

Light Stability and Electrophotographic Properties of Polycarbonate Layers Doped by Organic Photoconductors

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Abstract

Possible reasons of a fatigue of organic photoreceptors such, as the photochemical processes in charge transfer layers (CTL) are investigated and discussed. The results concern a study of influence of corona discharge, exposure and joint action of both the factors on cyclic stability of organic photoreceptors. The charge generation layers (CGL) use titanyl phthalocyanine (TiOPc), bisazo dye and effective stabilizers. The organic photoconductor (OPC) in CTL are p-diethylaminobenzaldehyde diphenylhydrazone (DEH), N-phenyl-4-tolyl- β -naphthylamine (PTNA) or N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) without stabilizers. It was established, that the values of a residual potential and dark decay of potential greatly depend on the exposure conditions such as light wavelength in cycle "charging-exposition". It can be conditioned by reactions of bication radicals or photoexcited monocation radicals of OPC molecules, for example with impurities involved in CTL.

Introduction

Our previous paper¹ reported on electrophotographic and hole transport properties of polycarbonates doped with OPC and their light- and corona discharge stabilization. The investigation have shown that a simultaneous use of antioxidants in both charge generating layer CGL and charge transporting layer CTL allows to sharply increase cyclic stability of drums to cycle "charging-exposition". That is, both of functional layers contribute to a cyclic fatigue of a drum. However, the mechanism which is responsible for cyclic fatigue of drum has not been determined with certainty. In a number of paper is supposed, that the reason of a fatigue of CTL is the photooxidation (especially UV-component of light)² or oxidation of OPC of CTL by products of corona (ozone, nitrogen oxides, etc.)³⁻⁴.

In order to prevent above mentioned harmful influences, in a number of the patents an electron-accepting compound or amines were added into a CGL⁵⁻⁷.

In this paper we have continued an investigation of cyclic fatigue of drums (cycles "charging", "exposition", "charging-exposition") - their residual potential and dark decay of potential. The effective stabilizers was entered into CGL, but CTL was used without stabilizers. It should allow to clarify influence of processes taking place mainly in CTL on a cyclic fatigue of drums. For the same reason it was interesting also to determine the effect of wavelength of light on the characteristics of drums after cycle "charging-exposition".

Experimental

The methods of an investigation of drums and their manufacture were described in the previous paper¹.

The CGL of OPC Drums contains TiOPc (ST10.10/2 of SynTec GmbH) dispersed in copolymer vinylchloride and vinylacetate VAGH (Du PONT de NEMUR) or bisazo pigment (ST- 1017 of SynTec GmbH) dispersed in polyvinylethylale PVE. The CTL were N-phenyl-4-tolyl- β -naphthylamine PTNA, DEH or TPD doped bisphenol-A-polycarbonate PC-A (PC-3, PO "Zarya" Russia).

Dark decay was determined by a decrease of the initial surface potential after left in the dark for 5 or 10 seconds (DD_5 , DD_{10} , %). Residual potential V_R was determined by a surface potential after exposure $10 \times E_{1/2}$.

Sometimes we used so-called relative values - relative residual potential V_R/V_{R0} and relative dark decay DD_{10}/DD_{10}^0 , where V_{R0} and DD_{10}^0 are initial values.

The corona-, light- and corona+light stability of samples were investigated by using a special rotate machine. Initial electrophotographic characteristics of OPC Drum (V_R , $DD_{5\%}$ and so on) were determined. The rotating drum was treated by light or corona discharge (with different intensity) or light + corona discharge. After 5000 - 35000 revolutions (cycles) the electrophotographic characteristics were determined immediately and after dark-resting for 48 hour.

Halogen lamp ($T_{color} = 2850$ K) with fixed intensity without or with colour filters was used. The colour filters were

transparent to wavelengths more than 440, 550, 700, 800 or 1000 nm (Fig.1). The spectrum of the halogen lamp radiation without filters herewith was in the wavelengths region of more than 300 nm. Intensity of the light was all the time equal 250 W/cm^2 (or 3200 Lx).

