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FUJI ELECTRIC REVIEW

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2011 VOL.57

Photoconductor

Fuji Electric Group

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Cover photo:

Demand for printers and copiers is anticipated to increase in the future along with the advancement of information technology, growth of emerging countries, and other related factors. Fuji Electric contributes to boosting the speed and image quality of printing, reducing the size of machines, making equipment more energy efficient, and cutting printing costs through working to make photoconductors smaller, more durable, more sensitive, and better responsive. During this process Fuji Electric has developed more sophisticated commercialization, production, and image assessment technologies, while also establishing material design technologies.

The cover photo represents our products as well as our company's unique proprietary computer-aided molecular design and chemical synthesis technologies. Fuji Electric will continue to contribute to realizing an affluent society and protecting our global environment via the provision of eco-friendly photoconductors that match advancing and diversifying market needs.

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Photoconductors: Current Status and Future Outlook

Mitsuru Narita † **Takashi Obinata** †

ABSTRACT

From the perspectives of energy and the environment, energy savings is also needed in the field of electrophotography. The market for electrophotography-based printers and copiers is forecast to grow at an annual rate of approximately 8%. Accordingly, that same growth rate is also forecast for photoconductors, which are key electrophotographic devices. Fuji Electric is consolidating its OPC production facilities in Shenzhen, China in order to meet worldwide demand. Also, newly adding positive electrification multi layer-type photoconductors for greater energy savings, Fuji Electric offers five lines of photoconductor products, i.e., negative electrification type photoconductors for printers, analog copiers and digital copiers, and monolayer type and multi layer-layer type positive electrification photoconductors for printers, and delivers products that are well suited for energy savings and that are friendly to the global environment.

1. Introduction

Advances in information technology, the rise of the emerging economies, and other factors have given access to information networks to huge numbers of people around the world. There has been a concomitant massive increase in the numbers of running computers, mobile phones, and other networked devices, as well as printers and digital copiers. There are concerns that the energy consumed by these devices will have a large impact on the global environment, creating a strong demand for energy efficiency (energy conservation) in the field of information devices as well.

In reaction to this situation, Fuji Electric wants to be friendly to people and the environment. It aims to contribute to society through energy and environmental businesses, in order to create harmony between the Earth and society. This includes mitigating global warming, creating a closed-loop economy, and ensuring biodiversity.

In its photoconductor business as well, it is contributing to the energy efficiency of printers, copiers, and other electrophotographic devices, by developing energy-efficient photoconductor products that are friendly to the global environment.

This paper describes the trends in the printer and copier markets; highlight the latest energy-efficient technologies and products using photoconductors as key device for electrophotographic technologies; and describe the outlook for Fuji Electric's photoconductors in the global environment.

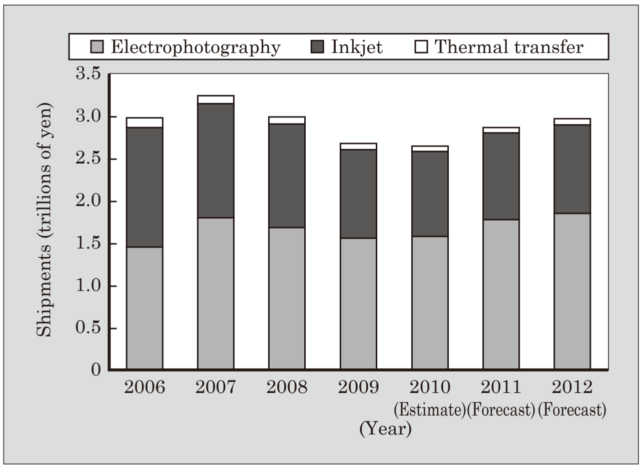
2. Trends in the Printer and Copier Markets

There are two methods for displaying text and image information: soft copy (shown on a display) and hard copy (printing). There have been remarkable advances in soft-copy technology, most notably in LED and organic light-emitting diode (OLED) displays, and the adoption of these technologies is expected to continue to increase.

