Development of Positive Charging Multi-Layered Organic Photoconductor for Liquid Electrophotographic Process

Nam-Jeong Lee, Hae-Ree Joo, Kyung-Yol Yon, and Young No
Digital Printing Division, Samsung Electronics Co., Ltd.
Suwon, Kyungki-Do, Korea

Abstract

The development of positive charging multi-layered OPC drum for liquid electrophotographic (LEP) process is presented in this study. This includes a) the investigation of optimum CGL solvents to coat CGL on CTL, b) the formula optimization of CTL and CGL to get high sensitivity and low discharge voltage, and c) OCL material development using aqueous dispersion of polyurethane to achieve the resistance against carrier liquid. Using the proprietary positive charging multi-layered OPC drum and liquid toner, excellent full color image could be obtained.

1. Introduction

Liquid electrophotographic (LEP) process for color printing has been developed due to its various advantages such as superior image quality and low TCO and so on. For LEP process, there has been a need for developing organic photoconductor (OPC) for liquid toner. Thin OPC for high charge capacitance is required to develop liquid toners having smaller particle size and higher charge on it, i.e. high Q/M. In addition, OPC should have resistance against carrier liquid, i.e. paraffin oil. In this study, it was investigated how to improve the performance of positive charging multi-layered OPC for liquid toner and the coating quality.

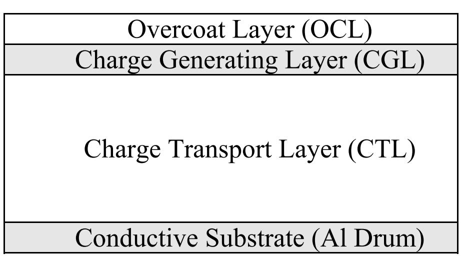

Figure 1. Schematic of positive charging multi-layered organic photoconductor.

Positive charging multi-layered OPC is composed of conductive substrate, charge transport layer (CTL), charge generating layer (CGL) and overcoat layer (OCL) as shown in Figure 1.

One of the main issues of this type of OPC is to coat CGL on the top of CTL with the formation of proper interface. Another is to develop OCL that can show excellent paraffin oil resistance, mechanical wear resistance and electrostatic characteristics.

2. Experimental

Polished aluminum drum was used as a conductive substrate. CTL coating solution was prepared by dissolving CTM (charge transport material) and binders (polycarbonate-Z, 95% + O-PET, 5%) in THF and filtering with syringe filter (1um). For CGL solution, titanyloxyphthalocyanine (TiOPc) and polyvinylbutyral was dissolved in ethanol (EtOH) and milled for 2hrs. The millbase was diluted with EtOH and butyl acetate (BuAc) and filtered with 5um syringe filter. As an OCL coating solution, aqueous dispersion of polyurethane (HepceChem Co., Korea) was diluted with water and isopropyl alcohol and treated with ultrasonic and filtered with 5um syringe filter.

A ring coater was used for OPC drum coating. Coating speed and drying temperature and time are shown in Table 1.

Table 1. Coating and drying condition

Layer	%solid	Speed (mm/min)	Drying temperature & Time (^oC & min)
CTL	23	300	100 & 10
CGL	4	250	110 & 15
OCL	5	200	120 & 20

Drum photoconductor evaluation apparatus (PDT2000, QEA) was utilized to measure electrostatic properties of OPC drum (charging voltage (Vo), discharge voltage (Vd, when 1uJ/cm^2 was exposed)). Repetitive electrophotographic (EP) cyclic property was evaluated with custom-made EP cyclic tester. Wear test by liquid toner and cleaning blade was done as described in Figure 2.

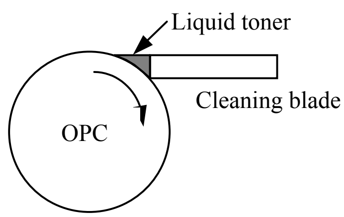

Figure 2. Schematic of wear tester.

3. Results and Discussion

CGL Coating

In order to get positive charging OPC, CGL should be coated on CTL (inverse structure to negative charging OPC). However, when a general CGL coating solution is used, it is frequently observed that CGL solvent dissolves precoated CTL during CGL coating. Or sometimes, poor interfacial contact between the two layers is also observed. Control of CGL co-solvent composition was tried to make it possible to coat CGL on CTL and to get good EP property simultaneously.

As a CTM, a dimer type of carbazole hydrazone derivative was used. It is known to have good paraffin oil resistance and is nominated as 'CTM1' in this study.