The drums used have following compositions: **Drum No 1:** CGL = TiOPc + VAGH (2:1) + Stabilizer Ph1; CTL= DEH + PC-3 (1:1). **Drum No 2:** CGL = TiOPc + VAGH (2:1) + Stabilizer Ph1; CTL= PTNA + PC-3 (1:1). **Drum No 3:** CGL = bisazo pigment ST 1017 + PVB (2:1) + Stabilizer Ph1; CTL= DEH + PC-3 (1:1). **Drum No 4:** CGL = bisazo pigment ST 1017 + PVB (2:1) + Stabilizer Ph1; CTL= PTNA + PC-3 (1:1). **Drum No 5:** CGL = TiOPc + VAGH (2:1) + Stabilizer Ph1; CTL= TPD + PC-3 (1:1). **Drum No 6:** CGL = bisazo pigment ST 1017 + PVB (2:1) + Stabilizer Ph1; CTL= TPD + PC-3 (1:1).

Results and discussion

Fig.1-3 are shown absorption spectra of pigments (in CGL), OPC (in CTL) and transmission spectra of colour filters.

Fig. 4-7 are shown Light- or Corona intensity dependences of relative residual potential V_R/V_{R0} (cycle "charging-exposition") for Drums 1-2.

As shown in Figs. 4-7, the increase of the relative residual potential V_R/V_{R0} for drums No 1, 2 after the ending of cycles both at once and after 48 hour with increasing of initial surface potential (ISP) indicates that reversible and irreversible processes there are mainly in the CTL, since CGL was well sensibilized.

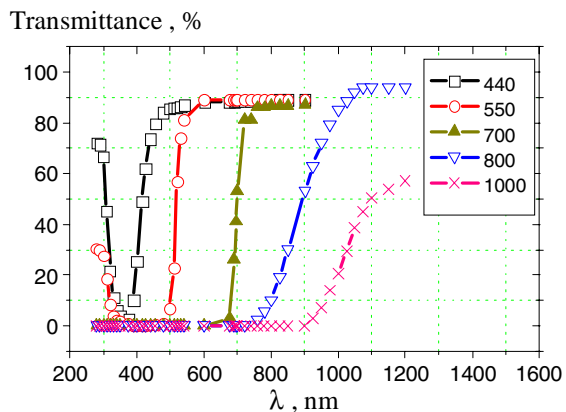


Fig. 1. Transmission spectra of the colour filters.

Simultaneously the growth of magnitudes of DD_5 and DD_{10} was observed also. The same dependencies were obtained and for drums No 3, 4, which consist of stabilized bisazo dye.

Figs. 4-7 show that stability of CTL to exposure or corona discharge is smaller for DEH than for PTNA.

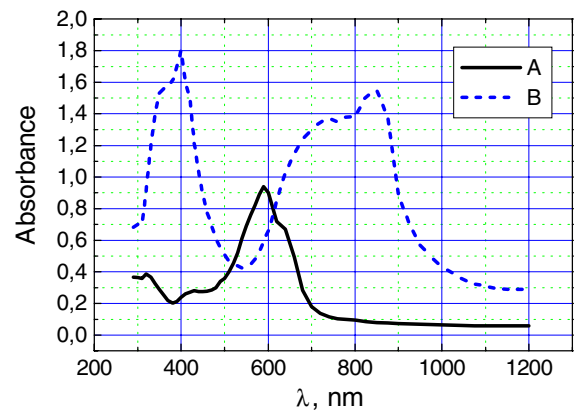


Fig. 2. Absorption spectra of A - bisazo pigment ST 1017/PVB, B - TiOPc/VAGH.

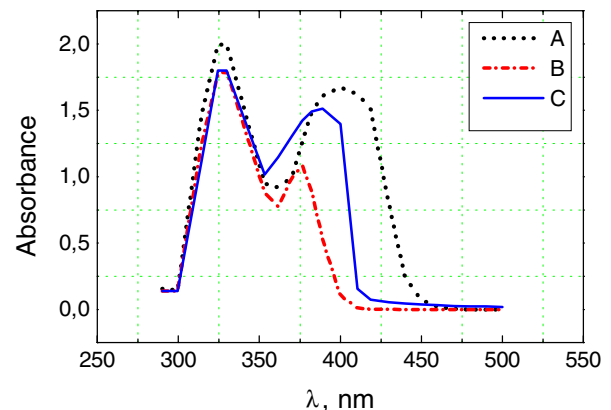


Fig. 3. Absorption spectra of A - DEH, B - PTNA, C - TPD.

This especially evidently when light intensity are higher 1500 lx, and immediately after acting of the cycle "charging - exposition".

The same data are obtained and for drums No 3, 4 (containing bisazo dye). It confirms the conclusion that the processes taking place mainly in CTL are responsible for the growth of V_R and DD.

As indicated earlier¹, the V_R and DD values (measured at once and after dark resting) vary more at the action of both corona discharge and exposure simultaneously, than at the action of each factor by itself.

