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Absorption Spectra and Electrophotographic Properties of Squarylium Dyes Containing a Nitro Group

Seok Hwan Hwang,[a] Nok Kyung Kim,[a] Kwang Nak Koh[b] & Sung Hoon Kim[a]*

[a]Department of Dyeing and Finishing, College of Engineering, Kyungpook National University, Taegu, 702-701, Korea
[b]Sensor Technology Research Center, Kyungpook National University, Taegu, 702-701, Korea

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ABSTRACT

Squarylium dye containing a nitro group, absorbs at 676 nm in chloroform and showed a bathochromic shift of 22 nm in comparision to the unsubstituted analogue. The reaction between squaric acid and 2,3,3-trimethyl-5-nitro-indolenine proceeded readily giving a product in 97% yield. Electrophotographic characteristic of negatively charged dual-layered photoreceptors with squarylium dyes for charge generation materials and five charge transport materials have been investigated. Photoreceptors that used squarylium dyes containing a nitro group, exhibited high sensitivity under light exposure.

Keywords: electrophotographic, dark decay, photosensitivity, squarylium dye, organic photoreceptor

INTRODUCTION

Research and development of organic photoreceptors for electrophotography has undergone significant development during the past two

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*Corresponding author.

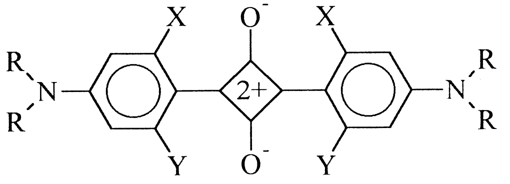
decades. Organic photoreceptors have many advantages compared to inorganic ones, and they can be readily manufactured at low cost.

The first organic photoreceptor used in a commercial application was based on the charge transfer complex formed between poly(N-vinylcarbazole) and 2,4,7-trinitro-9-fluorenone (PVK:TNF), which was applied in the IBM Copier I in 1970 [1]. The photoreceptor is a principal part of the electrophotographic system, and involves the use of materials that generate and transport the electrons or holes in response to absorbed photons. Current research activities are directed to both improving the characteristics of existing photoreceptors and developing new materials for future applications.

Recently, almost all the photoreceptors are of a layered structure. They exhibit high sensitivity and long copying life. This structure was introduced by Kalle in 1976. They have a thin charge generation layer (CGL) which is coated onto a substrate. The CGL consists of a pigment dispersed in the polymer, or by vapor deposition. The upper layer is an approximately 20 μm of charge transport layer(CTL), which is made from a molecularly doped polymer. Organic photoreceptors include azo dyes [2], phthalocyanines [3] and squarylium dyes [4].

Certain squarylium dyes are known to have photoconductive properties. They have been shown to be useful for electrophotographic applications [5], organic solar cell [6], and optical recording systems [7]. Squarylium dyes were initially used as sensitizers for ZnO photoconductors [8]. In the late 1970s, IBM developed dual layered photoreceptors utilizing dispersions of squarylium dyes as charge generating layers with charge transport layers based on both pyrazolines and hydrazones.

Some squarylium dyes containing N,N-dialkylaminobenzene such as SQ **9**, were often to exhibit low dark decay and high charge accepting properties in electrophotographic devices [9, 10].



SQ **9**

R = alkyl
X = H, OH, F
Y = H, OH, OR, alkyl

We have previously reported the synthesis [11] and electrochromic [12] properties of squarylium dyes containing an indoline moiety. Introduction of an electron accepting group, such as nitro, into the indoline moiety afforded considerable protection against photobleaching.

In this paper, we report the absorption spectra and an electrophotographic evaluation of some squarylium dyes containing a nitro group.

EXPERIMENTAL

Melting points were determined using an Electrothermal IA 900 apparatus and are uncorrected. Visible spectra were measured using a Shimadzu UV-2100 spectrophotometer. Elemental analysis were recored on a Carlo Elba Model 1106 analyzer.

Materials

SQ **2–3** were prepared by reacting squaric acid **3** with the indolenine derivative**1** in an azeotropic solvent. The procedures of preparation and characterization data of SQ **3–4** have been reported earlier [11]. SQ **9** was prepared according to a procedure published by Law and co-workers [13] and was purified by Soxhlet extraction with chloroform. All compounds used in this work where analytically pure. Compounds **4, 5, 6, 7** and bisphenol-A-polycarbonate(PC) were obtained from Toyo Ink Co. Compound **8** was prepared using previously described procedures [14]. Polyvinylbutyral(PVB) was a commercial sample from Sekisui Chem.