Meanwhile, hard copies consume paper as their medium. In 2009, a keynote address at NIP25 (IS&T's NIP25: Imaging Science & Technology's 25th International Conference on Digital Printing Technologies) reported that printing both sides of a sheet of A4 paper resulted in the same level of carbon-dioxide emissions as reading the equivalent A4 document on a computer screen for five minutes[1]. The production of paper has a long history. Its manufacture has been made extremely energy efficient, and it is likely to continue to be used as a lightweight and highly convenient medium.

Computer output devices that produce hard copy

Fig.1 Trends in Worldwide Color Hard-copy Devices by Shipment Value



† Semiconductors Group, Fuji Electric Systems Co., Ltd.

Fig.2 Trends in Worldwide Electrophotographic Devices by Units Shipped

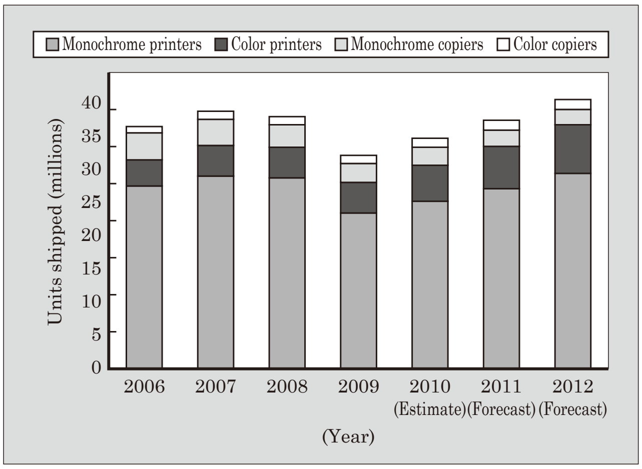
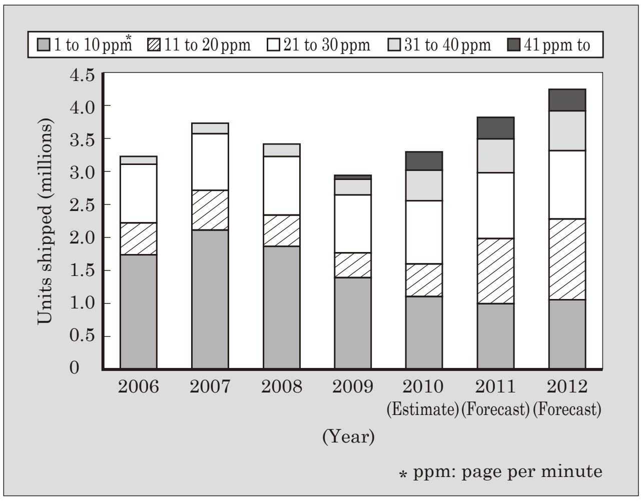


Fig.3 Trends in Worldwide Color Laser Printers by Speed and Units Shipped



can be classified into two types: inkjet printers, which are popular for personal use, and electrophotographic printers, which are popular for office use. Inkjet printers are inexpensive, support color, and use special inkjet paper. Meanwhile, electrophotographic printers have lower running costs, are fast, and support ordinary paper.

Figure 1 shows the trends in the market for color hard-copy devices of each category, by shipment value[(2)]. In 2011, the overall color hard-copy market is expected to grow by about 8% year on year. In particular, the electrophotographic market is expected to grow by a large margin of about 13%, driven by growth in color printers and color copiers, and the market is expected to continue to grow moving forward.

3. Trends in Electrophotography

Figure 2 shows the trends in numbers of electrophotographic printers and copiers shipped. In 2009, the year after the global financial crisis precipitated by the collapse of the Lehman Brothers, shipments plummeted by 15% year on year, to 29 million units. The markets of China and the other emerging economies subsequently recovered, and manufacturers launched products meeting the specifications of these markets, resulting in 8% year-on-year growth worldwide in 2010. As document expression becomes increasingly diverse and sophisticated, there has been a growing trend toward color electrophotography, and a year-on-year growth of about 16 to 17% is expected. It is also expanding into the light printing field, as it expands into production printing.