These data are confirmed also by the results of the present work.

Indeed, Figs. 8-11, Tables 1, 2 show, that an effect of only halogen lamp (without filters) on CTL (Drums 1-4) in a cycle "exposition" ($ISP = 0$), or an effect of only corona discharge in a cycle "charging" give only weak changes of the values V_R , V_R/V_{R0} and DD_{10}/DD_{10}^0 .

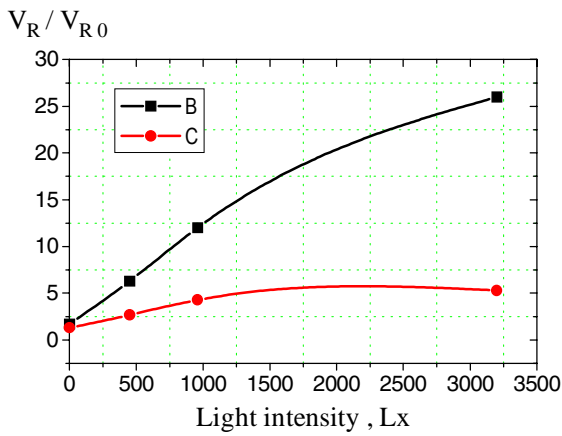


Fig. 4. Light intensity dependence of relative residual potential V_R / V_{R0} for Drum No 1. Cycle "charging-exposition". The initial surface potential was -1000 V; B - after 15000 cycles immediately, C - dark-rested for 48 hours after 15000 cycles.

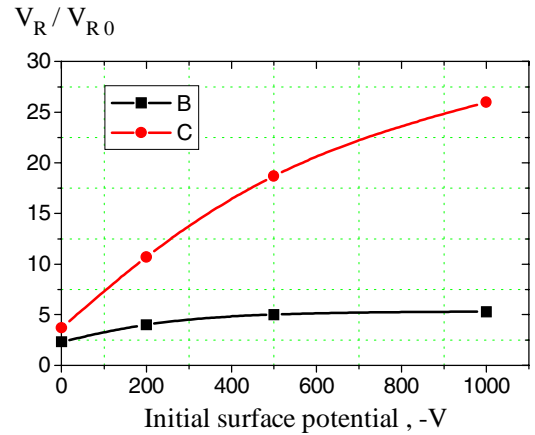


Fig. 6. Corona intensity (initial surface potential) dependence of relative residual potential V_R / V_{R0} for Drum No 1. Cycle "charging-exposition". The light intensity was 3200 Lx (250 W/m^2). C - after 15000 cycles immediately, B - dark-rested for 48 hours after 15000 cycles.

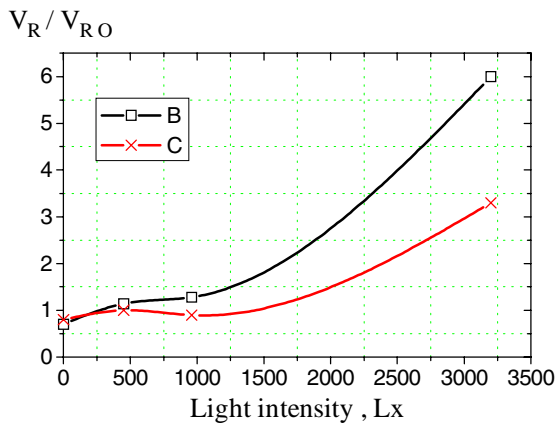


Fig. 5. Light intensity dependence of relative residual potential V_R / V_{R0} for Drum No 2. Cycle "charging-exposition". The initial surface potential was -1000 V; B - after 15000 cycles immediately, C - dark-rested for 48 hours after 15000 cycles

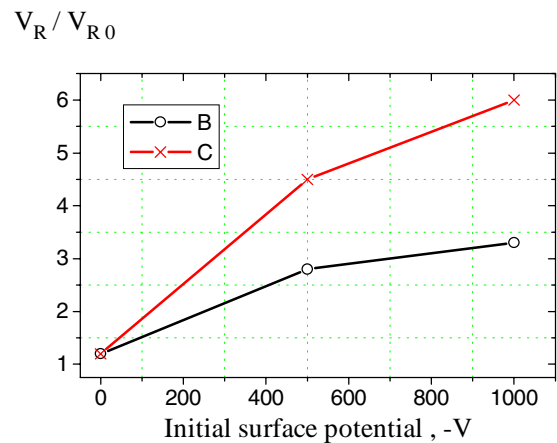
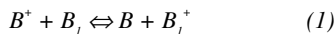


Fig. 7. Corona intensity (initial surface potential) dependence of relative residual potential V_R / V_{R0} for Drum No 2. Cycle "charging-exposition". The light intensity was 3200 Lx (250 W/m^2). C - after 15000 cycles immediately, B - dark-rested for 48 hours after 15000 cycles.

