Organic photoconductive materials*

Rafik O. Loutfy, Ah-Mee Hor, Cheng-Kuo Hsiao, Giuseppa Baranyi and Peter Kazmaier

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, CANADA

Abstract - A brief survey of the fabrication, evaluation and uses of organic photoconductive materials as xerographic photoreceptors is given. Included is a discussion of the basic material design roles required for successful operation of photoreceptor devices. The review includes present organic material classes used in commercial copiers/printers and future potential of organic photoreceptors based on phthalocyanines and squaraines.

INTRODUCTION

The Xerographic process, invented by Chester Carlson in the 1930's, has played a major role in revolutionizing the way in which information is processed and disseminated (ref.1). The technology derived from this invention provided a cheap, simple and reliable way of reproducing and more recently creating original documents. Xerox first introduced this process to the world with its 914 xerographic copiers in 1959. Since then, xerography has truly revolutionized office procedures by eliminating the need for carbon paper and making available quickly and conveniently high quality copies of documents. A second major technological breakthrough by Xerox was the introduction, in 1977 of a two page per second non-impact laser printer. The electronic printing process that uses a computer controlled laser beam to create images on a photoreceptor which then are xerographically transferred directly to paper, is now known as "Lasography". Lasography, like xerography, has brought about an amazing range of benefits in creating, processing and transmitting efficiently large body of information.

An enabling part of these technologies is the "photoreceptor" which by the combined use of photoconductivity and electrostatics captures information optically projected onto it. Photoconductivity is the conversion of electromagnetic radiation into electrical current. This radiation usually consists of ultraviolet, visible and/or infrared light. Materials responding to this type of radiation are termed photoconductors. Thus, photoconductors are materials which conduct electricity when illuminated by light of specific wavelengths but act as electrical insulators when kept in the dark. The photoconductors can be fabricated into drum, sheet or flexible belt photoreceptor devices for use in office copiers and laser printers. Acceptable performance of xerographic photoreceptor requires materials of unusual properties: The material must be a good insulator in the dark, highly conductive in the light, mechanically stable and should be easily manufactured into photoreceptors. Until recently, inorganic materials such as selenium, selenium alloys, zinc oxide and cadmium sulfide have been widely used as photoreceptors. In recent years those materials are being rapidly replaced by organic photoreceptors. The major advantages of organic photoreceptors are non-toxicity (i.e. disposable), low cost, ease of manufacturing, flexibility (in sheet and belt form), panchromaticity and high photosensitivity. Performance stability of organic photoreceptors has been improving significantly in recent years.

This paper is composed of a brief review of the xerographic process, the development of organic photoreceptors, fabrication and evaluation of xerographic organic photoreceptor and a description of the basic materials parameters that are necessary to develop acceptable photoreceptors. Following this a comparative description will be given of different classes of organic photoconductive materials that are of potential application as future photoreceptor in diode laser printers.

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THE XEROGRAPHIC PROCESS

Figure 1 outlines the basic steps in the xerographic process:

i) The free surface of the photoconductive layer (typically tens of microns thick) deposited onto a conductive substrate is charged to an initial potential, $V_0$, of several hundred volts. This is done by depositing ions from a charging device, utilizing air breakdown, known as a corotron. The dark resistivity of the photoconductor must be sufficiently high i.e. the materials should be reasonably insulating in the dark to give sufficient charge acceptance at reasonable charging current and charge retention through a low dark decay. ii) The charged device is then exposed to reflected light from the document to be copied. Where light strikes the photoreceptor, photocarriers are created proportional to the light flux striking a particular region, and their subsequent transport across the film produces a reduction in the initial surface potential. A latent electrostatic image of the unexposed (dark) areas thus replicates the information on the document. iii) This latent image is rendered visible by use of a triboelectrically charged toner consisting of small polymer particles ~10 microns, impregnated with carbon black and is charged with opposite polarity to the photoconductor. The toner particles are attracted to the still charged dark areas of the photoreceptor. iv) Next the toner image is transferred to a sheet of paper and finally, v) The transferred image is made permanent or fixed by thermal fusing.