Synthesis of squarylium SQ 1,2

Squaric acid (0.68 g, 5.96 mmol) and 2,3,3-trimethylindolenine (1.9 g, 11.9 mmol) were heated under reflux for 3 h in a mixture of 6 ml of *n*-butanolbenzene (4:1/v:v) containing 3 ml of quinoline. Water was removed azeotropically using a Dean–Stark trap. The reaction mixture was cooled to room temperature. The precipitated crude product, SQ **1**, was separated by filteration and washed with *n*-hexane. SQ **2** was obtained from 2,3,3-trimethyl-5-nitroindolenine using a similar procedure. Structures were confirmed by the following:

SQ1
Yield: 55 %, M.P.: 270–272°C
Found: C; 78.45, H; 6.20, N; 7.09%
Calcd: C; 78.45, H; 6.10, N; 7.06%

SQ2
Yield: 97%, M.P.: > 300°C
Found: C; 64.19, H; 4.85, N; 10.93
Calcd: C; 64.19, H; 4.55, N; 11.51

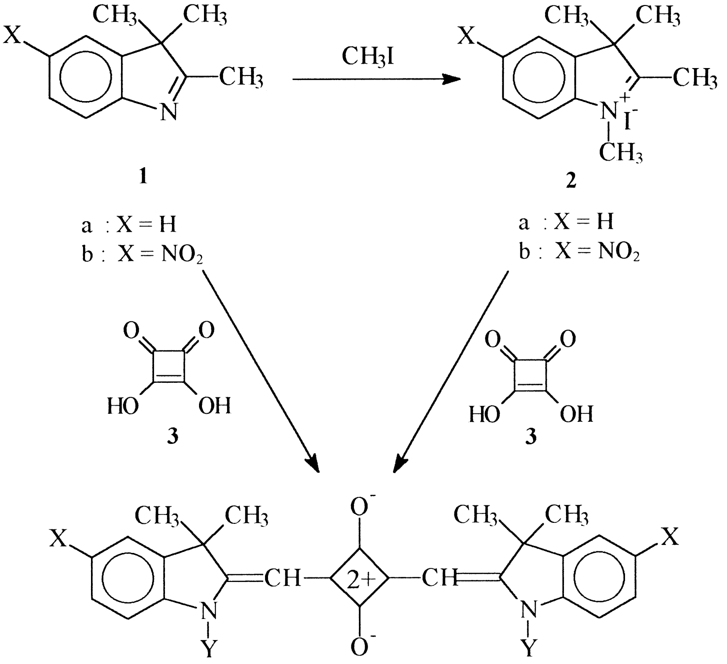
Preparation of evaporated film

The evaporated films for measurement of visible absorption spectra were prepared on plain glass. The evaporation was carried out at about 200°C under a vacuum of 10^{-6} Torr.

Device fabrication and electrophotographic measurement

The electrophotographic properties of the squarylium dyes synthesized were studied in negative charging dual-layered photoreceptor devices, a system currently utilised in commercial photoreceptors. Materials used for the charge generation layer (CGL) and the charge transport layer (CTL) are shown in Scheme 1 and Fig. 1, respectively.

The charge generation materials(CGM) used were the five squarylium dyes (SQ **1**–**4** and SQ **9**), and the charge transport materials (CTM) were



SQ **1** X = H, Y = H
SQ **2** X = NO_2, Y = H
SQ **3** X = H, Y = CH_3
SQ **4** X = NO_2, Y = CH_3

Scheme 1.