In other words, the essential changes of values V_R , V_R / V_{R0} and DD_{10} / DD_{10}^0 are present only if both light and corona discharge effect together.

On the base of these results we can suppose, that the fatigue of CTL in this case is connected mainly with holes drifting in CTL, i. e., with a following reaction (1):



where B and B_1 - neutral molecules of OPC, and B^+ , B_1^+ - their monocation radicals.

Furthermore the fatigue of CTL can also be associated with reversible and irreversible interactions of these cation radicals with molecules of active impurities involved in CTL. Such impurities can operate as different types of the

traps for charge carriers⁸, which can influence on CTL characteristics.

To clarify possible mechanisms of such interactions the influence of light wavelength in cycle "charging-exposition" was further investigated.

The used colour filters have removed practically completely a light with wavelength below 440, 550, 700, 800 and 1000 nm respectively. The intensity of exposure was always constant and equal 250 W/m^2 .

Some data obtained are shown in Figs. 8-11 and Tables 1, 2.

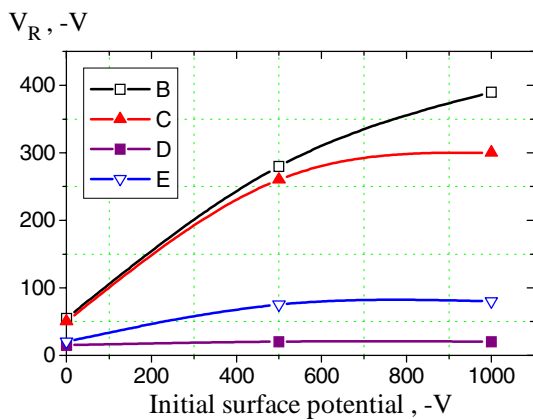


Fig. 8. Corona intensity (initial surface potential) dependence of residual potential V_R for Drum No 1. Immediately after 15000 cycles "charging-exposition" with different spectrum of light of halogen lamp ($T_c=2850$ K); B - without colour filters, C- with colour filters transparent at >440 nm, D - at >550 nm, E - at >700 nm. The light intensity was 250 W/m².

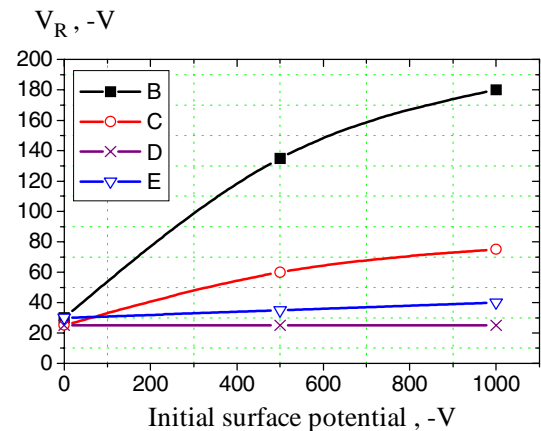


Fig. 10. Corona intensity (initial surface potential) dependence of residual potential V_R for Drum No 2. Immediately after 15000 cycles "charging-exposition" at different wavelengths of halogen lamp ($T_c=2850$ K); B - halogen lamp without colour filters, C- with colour filters transparent at >440 nm, D - at >550 nm, E - at >700 nm. The light intensity was 250 W/m².

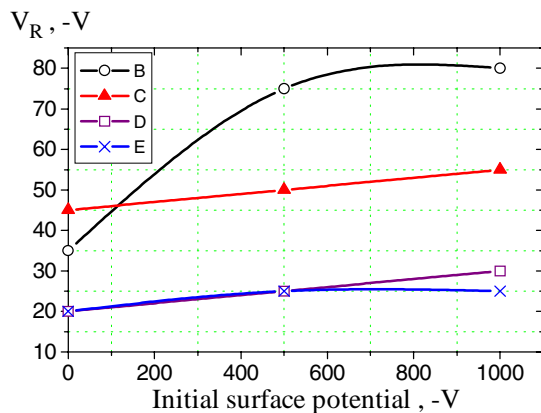


Fig. 9. Corona intensity (initial surface potential) dependence of residual potential V_R for Drum No 1. Dark-rested for 24 hours after 15000 cycles "charging-exposition" with different spectrum of light of halogen lamp ($T_c=2850$ K); B - without colour filters, C- with colour filters transparent at >440 nm, D - at >550 nm, E - at >700 nm. The light intensity was 250 W/m².