![Figure 1. Basic Steps in Xerographic Process](image)

The discussion will now focus on the development of organic photoreceptors, their electrical and photoelectronic properties that play a determining role in the photodischarge characteristics.

DEVELOPMENT OF ORGANIC PHOTORECEPTOR

It has long been known that anthracene and other polyaromatic hydrocarbon display photoconductive properties, however, application in practical photoreceptor was not possible because of their low photosensitivity and limited spectral response to the ultra-violet. The first commercial-organic photoreceptor used in laser printer was introduced by IBM which was a single layer photoreceptor (see figure 2a) based on polyvinyl carbazole (PVK) and trinitrofluorenone (TNF) charge transfer complex system. However, the photoconductivity of this photoreceptor is about one-third that of amorphous selenium. To improve the quality of organic photoreceptor a multilayer structure was developed. Most of these multilayer photoreceptors have a double-layer structure made of a thin charge generation layer (CGL) in continuous contact with a much thicker charge transport layer (CTL), as shown in Figure 2b. The function of the charge transport layer is to transport the charge photogenerated in and injected from the charge generation layer. The charge generation layers in the majority of commercial organic photoreceptors consists of a dispersion of the photoconductive organic pigment in an electrically inert polymer matrix and are known as binder-generator layer (BGL). By adopting the structure of Figure 2b. to organic photoreceptors, photosensitivity has been raised over ten times more than the PVK/TNF photoreceptors. Many companies including Xerox Kalle, IBM, Kodak, Ricoh, Sharp, Canon, Hitachi, Mitsubishi and others have introduced double-layer organic photoreceptors for use in copiers and laser printers. Currently organic photoreceptors represent about 40% of the world market for photoreceptors.
In Table 1, some examples are shown of organic photoconductive materials developed primarily for copiers. The charge generation material in these examples is designed to absorb light in the visible region of the spectrum. Many of the charge transport materials are compounds containing tertiary amines, which are designed with low ionization potential to allow hole injection and transport. All these organic photoreceptors show high photosensitivity in the visible light range 400-700 nm and moderate life stability 2-10 Kilo copies.

The emergence of semiconductor diode-laser print head operating in the near infrared (750-850 nm) has dictated the need for new photoreceptor materials with long wavelength sensitivity. The search for new near infrared sensitive photoreceptor materials has been the most actively researched area in the field of electrophotography in the past six years. The reason for this activity is the extremely challenging set of properties that the photoreceptor must exhibit. As mentioned previously, the new photoreceptors must sustain high voltages in the dark and discharge rapidly upon exposure to the diode-laser wavelength 750-850 nm, have high charge mobility and satisfactory electrical properties such as low dark decay and minimal fatigue. It should be durable, non-toxic, and readily manufactured in high yield. Organic photoconductors meet many of these requirements. As a result, great variety of infrared sensitive organic photoreceptors have been developed. Examples are the Ricoh azo-based charge generation materials (ref.2), the IBM (ref.3), Xerox (ref.4) and Pitney Bowes (ref.5) work on squaraine dyes, Kodak trimethine-chiopyrylium dyes (ref.6), NTT chloroaluminum phthalocyanine...
chloride generator (ref. 7), Oki (ref.8) and Kodak (ref.9) chloro indium phthalocyanine chloride, Hitachi's τ-metal free phthalocyanine (ref.10), Xerox (ref.11) Vanadyl phthalocyanine based photoreceptors. In Table 2 some examples are shown of organic photoconductive materials developed primarily for diode-laser printers. In our laboratory, our work has focused on xerographic evaluation of two classes of IR-sensitive charge generator materials: squaraines and phthalocyanines. The results of our investigation will be reported below.

**EXPERIMENTAL DETAILS**

**Materials:** A series of fifteen squaraine pigments (see Table 3) were prepared by reacting the aromatic amine with squaric acid as described in ref. 12. The phthalocyanines were either purchased from Eastman Chemicals or in-house synthesized by reacting the metal chloride with phthalonitrile in α-chloro-naphthalene. All phthalocyanines were purified by the train sublimation procedure (ref. 13). All other materials were commercially available and were used without further purification.