As a technical trend, more energy-efficient electrophotographic printers, copiers, and other devices are being developed as a measure for the global environment. In particular, manufacturers are working actively to improve the energy efficiency of the process for fusing toner on paper, as this consumes about 60% of the total electric power. One example is the switch from thermal-heater fusing to belt fusing, using electromagnetic induction heating. This enables operation without preheating, greatly reducing both standby time and power consumption. Another example is the development of low-temperature toner, which can fuse at lower temperatures. In response to these trends in electrophotography, the trend in photoconductor technology is toward helping to reduce rotation torque, and ensuring durability and high lubrication that resists filming, even when low-temperature toners are used. Fuji Electric is committed to quickly developing and marketing highly environment-friendly photoconductors.

3.1 Printers

As shown in Fig. 2, shipments of monochrome printers are expected to grow by 5% year on year by units shipped in 2011, while shipments of color printers are expected to grow by a massive 16%. This high rate of growth in numbers of color printers shipped is expected to continue.

Figure 3 shows trends in shipments of color laser printers by speed and units shipped. As shown in Fig. 3, there has been almost no growth in shipments of color printers with an output speed of 10 pages per minute (ppm) or lower, and printers with speeds of 11 ppm and higher are expected to become the norm starting in 2010. Low-speed devices employ a method of printing four colors, using one photoconductor at a time (four-cycle method), while medium-speed devices largely use the tandem method, where four photoconductive drums are arranged in an array, and each drum prints one color.

One of the features required of photoconductors for color printers is stable light attenuation, which is required in order to ensure image quality, and high resolution and color reproducibility in particular. High dimensional accuracy is particularly required of photoconductors using the tandem method, in order to su-

Fig.4 Trends in Worldwide Copiers by Units Shipped

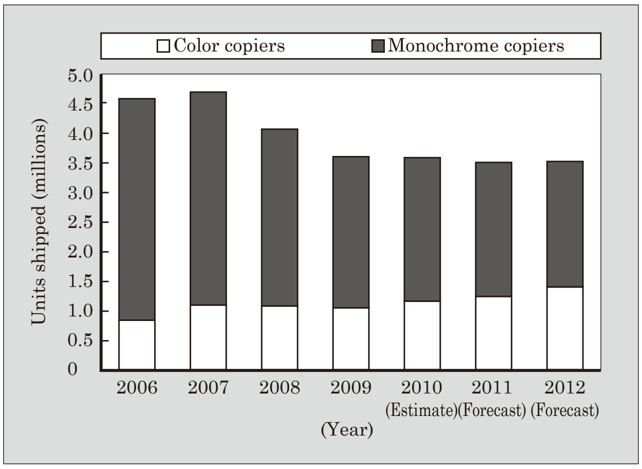
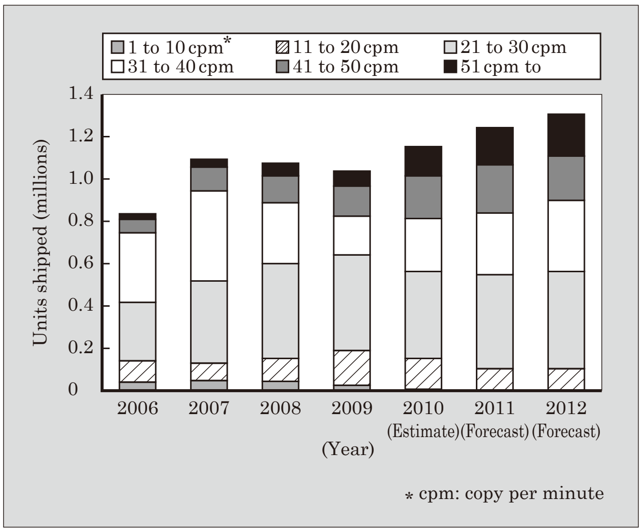