As follows from these data the essential rise of V_R after exposure of halogen lamp without filters (wavelength is longer 300 nm) and (to a lesser degree) with colour filter transparent at $\lambda > 440$ nm is observed.

Under effect of light with wavelength more than 550 or 700 nm (i. e., in the area of a spectrum, where the molecules of OPC have not absorption) essentially smaller influence of cycle "corona-exposition" on V_R and V_R/V_{R0} was observed.

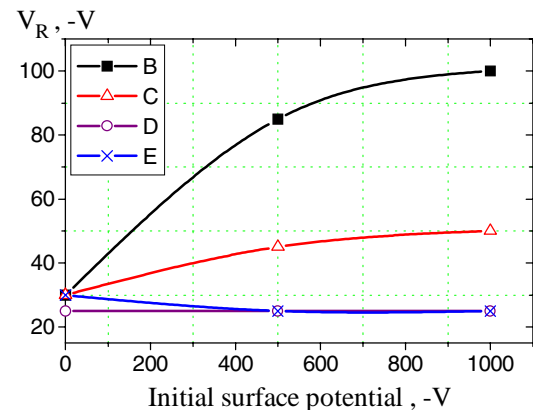


Fig. 11. Corona intensity (initial surface potential) dependence of residual potential V_R for Drum No 2. Dark-rested for 24 hours after 15000 cycles "charging-exposition" at different wavelengths of halogen lamp ($T_c=2850$ K); B - without colour filters, C- with colour filters transparent at >440 nm, D - at >550 nm, E - at >700 nm. The light intensity was 250 W/m².

It is necessary to take into account, that used TiOPc and bisazo dye absorb light in all this spectral region.

As this takes place, the values of sensitivity $S_{1/2}$ of these drums for light of halogen lamp without and with colour filters (wavelength is longer 300, 440, 550 and 700 nm) are close.

It means, that an amount of holes passed through the CTL by the action of halogen lamp with or without the colour filters in the cycle "charging - exposition" (and with constant intensity of light) is also practically equal.

Table 1. The effect of wavelength of exposure on the relative residual potential V_R / V_{R0} and relative dark decay DD_{10} / DD_{10}^0 immediately after 30000 cycles "charging-exposition" and after dark-rested for 48 hours for Drums No 1, 2, 5 (CGL= TiOPc+...). Exposition was: without colour filters (at $\lambda > 300$ nm), with colour filters transparent at > 440 nm; - at > 550 nm, - at > 700 nm. The light intensity was 250 W/m^2 .

λ , nm	OPC	V_R/V_{R0}		DD_{10}/DD_{10}^0	
		at once	after 48 h	at once	after 48 h
> 300	DEH	10,5	4,3	1,5	1,4
> 440	DEH	14,2	4,5	1,4	1,2
> 550	DEH	1,0	1,0	2,6	1,2
> 700	DEH	1,0	1,0	2,4	1,1
no light*	DEH	1,0	1,0	1,5	1,5
no corona**	DEH	1,0**	1,0	1,2	1,0
> 300	PTNA	7,4	4,6	1,4	1,3
> 440	PTNA	4,8	3,4	2,0	1,6
> 550	PTNA	1,0	0,9	2,0	1,7
> 700	PTNA	1,1	1,0	2,0	1,8
no light*	PTNA	1,0	1,0	1,4	1,0
no corona**	PTNA	1,0	1,0	1,2	0,9
> 300	TPD	0,6	0,3	3,6	1,7
> 440	TPD	0,3	0,3	2,4	1,1
> 550	TPD	0,7	0,3	3,3	1,1
> 700	TPD	1,2	0,5	3,1	1,6

* - in cycle "corona", ** - in cycle "light".

Taking into account these data, we can suppose, that greater (reversible and irreversible) change of values of V_R and V_R / V_{R0} and also DD and DD_{10}/DD_{100} for drums No 1-6 under the effect of light with wavelength more than 300 or 440 nm simultaneously with effect of a corona discharge are determined by absorption of light by molecules of OPC (Fig. 3).

These results are in good agreement with the fact, that the growth of values of V_R and V_R / V_{R0} for CTL on the base of DEH is more significant, than for CTL on the base of PTNA and TPD for all other equal conditions, that correlates with values of their integrated and spectral light absorption (Fig. 3).