**TABLE 3. Chemical Structure of the Organic Photoconductors Studied**

<table>
<thead>
<tr>
<th>PHTHALOCYANINES</th>
<th>SQUARAINES</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = Mg, Zn</td>
<td></td>
</tr>
<tr>
<td>ClI, ClZn, ClGa</td>
<td></td>
</tr>
<tr>
<td>ClI Ge, ClI Si, VO</td>
<td></td>
</tr>
</tbody>
</table>

Photoreceptor design and fabrication: The photoreceptor device configuration used to evaluate the squaraines and phthalocyanine pigments was a dual layer structure as shown in figure 2b. The substrate was 3 mil aluminized Mylar (Dupont), overcoated with a thin (0.1 μm) silane charge blocking layer prepared from the monomer, N-methyl-3-aminopropyltri-methoxysilane (ref.14). The generator layer consisted of 30% by weight photoconductive pigment dispersed in Vital PE-200 polyester (Good-year) resin. The charge transport layer was a solid solution of N,N'-diphenyl-N,N'-bis(3-methyl phenyl)-[1,1'-bisphenyl]-4,4'-diamine (TPD) in Makrolon polycarbonate (1:1 weight) (see ref.15).

The pigment dispersion was carried out in a roll mill in a small amber glass bottle with added solvent, polymer, and 1/8-in. steel shot. The polyester was dissolved in methylene chloride and then the pigment was added and ball milled for 1.5 hr. Uniform films of binder generator layers were coated using the draw-down film application technique. The dry binder generator film thicknesses were typically one micron.

The TPD/Makrolon polycarbonate hole transport layer was coated from a 10-ml methylene chloride solution of 0.66 g of TPD and 0.66 g of Makrolon. The transport layer was coated using a modified Gardner mechanical drive film coating apparatus with a multiple clearance film applicator. The sample was dried in a vacuum oven at a temperature of about 270 for 24 hours to produce an approximately 30 ± 1 μm thick hole transport film.

**Xerographic Measurements:** The xerographic discharge measurements were carried out using a computer controlled xerographic cycling system. The samples were mounted onto the flat-plate scanner. A corotron wire was used for charging the samples. The surface potential was measured using a wire loop connected to a Keithley 616 electrometer. Light from 75W Xenon lamp was passed through a colored band pass filters and neutral density filters to obtain monochromatic light between 400 and 900 nm. Light exposure and erasure energies were measured using a Karl Lambrecht dc 1010 light meter. This light meter is equipped with a PLL light probe which has a near-flat irradiance response from 400 to 1000 nm.

**a. Single Discharge Measurements:** The single discharge experiments produced a single photoinduced discharge curve portraying surface potential versus time. The experiment was run so that there was a 0.5-sec dark decay period, a brief flash-type exposure (20 msec), a 1.0-sec discharge period, a 0.75-sec erasure period, and a final 0.25-sec after-erase rest period.
Organic photoconductive materials

A single photoinduced discharge curve (PIDC) for a dual layer photoreceptor device is shown in Figure 3. Where Vo is the initial dark potential, VDDP is the dark development potential, Vbk is background potential at 0.25 and 1.0 sec after exposure, Vr is the residual potential after erase, and dv/dt is the dark decay in V/sec. A caption is printed giving the important xerographic parameters calculated from the experimental data using the HP-85 microcomputer.

b. Surface Potential versus Exposure (SPE) Measurements: The surface potential versus exposure (SPE) curves are obtained by performing a number of photoinduced discharge experiments at varying exposures. From these PIDC’s, surface potentials at given times after exposure are plotted against exposure energy. A typical SPE curve for photoreceptor device is shown in Fig. 4. The three surface potentials (V1, V2, and V3) versus exposure curves were obtained at time (t) equal to 0.25, 0.75 and 1.5 sec after exposure, respectively. Surface potential versus exposure measurements are important for showing the behavior of the photoreceptor toward exposure energy and for providing the information from which the "Contrast Potential vs. Exposure" curve is obtained.

c. Spectral Sensitivity Measurements: The spectral sensitivity of the dual-layer photoreceptors was measured by determining the exposure required to reduce the surface potential (from -830 V) to (-415V) i.e. E+ at different wavelengths from 400 to 900 nm. Figure 5 shows the spectral sensitivity of a typical IR-sensitive photoreceptors from 400 to 900 nm.