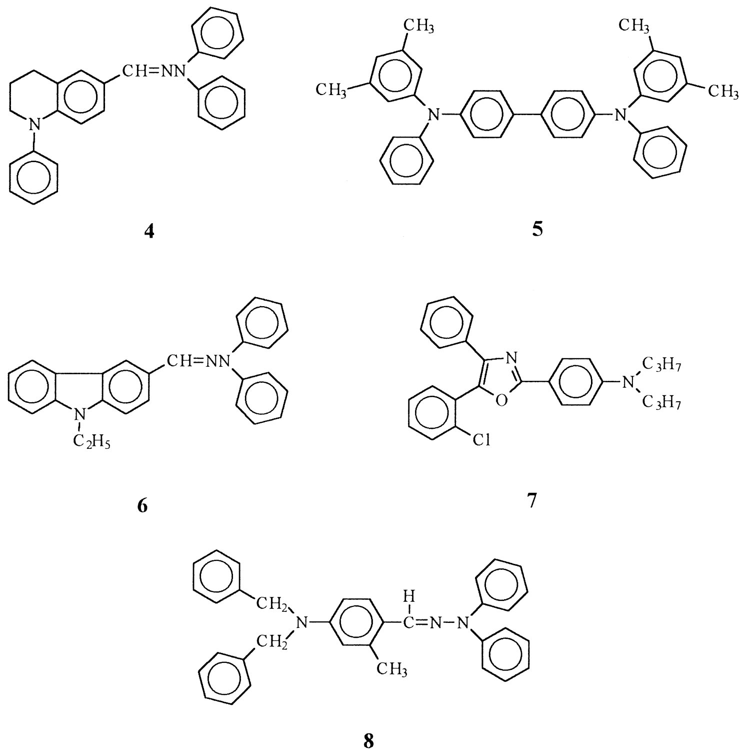


Fig. 1. Structure of charges transport materials.

1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline-6-carboxyaldehyde-1, 1'-diphenylhydrazone(**4**), N,N'diphenyl-N,N'-bis(3,5-dimethylphenyl)-(1,1-biphenyl)-4,4'-diamine(**5**), 9-ethylcarbazole-3-carbaldehyde diphenylhydrazone(**6**), 2-(*p*-dipropylaminophenyl)-4-(phenyl)-5-(*o*-chloro-phenyl)-1,3oxazole(**7**) and 4-dibenzylamino-2-methyl-benzaldehydediphenyl hydrazone(**8**).

Photoreceptors were coated by wire bar solvent coating on aluminized Mylar film. Each CGL was $\sim 0.5\,\mu m$ thick and 30 wt% of SQ dye in PC was used as a binder. CTLs were composed of 40 wt% CTM prepared by dissolution in each polymer binder and methylene chloride, and coated onto the CGL at thickness $\sim 30\,\mu m$. A schematic of the cross section of a dual-layered photoreceptor device is given Fig. 2.

The electrophotographic discharge measurements were carried out on a computer controlled flat-plate scanner. Samples were charged up negatively to about -600 V by a wire corotron device. The surface potential was measured by probe connected to a Trek electrometer (Model 3601). The characteristic of the photoreceptor was measured by the apparatus, shown in Fig. 3.

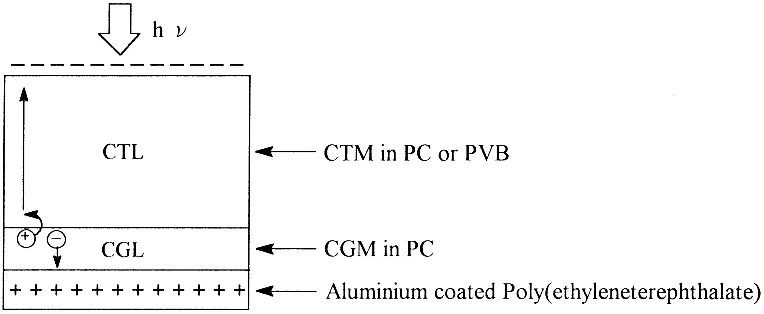


Fig. 2. Composition of dual-layer photoreceptor.

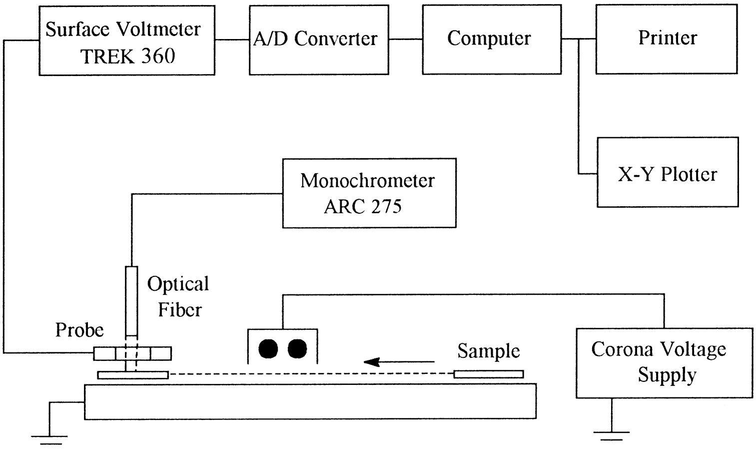


Fig. 3. Schematic diagram of apparatus for the photoinduced discharge curve.