BuAc and EtOH were used as a co-solvent for CGL and relative amount of each solvent was varied. As can be seen in Table 2, when 100% of BuAc was used for CGL solution (Ex1), CTL was dissolved during coating and consequently it was not possible to coat CGL on CTL without deterioration. When the ratio of BuAc/EtOH was 7/3 (Ex2) or 5/5 (Ex3), CGL was coated with good coating quality and the discharge voltage was low. This might be due to the effective contact between TiOPc particles and CTM in a swollen state of CTL by the existence of BuAc. Whereas, when 100% of EtOH was used as a CGL solvent (Ex4), CGL was coated on CTL with good coating quality. However, its discharge voltage was much higher than those of the use of BuAc/EtOH co-solvent. It is because EtOH cannot dissolve or swell CTL materials, and consequently the close contact between CGM and CTM is not formed.

Table 2. EP characteristics of the OPC with varying the composition of CGL solvents

Exp. No.	Ex1	Ex2	Ex3	Ex4
BuAc/EtOH	10/0	7/3	5/5	0/10
Coating quality	CTL dissolution	Good	Good	Good
Vo (V)*	-	500	500	510
Vd (V)*	-	42	84	134

* : PDT2000(QEA) data

Optimization of CTL/CGL

CGL could be successfully coated on CTL using BuAc/EtOH co-solvent system. However, it is needed to reduce the amount of BuAc in CGL solvent. It is because the inclusion of relatively large amount of BuAc can still cause the contamination of CGL coating solution in large scale production, especially in dip coating case. Additionally, higher sensitivity of OPC becomes crucial as printing speed is increased. In an effort to achieve the above two goals simultaneously, the CTL composition and the ratio of each co-solvent were optimized.

One of enamine stilbene derivatives was selected as the second CTM (CTM2) in CTL composition. CTM2 is known that its hole mobility is higher compared to CTM1. In addition, CTM2 was slightly soluble in BuAc from our feasible dissolution test.

As shown in Table 3, those OPCs in which CTM2 is included in CTL as the case of Ex6 and Ex7 showed high charge voltage (Vo) and low discharge potential (Vd) in spite of low content of BuAc in CGL co-solvent (30%). It might be due to the slightly high solubility of CTM2 in BuAc. After CGL solution is coated on CTL, CTM2 is dissolved by BuAc at the interface and it takes its position at CGM's surface more effectively. Additionally, the higher hole mobility of CTM2 than CTM1 can contribute to the enhancement of sensitivity and consequent lowering of discharge potential.

Table 3. EP characteristic of the OPC with varying the composition of CTMs and CGL solvent

Exp. No.	Ex5	Ex6	Ex7	Ex8	Ex9	Ex10
CTM1/CTM2 (in CTL)*	10/0	5/5	7/3	0/10	0/10	10/0
BuAc/EtOH (in CGL)	3/7	3/7	3/7	3/7	7/3	7/3
Vo (V)	467	464	451	412	456	449
Vd (V)	96	69	78	37	55	81

* : [CTM1/CTM2]/[PCZ200]=50/50

When 100% of CTM2 is used as CTM and 70% of BuAc was used as CGL solvent (Ex9), the OPC showed the lowest Vd. However, in this case, CTL was severely dissolved by large amount of BuAc and resulted in uneven coated surface.

Conclusively, with proper selection of CTMs, we could get (+) charging multi-layered OPC with enhanced EP performance with the least damage on coating quality.

OCL Development

It is inherently very difficult for (+) charging multi-layered OPC to endure the repetitive electrophotographic cycling process. It is because CGL is very thin and weak from the low amount of binder resin. Therefore, OCL might be necessary to protect CGL. Especially when liquid toner is applied to this OPC, OCL should have another function like high abrasion resistance against the paraffin oil of liquid toner and cleaning blade.

In this study, polyurethane, particularly aqueous dispersion of polyurethane particles, was selected as an OCL material. As CGL is very thin and weak to general organic solvent, the use of organic solvent in OCL coating solution was excluded. Therefore, water was chosen for

OCL solvent. As a polyurethane aqueous dispersion, HWU1123A and HWU305A (solid concentration : 40%, water 55%, NMP 5%, HepceChem Co., Korea) were utilized. They are anionic polyurethane particles of which the size is a few tens nanometers. For comparison, Hybridur-580 (urethane acrylic hybrid dispersion, solid concentration : 10%, Air Products and Chemicals, USA) was also used.