d. Xerographic Cyclic Stability Measurements: The samples were preconditioned by precycled (charge/discharge) one hundred times, then xerographically cycled 1000 times. In each cycle, five surface potentials were measured, the initial potential (Vo), the potential just before exposure (VDDP), the potential 1.0 sec and 1.75 sec after exposure, and the potential after erase (Vr). These data as a function of cycles were automatically monitored and recorded by the HP-85 microcomputer. Figure 6 show a "cyclic" plot of a dual layer photoreceptor exposed to 830 nm light.
RESULTS AND DISCUSSION

The immediate objective of our work was to produce IR-sensitive photoreceptors which incorporate a dispersion of microcrystalline particles of squaraines and phthalocyanines pigments, using simple and economical synthetic and fabrication procedures. For comparison purposes, all the squaraines and phthalocyanines photoreceptor devices were fabricated under similar conditions. It should be noted, however, that the results are for comparison purpose only and do not reflect the optimum performance of any of these materials. Extensive optimization studies were carried-out for few promising materials such as fluoro/methyl squaraine and chloroindium phthalocyanine (ref. 12 and 16).

SQUARAINES

Table 4 summarises the xerographic performance of squaraine photoreceptors. Of the fifteen bis(4-dialkylamino phenyl) squaraine pigments investigated, all were found to have some IR-sensitivity in dual-layer photoreceptor structure, except the methoxy squaraine (CH3OSQ) which was not photoactive at all and the dihydroxy squaraine (diOHSQ) which was only photoactive to visible light. In general the bis(4-dimethylamino phenyl) squaraine pigments were more photoactive than the Julolidine, diethylamino or dibutylamino analogous. The major reason for this difference relates to the increase in pigment solubility which detrimentally affects the photosensitivity and increases residual potential. The dibutylamino phenyl squaraines are more soluble in the polymer matrix forming molecular solid-solution (spectroscopically observable) leading to desensitization and trapping of charge carrier. It is therefore important to minimize pigment solubilization in the evaluation of novel photogenerators materials. Of the photoactive squaraines examined, four were highly IR-photosensitive (EI @ 830 nm, < 5 ergs/cm²). These were the hydroxy squaraine (HOSQ); fluoro squaraine (FSQ); squaraine (HSQ); and fluoro/methyl squaraine (F/MeSQ). Two squaraine pigments showed intermediate IR-photosensitivity (EI < 15 ergs/cm²) these are methyl squaraine (MsSQ) and hydroxy methyl squaraine (HO/MeSQ). The remaining seven squaraines exhibited low photosensitivity (EI > 30 ergs/cm²). The material with highest photosensitivity, lowest dark decay and good cyclic stability is the hydroxy squaraine pigment (HOSQ) which is currently being used by IBM in their 3820 photoreceptor. Although, FSQ and HSQ are equally photosensitive to HOSQ photoreceptors incorporating these pigments exhibit higher dark decay and are less stable in cyclic tests. The squaraine pigment F/MeSQ is quite interesting since it combines the high photosensitivity of FSQ and the low dark decay of MsSQ.

The photosensitivity and dark decay of organic photoreceptors depend not only on the type of organic photoconductor pigment used but also on the loading of the photoconductive pigment; the thickness of the charge generator layer (CGL) and the thickness of the charge transport layer (CTL). Figure 7 shows the dependence of photosensitivity, dark decay and residual potential on charge generator layer (CGL) and charge transport layer (CTL) thickness for some squaraine pigments. At a given pigment loading, both the photosensitivity and the dark decay increases with increased CGL thickness. A point is reached beyond which further increase in CGL thickness has little effect on photosensitivity, however, dark decay keeps on increasing.