It is possible to explain the observable facts by existence of chemical reactions of photoexcited monocation radicals $(B^+)^*$ of OPC, formed, for example, on the Eq. 2:



These photoexcited monocation radicals can have

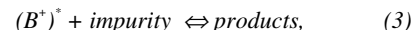
Table 2. The effect of wavelength of exposure on the relative residual potential V_R / V_{R0} and relative dark decay DD_{10} / DD_{10}^0 immediately after 5 000 cycles "charging-exposition" and after dark-rested for 48 hours for Drums No 3, 4, 6 (CGL= Bisazo dye+...). Exposition was: without colour filters (at $\lambda > 300$ nm), with colour filters transparent at > 440 nm; - at > 550 nm, - at > 700 nm, at > 1000 nm. The light intensity was 250 W/m^2 .

λ , nm	OPC	V_R/V_{R0}		DD_{10}/DD_{10}^0	
		at once	after 48 h	at once	after 48 h
> 300	DEH	20	3	1,3	1,1
> 440	DEH	13	2,5	1,5	1,1
> 550	DEH	7,5	0,5	1,5	1,1
> 700	DEH	3,5	0,5	1,3	0,9
> 1000	DEH	1,0	0,5	1,1	0,7
no light*	DEH	1,0	1,0	1,0	0,7
no corona**	DEH	1,0	1,0	1,5	0,9
> 300	PTNA	3	2	1,3	0,3
> 440	PTNA	2,4	1,4	1,3	0,3
> 550	PTNA	2	1,2	2,3	0,7
> 700	PTNA	2,5	1,5	1	0,7
> 1000	PTNA	3,6	1,3	0,25	0,3
No corona**	PTNA	1,0	1,0	0,8	0,5
> 300	TPD	1,5	1	2,2	2,3
> 440	TPD	1	1	1,8	1,6
> 550	TPD	1	1	1,6	1,4
> 700	TPD	1	1	1,2	1,2
> 1000	TPD	1	1	0,7	0,9

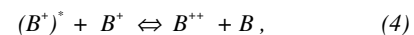
* - in cycle "corona", ** - in cycle "light".

irreversible or reversible interaction with the impurities, for example,

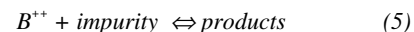
- on the reaction (Eq. 3):



- or generate bication radicals B^{++} , for example, on the reaction (Eq. 4):



which then can interact with impurities (Eq. 5):



and so on.

From the obtained experimental data we can suppose, that bication radicals and photoexcited monocation radicals have higher reactivity in reactions with impurities, than monocation radical B^+ (or their relaxation time greater, than for B^+).

Some differences in behavior of investigated OPC (greater or smaller changes of values of V_R or DD, etc.) are possibly explained by existence of various types and amounts of impurities in CTL (depending on ways of synthesis and a degree of purification of OPC), and also by influence of a chemical structure of the OPC.

As shown previously^{1, 5-7}, the adding into CTL of stabilizers - hindered phenols or electron acceptors allows to significantly improve the cyclic stability of drums.

The mechanism of a stabilization by such substances has not been determined with certainty and requires a further investigations.

However it is possible to suppose, that the molecules of stabilizers interact with impurities and reduce their reactivity and / or interact with cation radicals of OPC (B^+ , B^{++} , $(B^+)^*$) and facilitate their relaxation.

Conclusion

The investigation of light-, corona- and light + corona influence on electrophotographic characteristics of OPC drums with stabilized CGL and nonstabilized CTL demonstrates, that a simultaneous effect of light and corona on CTL promote a large reversible and irreversible fatigue of drums. . An active part of a spectrum, which is greatly absorbed by molecules of OPC, affects on the CTL especially efficiently.

It can be conditioned by photochemical reactions of cation radicals of OPC molecules, for example with impurities involved in CTL

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Biography

Konstantin K. Kochelev graduated in 1971 from Novosibirsk's State University (Chemistry). In1980 he received his Dr. chem. sci. degree in physical-chemistry of polymers (Tomsk's State University). Since 1980 he researched electrophotographic (EPG) materials at the Scientific Research Phototechnical Institute on Company Slavich ("NIFTI-Slavich", Pereslavl- Zalessky). His work has focused on Electrophotographic Drums and Toners and special polymer materials (EPG, PTP, heat mirror films and so on). He is a member of the IS&T. cca 150 patents and publications.

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