Fig.5 Trends in Worldwide Copier Market by Copying Speed



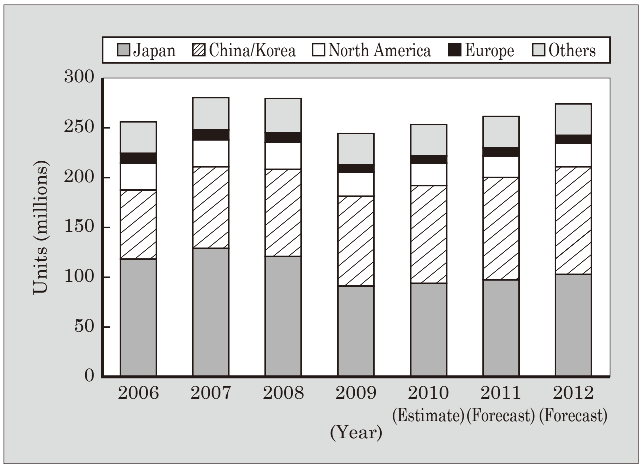
press color drift by the four colors.

One trend in the printer field is expansion into the light printing field. As electrophotographic technology becomes more advanced, electrophotography is expanding into the printing field. In particular, toner-fusing methods and printer paper have advanced to the point where they offer the same quality as printed images. Photoconductors used in the light printing field must have high resolution and durability. The papers in this special issue describe photoconductors for digital copiers and latent-image evaluation techniques in detail.

3.2 Copiers

Copiers are also becoming increasingly energy efficient and digital. Figure 4 shows trends in shipments of copiers by numbers of units. Although the overall number of units shipped is declining, shipments of color copiers are increasing. Figure 5 shows shipments of color copiers by copying speed and numbers of units. Shipments of medium and high-speed copiers with speeds of 21 copies per minute (cpm) and above are

Fig.6 Trends in Worldwide Organic Photoconductors by Region and Units Produced



strong, while shipments of 20 cpm and lower copiers are falling. Shipments of 51 cpm and higher copiers are also growing. Particular focus is being placed on energy efficiency, and more copiers are changing from thermal fusing to induction-heat fusing in order to improve the fuser, and are using toners that fuse at lower temperatures.

Some of the features demanded of photoconductors for copiers are high responsiveness, durability, and light attenuation suited to the copier processes, such as gradations that can reproduce halftones in graphical images.

3.3 Photoconductors

Some of the photoconductors used in electrophotographic printers and copiers include organic photoconductors (OPCs), selenium photoconductors, and amorphous silicon photoconductors.

99.6% of all photoconductors produced are OPCs. Figure 6 shows trends in numbers of OPCs produced by region[(3)]. After the global financial crisis, the production volume in Japan plummeted by about 25% in 2009, while produciton levels in China and Korea remained nearly unchanged and reached the same volume as Japan. The economy subsequently stabilized, and production is growing at a strong rate of about 8% per year. North America and Western Europe account for the majority of consumption. Moving forward, demand is expected to grow in such regions as Eastern Europe, Russia, China, Asia, South America, and Africa (the BRICs and VISTA). In the field of electrophotographic devices using photoconductors, demand will be captured by low-priced, compact monochrome printers. Products will also need to match the distinctive characteristics of each market country. For example, a distinctive type of paper is used in China that has rougher surfaces that in Japan, and printers sold there must have an internal structure that supports this type of paper.

Table 1 Organic Photoconductor (OPC) Product Series

Type	Features		Applications
	Electric charging polarity	Layer composition	
Type 8	Negative	Multilayer	Printers, facsimiles, multifunctional devices
Type 9	Negative	Multilayer	Analog copiers
Type 10	Negative	Multilayer	Digital copiers, multifunctional devices, convenience printings
Type 11	Positive	Single layer	Printers, facsimiles, multifunctional devices
Type 12	Positive	Multilayer	Printers, facsimiles, multifunctional devices, convenience printings

4. Overview of Fuji Electric Products

Fuji Electric developed and began marketing selenium photoconductors in 1973, and OPCs in 1988. OPCs are a key device for printers and copiers. Fuji Electric develops, produces, and markets OPCs and peripheral devices on a global scale, responding swiftly and flexibly to the rapid advances in electrophotographic technologies.