### Table 4. Xerographic Data for negatively Charged Dual-Layer Photoreceptors Incorporating Squaraines as Photogenerator

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>R</th>
<th>E dark decay (V/Sec)</th>
<th>E_i</th>
<th>E_opt</th>
<th>% discharge @ 10 ergs/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>H</td>
<td>CH₃</td>
<td>35</td>
<td>3.0</td>
<td>10</td>
<td>79</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>42</td>
<td>3.5</td>
<td>10</td>
<td>79</td>
</tr>
<tr>
<td>F</td>
<td>H</td>
<td></td>
<td>70</td>
<td>3.5</td>
<td>10</td>
<td>68</td>
</tr>
<tr>
<td>F</td>
<td>CH₃</td>
<td></td>
<td>35</td>
<td>5.5</td>
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<td>50</td>
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<tr>
<td>H</td>
<td>CH₃</td>
<td></td>
<td>20</td>
<td>13.0</td>
<td>40</td>
<td>38</td>
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<tr>
<td>H</td>
<td>SCH₃</td>
<td></td>
<td>40</td>
<td>33</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>HO</td>
<td>HO</td>
<td></td>
<td>Not IR-Sensitive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>OCH₃</td>
<td></td>
<td>Not photosensitive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO</td>
<td>H</td>
<td>Et</td>
<td>&gt;50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>Bu</td>
<td>&gt;100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO</td>
<td>CH₃</td>
<td></td>
<td>&gt;100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO</td>
<td>HO</td>
<td>Jl</td>
<td>&gt;100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO</td>
<td>H</td>
<td>15</td>
<td>50</td>
<td>130</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>HO</td>
<td>HO</td>
<td>20</td>
<td>52</td>
<td>135</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

a. V_DPP = -830 volts.  b. Exposure 830 nm

c. E_i exposure required to reduce surface potential from -830 V to -415 V.

d. E_opt optimum exposure required to achieve maximum contrast potential.

e. CGL: 1 micron of 30wt.% pigment dispersed in PE-200 polyester.

CTL consists of 50 wt.% TPD in PC(A) of thickness of 30 microns.
The optimum CGL thickness should correspond to this critical thickness at which the maximum photosensitivity is attained at the lowest dark decay. Increasing the CTL thickness results in a decrease of dark decay (for constant voltage charge) and slight increase of both sensitivity and residual potential. At a given CGL and CTL thicknesses the photosensitivity and dark decay increases with increased photoconductive pigment loading in the CGL. In some cases, charge acceptance also decreases with the increase in pigment loading placing a limit on the usable contrast potential. Optimization of photoreceptor, performance for any given photoconductor involves a matrix of a large number of experiments in an attempt to find the optimum CGL, CTL thickness, pigment loading, best polymer binder, coating solvent, blocking layer, adhesive, ground plan, coating technique, pigment particle size and morphology, dispersion quality, additives and purification techniques. All these variables affect greatly the key photoreceptor attributes: charge acceptance, dark decay, photosensitivity, print quality, cyclic stability, residual potential and yield. Optimization of the performance of a photoconductor incorporating F/MeSQ pigment was carried out in our laboratory; some of the results will be given. Figure 5 shows the spectral response of a dual layer photoreceptor incorporating the F/MeSQ pigment. The spectral response of such a device is flat between 500-900 nm spectral region. Photoreceptors incorporating the F/MeSQ pigment exhibit low dark decay and high IR (830 nm) and white light (400-700 nm) photosensitivity. Typical dark decay values are 35V/sec with optimum exposures of 13 ergs/cm² and 20 ergs/cm² for 830 nm and white light exposure respectively (VDDP = -800 volts, maximum contrast potential 480 volts, input density = 1.0). The best CGL binder was polyvinyl butyral, CGL thickness between 0.85 to 1 micron, and CGL pigment loading between 30 and 40%. F/MeSQ photoreceptors were cycled over 10 Kilocycle, gave excellent prints and exhibited good temperature and humidity stability.