Table 4. EP characteristic and wear resistance of the OPC with varying aqueous polyurethane dispersion and its concentration

Exp. No.	Ex11	Ex12	Ex13	Ex14	Ex15
OCL material	1123A 1.5%	1123A 3.0%	305A 1.5%	305A 3.0%	H-580 1.5%
Vo (V)	928 -> 923*	946 -> 952	922 -> 916	899 -> 916	911 -> 857
Vd (V)	56 -> 126*	99-> 142	80 -> 137	97 -> 130	91 -> 155
Scratch (Wear test)	A few	No	A few	No	Many

* : EP cyclic tester data (Charging->Exposure->Erasing) :
(the 1st cycle -> the 5000th cycle)

As can be seen in Table 4, when urethane acrylic hybrid dispersion was used as an OCL, a lot of scratches appeared on the surface of OPC and large drop of Vo and large increase of Vd were observed during 5000 EP cyclic test. Whereas, when the anionic polyurethane dispersion was coated on CGL as shown in Ex11 and Ex13, a small amount of scratches were observed but Vo was maintained or slightly increased and Vd ramp-up was not so high. Relatively thick coating of the polyurethane (Ex12 & Ex14) showed no scratches after 5000 cycle wear test and improved EP properties were realized.

Liquid Toner Developing Test

The (+) charging multi-layered OPC was tested by an apparatus of liquid toner developing system as schematically illustrated in Figure 3. Liquid toner was composed of pigment, organosol, charge director and a paraffin oil carrier (Norpar 12, Exxon) and was manufactured by using attritor-type mill.

After developing the liquid toner, the image was taped from OPC surface. Photographic micrograph of dot image is shown in Figure 4. It showed very sharp dot images.

Using prototype printing machine adopting the (+) charging multi-layered OPC and liquid toners, full color images could be produced. The image shows very good resolution and high optical density (Figure 5).

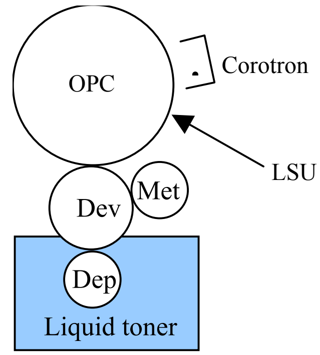

Figure 3. Schematic of liquid toner developing apparatus (Dev : developer roll, Dep : deposit roll, Met : Metering roll).

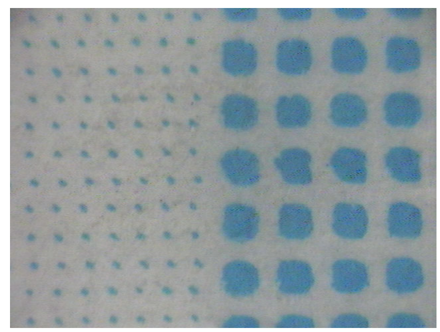

Figure 4. 1X1 and 4X4 dot images taped from OPC surface on which cyan liquid toner was developed.

Figure 5. Image sample.

4. Conclusion

We tried to make positive charging multi-layered organic photoconductor and the main conclusions are as follows:

1. Positive charging multi-layered OPC could be made successfully from CGL coating on CTL by adjusting CGL co-solvent composition.
2. With a proper selection of CTMs and CGL co-solvent composition, the electrophotographic properties of the OPC could be enhanced.
3. By applying aqueous polyurethane dispersion as an OCL, the OPC with high resistance to wear and liquid carrier could be obtained.
4. Using the positive charging multi-layered OPC and liquid toner, full color images with good optical density and high resolution were printed.

Acknowledgement

The authors would like to acknowledge the contributions of Samsung Electronics, Digital Printing Solution Laboratory (Woodbury, MN, USA) in supplying raw materials and manufacturing liquid toners for this study.

References

1. Y. Takahashi, Materials & Chemicals for Printer, pg. 121-134 (1995).
2. M. Croucher, et. al., Colloidal and Transport Properties of Electrostatically Based Liquid Developers, Photographic Sci. & Eng., 28 (3), pg. 119-124 (1984).
3. US patent 6,255,363, Liquid inks using a gel organosol (2001).
4. Tetsuo Murayama, Organic Photoconductors in Electrophotography, Japan Society of Electrophotography, 1987, pg. 3-13 (Japanese).
5. US patent 5,863,980, Preparation process of polyurethane prepolymer, preparation process of aqueous dispersion obtained therefrom, and use thereof (1999).

Biography

Nam-Jeong Lee received his B.S., M.S. and Ph.D. degree in Department of Chemical Technology from Seoul National University at Seoul in 1993, 1995 and 1999. Since 1999 he has worked in R&D team, Digital Printing Division at Samsung Electronics Co., Ltd. in Suwon, Korea. His work has focused on liquid toner imaging process including the materials for liquid toner and organic photoconductor since 2000.