The company had three bases of production: one in Japan, one in the United States, and one in China; but in early 2006, production was consolidated in Shenzhen, China, responding efficiently to worldwide demand.

Fuji Electric (Shenzhen) is a production site for peripheral products, such as mag sleeves and toner cartridges. Currently, many manufacturers of printers and copiers assemble their devices in Asia, including China. The production of OPCs and their peripherals in China thus offers a great deal of convenience.

4.1 Organic Photoconductors (OPCs)

The demands of Fuji Electric's customers are growing increasingly diverse. Fuji Electric has created an organization to respond to these demands. It develops OPC products matching the wavelengths of printer and copier light sources, in order to deliver crisp and clear images.

Table 1 shows the company's product series.

(1) Printer OPCs (Type 8)

Type-8 products were developed as OPCs for general printers. This type includes a lineup that can support a wide range of potential responses and sensitivities, from low-speed to high-speed devices. In particular, the company continues to develop technologies relating to organic materials (e.g. charge-generating materials and charge-transporting materials). These include a wealth of technologies for designing materials, including technologies for molecular design using computers, dispersion technologies for converting materials into coating liquids, and coating technologies for finishing OPCs. This type is able to meet a wide range of customer demands, including the high resolution and color-image reproduction demanded of color printers. The company won the Best Poster Award of the Imaging Society of Japan for its research into the mechanism of latent-image formation of OPCs, and for revealing the relationship between photoconductor characteristics and resolution[(4),(5)]. The aim of this research was to improve resolution, through support for color imaging and photo-image quality.

The company aimed to reduce toner usage, in order to make an OPC suited to energy-efficient electrophotographic devices. Focusing on photoconductors and toner adhering strength, Fuji Electric has proposed various physical models taking into account both the photoconductor and the toner[(6),(7)].

The company has also improved the dimensional precision of drums by developing outstanding rotational stability. This is achieved by advancing technologies for processing element tubes, and designing high-precision drive gears.

(2) Copier OPCs (Type 9 & Type 10)

Two series of photoconductors are developed: Type-9 products for analog copiers and Type-10 for digital copiers.

These lines of products satisfy the particular demands of copiers: high responsiveness, high durability, and gradations. Fuji Electric also continues to improve these characteristics through the design and development of new materials. Digital copiers in particular have strong demands for long lifetime and potential stablity. The company has thus created high-functionality OPCs via technologies for molecular design of OPC binder materials and additive technologies for potential stablity, in order to meet these demands.

(3) Positive Charge OPCs (Type 11 & Type 12)

As Fuji Electric expands its lineup of OPC products suited to negative electric charge, it has also been developing positive-charge OPCs. Positive OPCs have high possibility to improve image quality easily, and produce less ozone, which is better for the environment. The development of electron-transport materials with high mobility is essential for creating these OPCs. Fuji Electric succeeded at synthesizing unique materials, and released a product using them in 1999. As is well known, positive-charge OPCs generate low levels of ozone even when using an electric-charge process via corona discharge. They can also improve resolution, because light is absorbed and electric charge generated on the surface.

Then in 2009, Fuji Electric became the first in the industry to develop a multilayer positive-charge OPC as an energy-efficient laser light source. This has higher sensitivity, responsiveness, and environmental stability than single-layer OPCs, and moving forward will be able to make a contribution as an OPC friendly to the global environment. The company is taking advantage of these features to expand them to use in monochrome printers, color printers, and on-demand printers, as their application expands to high-speed devices as well.

4.2 Peripheral Products

Fuji Electric has developed electrophotographic process technologies over many years. Based on these technologies, the company develops and designs development sleeves and other peripheral products using process simulators that combine the electric-charge module, development module, and cleaning module. Development sleeves using development modules are also used in both monochrome printers and color printers, via more advanced OPC element-tube processing technologies, and more advanced minute surface-processing technologies and thin-film coating technologies.