RESULTS AND DISCUSSION

Some properties of squarylium dye

We have previously reported synthesis and photostability of SQ **3**,**4** and nitro substituted SQ **4** have superior photostability in solution and in polymer matrix. The general procedure to prepare squarylium dyes containing the indoline moiety is shown in Scheme 1. The effect of the nitro group on the absorption spectra of SQ **2** and SQ **4** compared with the parent SQ **1** and SQ **3** was evaluated by the $\Delta\lambda$ value. Introduction of the nitro group into the parent SQ **1** produced a 22 nm red shift (Table 1).

However, a large bathochromic shift of 32 nm in SQ **4** was obtained. It can be concluded that introduction of nitro groups into indolenine moiety of squarylium dyes produces a large bathochromic shift of the first transition.

TABLE 1
Data of SQ 1–4

Dye	*Yield (%)*	*ΔY (%)*	$L_{max}{}^{a}$*(nm)*	*Δλ (nm)*	ε^{a}*(x* 10^{-5}*)*
SQ 1	55	—	654	—	1.33
SQ 2	97	42^{b}	676	$+22^{d}$	1.45
SQ 3^{f}	61	—	633	—	3.21
SQ 4^{f}	92	31^{c}	665	$+32^{e}$	3.04

[a] Measured in $CHCl_3$.
[b] $\Delta Y = Yield_2 - Yield_1$.
[c] $\Delta Y = Yield_4 - Yield_3$.
[d] $\Delta\lambda = \lambda_{max2} - \lambda_{max1}$.
[e] $\Delta\lambda = \lambda_{max4} - \lambda_{max3}$.
[f] see ref. 11.

SQ **2** was synthesized by the reaction of squaric acid **3** with 2,3,3-trimethyl-5-nitroindolenine **lb** in 90% yield. Thus, compound **lb** was much more reactive than **la**.It is known that the λ_{max} value is shifted longer wavelength in the solid state compared with those in solution because of the strong molecular interaction of dye molecules in the solid state. In the solid state, the absorption spectra of SQ **3** and **4** exhibited a broad absorption covering the wavelength from 500 to 700 nm (Fig. 4).

Electrophotographic properties of squarylium dyes

The effect of charge generation layer fabrication variables on the electrophotographic sensitometry of a dual-layer photoreceptor prepared with bis(4-dialkylaminophenyl) squarylium dye, SQ **9**, have been extensively investigated [15]. The data showed that the dark decay value varied from 10

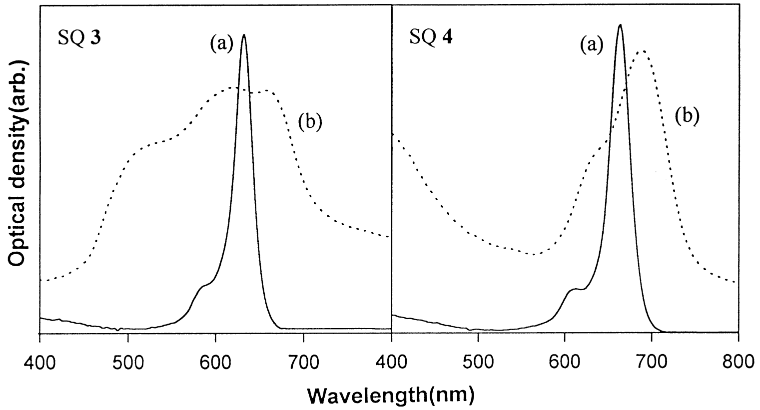


Fig. 4. Absorption spectra of SQ 3 and SQ 4 (a) in $CHCl_3$, (b) in solid film.

to 115 v/s. Structural variation of squarylium dyes has a large effect on the photosensitivity. $E_{1/2}$ values, which is the energy required to produce 50% discharge from the initial potential before light irradiation; radius ranging from 2.9 to > 1000 ergs/cm^2 are reported.

Commercial copying and duplicating machines are based on the principles of electrophotography in which latent electrostatic images produced in a photoconductive film are developed by charged pigment particles to produce real images [16]. The latent image formation involves the corona charging of a photoconductor, followed by its imagewise exposure. The photoconductor discharges in regions exposed to light, with the magnitude of the discharge depending on the light reflected from the document. The property of the photoconductor film that controls the tone reproduction curve is called the Photo-Induced Discharge Characteristics (or the PIDC) [17]. The PIDC is the relationship between the broad area surface potential of the photoconductor and the exposure.

