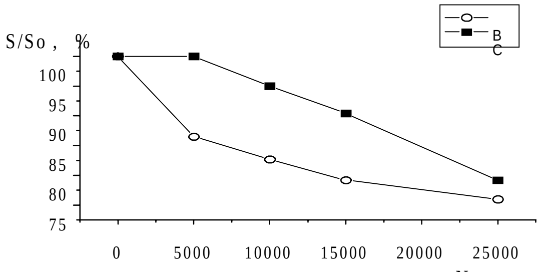

Figure 8. Cycle dependence of relative sensitivity S/So for Drum No 1. Cycle "charging –exposition". The initial surface potential was -1100 V). C –after 25000 cycles immediately, B – dark-rested for 12 hours after 25000 cycles.

CTL and CGL with Stabilizers

Drums of the type No 3.X and 4.X based on layers with various types of additives such as an antioxidant (hindered phenols, hindered amines, phosphites, sulfides, etc., and their mixtures), an ultraviolet absorbers, dyes, an electron accepting compounds as an agent for preventing light- , corona- and light+corona induced deterioration were investigated. The more suitable data were obtained for the layers with Irganox-565 (1 wt.%). For this sample, a rise of initial values of V_R (to - 85 V, after dark-resting – to -35 V) and a drop of initial values of S/S $_0$ (to 61 %, after dark-resting - to 77 %) after 35000 cycles were observed at the light intensity of 450 Lx and the initial surface potential of -1100 V. This composition of CTL was accepted in a future as "standard".

The more suitable data with 5 wt.% of chloranil, o-chloranil, TCNQ were obtained. For these samples a rise of initial values of V_R (to - 50 V, after dark-resting - to -25 V) and a drop of initial values of S/S $_0$ (to 61 %, after dark-resting - to 77 %) after 35000 cycles were observed at the light intensity 450 Lx and the initial surface potential - 1000 V.

For drums of type No 6.X in which the CTL includes PTNA instead of DEH (if the stabilizer in the CTL was absence) a rise of initial values of V_R (to - 180 V, after dark-resting - to -110 V) and a drop of initial values of S/S $_0$ (to 77 %, after dark-resting - to 89 %) after 35000 cycles are observed.

For the same drum in which the CTL includes Irganox-565, initial V_R increased up to -370 V and -210 V (after dark-resting) and initial S / S $_0$ decreased to 21 % and 34 % (after dark-resting). For CTL on the base of PTNA, a number of additives were investigated: dialkylamines, 2,2'- and 4,4'-bipyridyls (offered in the patent[5]), tetramethylpyrasine (offered in the patent[7]), electron-acceptor compounds (offered in the patent[6]) and their analogues, derivatives of tri- and tetranitrofluorenone and tri- and tetranitrofluorene. Promising data were shown by layers with 4,4'-bipyridyl, di- and mono- 1,1-dicyanoethylene- derivatives of benzene and carbazole. Initial V_R increased up to -85 V and -45 V (after dark-resting) and initial S/S $_0$ decreased to 91 % after 35000 cycles.

When TiOPc was used as pigment in CGLs, the most promising results were obtained for CTL on the base of DEH. For drums of the type No 7.X, following stabilizers show good data: Irganox-565 (1 wt.%), di- and mono- 1,1-dicyanoethylene- derivatives of benzene and carbazole. Initial V_R increased up to -60 V and -45 V (after dark-resting) and initial S/S_0 decreased to 93 % after 180000 cycles (at light intensity of 450 Lx); and initial V_R increased up to -75 V and -65 V (after dark-resting) after 70000 cycles (at light intensity of 1600 Lx).

Conclusion

The investigation of light- , corona- and light + corona influence on electrophotographic characteristics of OPC drums with stabilized or non stabilized CTL and CGL demonstrates that a simultaneous incorporation of antioxidants - hindered phenols and electron acceptors in compositions of both CGL and CTL allows to produce OPC drums promising for practical use in electrophotographic devices.

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Biography

Konstantin K. Kochelev graduated in 1971 from the Novosibirsk's State University (Chemistry). 1971-1980 - researcher at the Institute of Petroleum Chemistry (Tomsk). 1980-1995- senior researcher, head of the Laboratory at the Filial of GOSNIIKHIMFOTOPROECT (Pereslavl-Zalessky). 1995 - 1996 - Technical Director, since 1997 Deputy Director on Scientific Work at the "Scientific Research Phototechnical Institute on Company Slavich ("NIFTI-Slavich", Pereslavl- Zalessky). Dr. of Chem. Sci. (1981). cca 150 patents and publications.

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