5. Postscript

Electrophotographic technologies are increasing in adoption; the growth of the Internet has caused a dramatic increase in the adoption of digital and color devices. The functionality expected of OPCs includes crisper images and better durability; energy-efficient OPCs are also becoming increasingly friendly to the global environment.

Fuji Electric is committed to meeting these market needs with more advanced technologies for designing materials, creating products, and production. It is developing products that are attractive to its customers. Fuji Electric will continue to leverage the combined strength of the Fuji Electric Group to improve its technical capabilities, meet the needs of its customers, and offer highly capable products and services with the highest level of quality in the industry.

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Material Technology for Organic Photoconductors

Shinjiro Suzuki † Seizo Kitagawa † Yoichi Nakamura ‡

ABSTRACT

Fuji Electric is developing organic photoconductors (OPCs) in response to requests for image forming functions with higher sensitivity and higher stability, and to reduce the environmental impact of electophotographic machines. Fuji Electric is developing functional materials, polymer materials and additives applying proprietary computer-aided molecular designs and chemical synthesis technology. In order to support the miniaturization of equipment, promote resource conservation and recycling and achieve higher durability, Fuji is also developing new OPC underlayer resin materials, charge generating materials, and additives for the charge transport layer, and has accomplished to improve OPC environmental stability, enhance sensitivity, conserve energy, and improve printing durability. Additionally, Fuji Electric has established a system that complies with material safety standards and environmental regulations.

1. Introduction

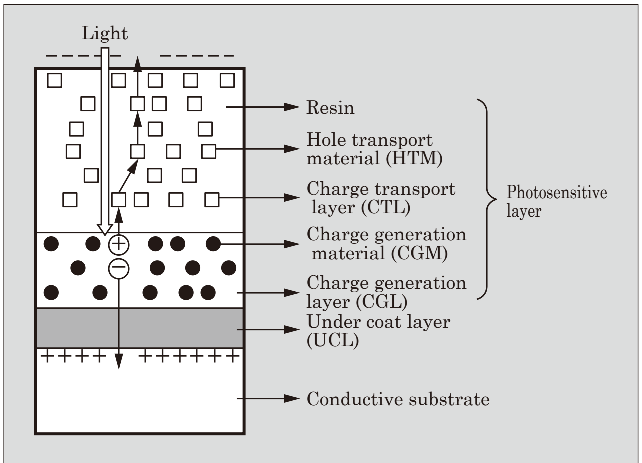
The photoconductor products developed by Fuji Electric are helping to make printers, copiers, and other electrophotographic devices more energy efficient and friendly to the global environment.

Electrophotographic devices using organic photoconductors are becoming increasingly digital, color capable, and networked. The public, corporate, and individual sectors are all using more documents containing larger amounts of information in greater density.

Assessments of environmental impact require the approach of life cycle assessment: the approach of focusing not just on reducing power consumption, resource usage, and waste/emissions, but on reducing the environmental impact of current products throughout their life cycle. For this reason, in addition to the conventional demands for image-formation functionality (e.g. high sensitivity and stability), photoconductors must be developed to support the technologies for reducing environmental impact demanded of electrophotographic devices. Users also demand that devices be made smaller and less expensive, and these demands must be met as well. Fuji Electric meets these diverse demands by creating proprietary organic photoconductor products having these characteristics.

This paper presents an overview of the materials and chemical technologies that are the core technologies of organic photoconductors, and an overview of the environmental initiatives by Fuji Electric for organic photoconductors, and describes their features.