Photoinduced discharge curves(PIDC) were measured in terms of surface potential vs time. V_o is the initial dark potential before white light irradiation. The photosensitivity of the device is expressed as $E_{1/2}$, the energy required to photodischarge half of the initial potential V_i. *DD* is the average potential of dark decay (Fig. 5).

Photoinduced discharge curves(PIDCs) of dual layered photoreceptors using the four squarylium dyes containing an indoline moiety as CGM and five CTMs are summarized in Tables 2 and 3. In order to examine the electrophotographic effect of SQ **1–4**, we chose the SQ **9** as our reference CGM. The photoreceptors using SQ **2** and SQ **4** exhibited low dark decay and good white light sensitivity. SQ **1** and SQ **3** used for CGM did not exhibited

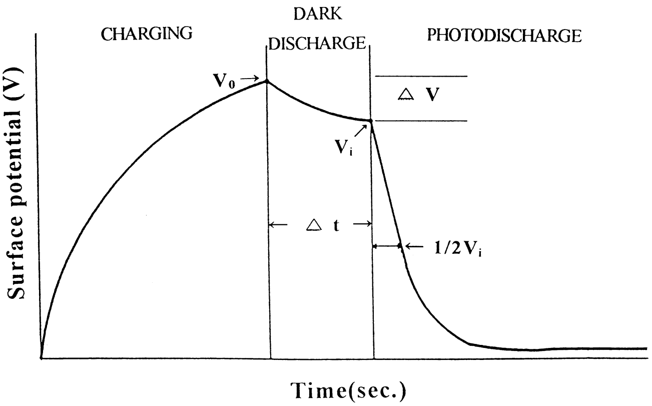


Fig. 5. Charging and photoinduced discharging characteristics of electrophotographic photoconductor.

TABLE 2
Electrical Properties of PC(CTL)/PC(CGL) Photoreceptors

		Electrophotographic data			
CGM	*CTM*	*Initial potential* $V_0(-V)$	*Exposure potential* $V_i(-V)$	*Dark decay* $DD(V/s)$	*Half exposure* $E_{1/2}(ergs/cm^2)$
SQ 1	**4**	565	535	15.2	416.8
	5	734	593	70.4	688.4
	6	656	591	32.4	635.2
	7	491	395	48	424
	8	735	663	35.9	Insensitive[a]
SQ 2	**4**	870	692	88.6	38
	5	576	473	51.9	9.2
	6	754	715	19.3	73.2
	7	458	400	28.8	15.2
	8	522	438	42.3	17.6
SQ 3	**4**	942	910	15.9	Insensitive[a]
	5	862	780	31.25	400
	6	799	778	10.5	Insensitive[a]
	7	696	626	34.9	Insensitive[a]
	8	551	532	9.6	Insensitive[a]
SQ 4	**4**	535	505	14.9	17.6
	5	603	480	61.3	14
	6	741	685	28.1	7.8
	7	510	461	24.7	10.2
	8	810	698	56.2	40.8
SQ 9[b]	**4**	637	610	8.5	59.6
	5	684	648	18	8
	6	679	594	42.5	20.8
	7	597	548	24.4	19.2
	8	602	538	32	9

[a] Insensitive defined as $E_{1/2} > 1000$ ergs/cm^2
[b] SQ **9**: $R = CH_3$, $X = H$, $Y = OH$.

electrophotographic properties. Introduction of a nitro group into the indoline moiety of squarylium dye decreases largely their solubility in organic solvents. SQ **1** and SQ **3** have a high solubility in organic solvents, tend to dissolve in the CGL-CTL interface, and causes a fabrication problem in dual-layered devices. Highly soluble SQ dyes, SQ **1** and SQ **3**, might have diffused or dissolved into the CTL during CTL coating process. Due to the poor solubility of SQ **2** and SQ **4**, the photoreceptors using SQ **2** and SQ **4** exhibit higher photosensitivity.