**TABLE 5. Xerographic Data for Negatively Charged Dual-Layer Photoreceptors Incorporating Phthalocyanine Pigment Particles as Photogenerators**

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Dark Decayb</th>
<th>E[sub+c]</th>
<th>E[sub+pc]</th>
<th>% discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evap. ClInPc</td>
<td>45</td>
<td>2.6</td>
<td>9</td>
<td>87</td>
</tr>
<tr>
<td>VOPc</td>
<td>30</td>
<td>4.1</td>
<td>18</td>
<td>71</td>
</tr>
<tr>
<td>x-H2Pc</td>
<td>20</td>
<td>4.5</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>ClInPc</td>
<td>60</td>
<td>8.0</td>
<td>38</td>
<td>60</td>
</tr>
<tr>
<td>CLAlPc</td>
<td>55</td>
<td>10.0</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>MgPc</td>
<td>80</td>
<td>30.0</td>
<td>50</td>
<td>22</td>
</tr>
</tbody>
</table>

a. CCL consist of 30 wt.% pigment dispersed in PE-200 polyester of thickness 0.1-0.35 microns; CTL consist of 50 wt.% TDP in PC(A) polycarbonate of thickness of 30 microns.

b. VDDP = -830 Volts
c. X exposure 810 nm.

**PHTHALOCYANINES**

Phthalocyanine pigments are inexpensive, non-toxic and many have broad spectral response, notably in the near-infrared region where the solid state diode laser emit (750-850 nm). In addition, many phthalocyanine complexes have been found to exhibit significant and potentially useful photoconductivity (ref.17 – 19). Recently, Kakuta et al of Hitachi (ref.8) developed dual-layer photoreceptor incorporating r-metal free phthalocyanine (r-H2Pc) which is reported to exhibit high IR photosensitivity (E[sub+c] ~ 5 ergs/cm² at 800 nm) and significant cyclic stability (50,000 cycle). Near infrared sensitive photoreceptor incorporating r-copper phthalocyanines are much less photosensitive, E[sub+c] = 32 ergs/cm² at 760 nm, (ref.20). Our work on phthalocyanine pigments as binder generator layer in dual-layer photoreceptor showed that many metallophthalocyanines exhibit high IR-photosensitivity, however, dark decay is rather high. As a result a much thinner CGL had to be used response of a dual layer photoreceptor microns for pigment loading of 30 wt.%). Table 5 list the xerographic results of negatively charged dual-layer photoreceptors incorporating phthalocyanine pigments as photogenerator.
Both vanadyl phthalocyanine and x-metal-free phthalocyanine exhibit high IR-photosensitivity $E \approx 4-4.5$ ergs/cm$^2$ and extremely good cyclic stability. The spectral response of vanadyl phthalocyanine (Fig. 3) is flat from 600-860 nm while that of x-H$_2$Pc sensitivity falls off rapidly past 800 nm. Another potentially useful IR-photoconductive materials are the trivalent metallophthalocyanine ClInPc and ClAlPc. The near infrared photosensitivity of photoreceptor devices incorporating chloroindium phthalocyanine dispersion is 8 ergs/cm$^2$ at 830 nm (ref.16), and that of chloroaluminum phthalocyanine is 10 ergs/cm$^2$. The cyclic stability of the ClInPc devices is the best we have seen so far for a binder generator layer (BGL) type photoreceptor. Further optimization of these devices should result in substantial improvements in performance. While the binder-generator solution coating technology used above enables low production cost for photoreceptors, it has been known that considerable cyclic instability and print defects can be traced to the non-uniformity of CGL. One approach to overcome this difficulty which we have adapted recently is to prepare a thin photogenerator layer by vacuum sublimation (evaporation). Highly photosensitive dual-layer photoreceptor devices containing 0.1 micron evaporated chloroindium phthalocyanine has been prepared with $E \approx 2.6$ ergs/cm$^2$ at 830 nm (ref.21). The cyclic stability and spectral response of evaporated ClInPc dual layer photoreceptor is shown in Fig. 8 and 9, respectively. The evaporated ClInPc photoreceptor device exhibits excellent cyclic stability and flat response from 600-850 nm. Highly sensitive dual layer photoreceptor devices containing evaporated chloroaluminum phthalocyanine chloride (ClAlPcCl) with $E \approx 6$ ergs/cm$^2$ between 800 to 850 nm (ref.7) and chloroindium phthalocyanine chloride (ClInPcCl) with $E \approx 3-4$ ergs/cm$^2$ between 800 to 850 nm (ref.8-9) have also been recently reported.

REFERENCES