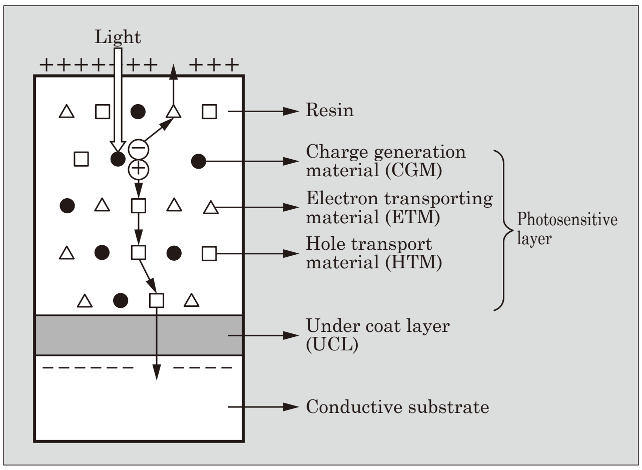
Fig.1 Layer Composition and Materials of Negative Charge Multilayer Organic Photoconductors



2. Organic Photoconductors

Organic photoconductors (OPCs) utilize the poten-

Fig.2 Layer Composition and Materials of Positive Charge Multilayer Organic Photoconductors



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‡ Fuji Electric Semiconductor (Malaysia) Sdn. Bhd.

tial difference created on a photoconductive surface to form an image. In principle, it makes no difference whether the polarity of the potential is positive or negative.

OPCs having image-formation potential that is positive are called positive-charge OPCs. Those having negative polarity are called negative-charge OPCs. Figure 1 shows the layer structure and principle of operation of negative-charge multilayer OPCs, and Fig. 2 does the same for positive-charge single-layer OPCs.

Negative-charge multilayer OPCs have a structure consisting of multiple layers with different functionality. They start with an aluminum tube or other conductive substrate, upon which is arranged an under coat layer (UCL) consisting of resin or the like. On the under coat layer is a charge generation layer (CGL) consisting of charge generation material (CGM) and resin or the like. Then on top of the charge generation layer is a charge transport layer (CTL), consisting of hole transport material (HTM) – which is a type of charge transport material (CTM) – and resin or the like.

Positive-charge single-layer OPCs also provide, as needed, a UCL made from resin or the like on an aluminum tube or other conductive substrate. On top of the UCL is a single photosensitive layer, consisting of an electron transport material (ETM) – which is a type of CGM/HTM/CTM – and resin or the like, thus forming the structure of the OPC.

Meanwhile, the structure of a positive-charge multilayer OPC includes a CTL consisting of HTM and resin or the like between the under coat layer and photosensitive layer of the positive-charge single-layer OPC.

When the surface of the photosensitive layer is charged by corona discharge or contact electrification and then exposed, both positive and negative charges are generated in the CGM. The positive charges move through the HTM. In the case of a negative-charge OPC, the charge reaches photosensitive layer surface, while in the case of a positive-charge OPC, it reaches the substrate after further passing through the CTL and UCL. Meanwhile, with a negative-charge OPC, the negative charge reaches the substrate after passing through the UCL, while with a positive-charge OPC, it passes through the ETM, and reaches the photosensitive layer surface. This neutralizes the surface charge of the photoconductor, and the potential difference with the surrounding surface forms an electrostatic latent image. Toner (color resin ink powder) is then used to make the latent image visible, and the print is completed by transferring, heating, melting and fixing the toner to the paper.

3. Fuji Electric's Commitment to Developing Organic Photoconductor Materials

Table 1 shows the main materials used in OPCs. These materials include UCL materials; CGM, HTM, ETM, and other functional materials; resins and other film-formation materials; and various additives whose purpose is to increase their functionality.

In order to gain wide acceptance of OPCs in the market, the functional materials, film-formation materials, additives, and other materials must each function properly. They must also be designed with the optimum mutual balance. This is one of the reasons for the complexity of OPC material technologies.

Fuji Electric reduces environmental impact, pioneers new markets, and offers new functionality by leveraging its proprietary materials technologies to match market trends. Next, we will describe the initiatives by Fuji Electric to develop materials technologies.

3.1 Designing Molecular Structures and Synthesis Technologies

The development of OPC materials includes molecular design based on chemical technologies. Fuji Electric has introduced a molecular-design system, and established computational molecular-design technology.