Polymers are key components of organic photoreceptors. They have been used as binder materials for both CTM and CGM. In this work, two kinds of polymer, such as PC and PVB have been used as binder materials. Table 2 and Table 3 summarize the results of the effect of polymer binder on the electrophotographic properties of dual-layered photoreceptor devices using

TABLE 3
Electrical Properties of PVB(CTL)/PC(CGL)) Photoreceptors

		Electrophotographic data			
CGM	*CTM*	*Initial potential* $V_0(-V)$	*Exposure potential* $V_i(-V)$	*Dark decay* $DD(V/s)$	*Half exposure* $E_{1/2}(ergs/cm^2)$
SQ 1	**4**	561	533	14.3	611.6
	5	904	863	20.3	Insensitive[a]
	6	668	587	40.7	Insensitive[a]
	7	469	391	39.2	508
	8	605	516	44.8	Insensitive[a]
SQ 2	**4**	609	568	19	264.4
	5	740	696	22.2	446.8
	6	822	677	72.6	153.2
	7	645	498	73.3	338.4
	8	748	649	49.5	144.4
SQ 3	**4**	572	549	11.3	538.8
	5	788	778	5.2	Insensitive[a]
	6	692	666	13	Insensitive[a]
	7	535	491	22	417.2
	8	860	765	47.9	Insensitive[a]
SQ 4	**4**	609	537	36.2	39
	5	853	824	14.4	279.2
	6	627	538	44.2	120.8
	7	614	426	94.3	82.8
	8	611	544	33.2	61.6
SQ 9[b]	**4**	627	566	30.6	12
	5	651	579	35.9	410.8
	6	348	250	49	311
	7	426	231	97.5	44.8
	8	605	448	78.4	9.6

[a] Insensitive defind as $E_{1/2} > 1000$ ergs/cm^2.
[b] SQ 9: $R = CH_3$, $X = H$, $Y = OH$.

squarylium dyes. Two kinds of photoreceptor devices, PC(CTL)/PC(CGL) and PVB(CTL)/PC(CGL), have been studied (Tables 2 and 3 respectively).

The dark decay and half exposure increased greatly when PVB is used for polymer binder of CTM; SQ **2** and SQ **4** where found to exhibit high dark decay and low photosensitivity in PVB(CTL)/PC(CGL) photoreceptors. However, an excellent sensitivity of 9.2 erg/cm^2 for SQ **2** and of 7.8 erg/cm^2 SQ **4** was obtained in PC(CTL)/PC(CGL). Although the SQ **1** and SQ **3** photoreceptors using PVB(CTL)/PC(CGL) exhibit electrophotographic properties of lower sensitivity and high dark decay, the nitro group introduced into squaryllum dyes, i.e. SQ **2** and SQ **4**, was also effective. Our results suggest that PC(CTL)/PC(CGL) devices are more efficient than PVB(CTL)/PC(CGL) Photoreceptors using squaryllum dyes containing a nitro group in PC(CTL)/PC(CGL) exhibit low dark decay, good white-light sensitivity, and low residual potential.

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REFERENCES

1. Gill, W. D., *Journal Applied Physics*,1972, **43**, 5033.
2. Arishima, K., Hiratsuka, H., Tate, A. and Okada, T., *Applied Physics Letter*, 1982, **40**, 280.
3. Arora, S. and Murphy, W., *SPSE Annual Meeting*, Rochester, April (1982).
4. Loutfy, R. O., Hsiao, C. K. and Kazmaier, P. M., *Photographic Science Engineering*, 1983, **27**, 5.
5. Champ, R. B. and Shattuck, M. D., USP 3824099 (1974).
6. Merritt, V. Y. and Hovel, H. J., *Applied Physics Letter*, 1976, **29**, 414,
7. Jipson, V. B. and Jones, C. R., *Journal of Vacuum Science Technology*, 1981, **18**, 105.
8. Kampfer, H., USP 3617270 (1971).
9. Chang, M. S. H. and Edelman, P. G., USP 4353971 (1982).
10. Chang, M. S. H. and Bergman, M. E., USP 4391888 (1983).
11. Kim, S. H. and Hwang, S. H, *Dyes and Pigments*, 1997, **35**, 111.
12. Kim, S. H. and Hwang, S. H., *Dyes and Pigments*, 1998, **36**, 139.
13. Law, K. Y. and Bailey, F. C., *Journal of Imaging Science*, 1987, **31**, 172.
14. Jin, E. and Kirn, Y. S., *Journal of Korean Society for Imaging Science*, 1996, **2**, 44.
15. Law, K. Y., *Journal of Physical Chemistry*, 1987, **91**, 5184.
16. Carlson, C., *Xerography and Related Process*, Focal Press, London, 1965, pp. 1–41.
17. Scharfe, M. E. and Schmidlin, F. W., *Advances in Electronic and Electron Physics*, Academic Press Inc., New York, 1975, pp. 83–144.