Table 1 An Example of OPC Material

Layer		Constituent Materials	
Photosensitive layer	Charge Transport Layer (CTL)	Hole transport material (HTM)	Arylamines; hydrazones; stilbenes; benzidines; etc.
		Electron transport material (ETM)	Azoquinons, etc.
		Film-forming material	Polycarbonates; polyesters; polystyrenes; etc.
		Additives	Materials to improve photoconductor characteristics; aid in film formation; prevent coating wear; etc.
	Charge Generation Layer (CGL)	Charge generation material (CGM)	Phthalocyanines; azos; etc.
		Film-forming material	Polyvinyl acetates; polyketals; etc.
		Additives	Materials to improve photoconductor characteristics; aid in film formation; prevent coating wear; etc.
Under Coat Layer (UCL)		Conductive material	Metal oxides, etc.
		Film-forming material	Polyamides; polyesters; melamines; etc.
		Additives	Materials to improve photoconductor characteristics; aid in film formation; prevent coating wear; etc.

As the company aims to further boost the functionality of OPCs, it is applying the system to the development of new functional materials, polymers, additives, and other new materials. Figure 3 shows a sample molecular structure of an OPC material that was actually developed.

Molecularly designed OPC materials are synthesized using chemical technologies. It is also necessary to obtain the purest possible materials from the perspective of green chemistry, and select high-yield synthetic reactions. For example, we break down the target molecule into precursors with pure structures, and consider efficient synthesis routes for deriving the desired synthetic compound[(1)]. It is also vital to select the appropriate catalyst, in order to synthesize the desired compound with high purity and high yield. Fuji Electric selects the appropriate catalysts for the Suzuki reaction and other innovative reactions, and establishes synthesis reactions that are safe, with high functionality and high yield[(2)].

When performing chemical synthesis, the approach to the reaction mechanism and purification technologies must be changed from a perspective of synthesizing materials for chemistry, to one of synthesizing materials for electronics. Fuji Electric leverages the plant technologies and process-control technologies unique to electronics manufacturers, while maintaining and improving the quality required to achieve the functionality of the OPC, by using such individual purification techniques as recrystallization, columns, distillation, and sublimation.

3.2 Designing the OPC Layer Materials

(1) Designing UCL materials

UCL materials must have a wide range of functionality, including adhesion to the conductive substrate, a smoother conductive substrate surface, charge blocking, easy application of an overcoat layer, and stability of the UCL coating solution. These functions are realized via conductive materials, film-formation materials, additives, and the like.

Devices are becoming more compact as a result of user preferences, and in order to conserve resources. There is also demand for photoconductors to have smaller diameters, and OPCs must be more durable and have good responsiveness. Fuji Electric employs a new, high-functionality film-formation material developed via its proprietary molecular-design technology. Due to the demands on devices, photoconductors must also be able to withstand a wide range of environments. A resin was thus also designed for UCL with the goal of environmental stability. The newly developed UCL resin has better moisture-absorption performance than conventional UCL resins. This improves the environmental fluctuation of the UCL membrane's volume resistance, improving the environmental stability of the photoconductor (Fig. 4).

This proprietary UCL-material design has made it possible to develop OPCs that balance high light response with environmental stability, optimizing the UCL's volume resistance for a wide range of environments, and adjusting the balance of the charge trans-

Fig.3 Molecular Structure of Material Developed by Fuji Electric

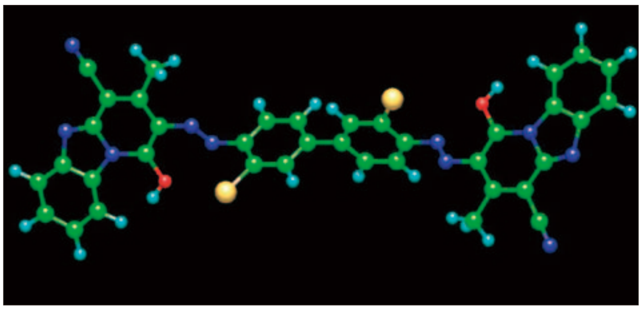


Fig.4 Environmental Dependence of Moisture Absorption

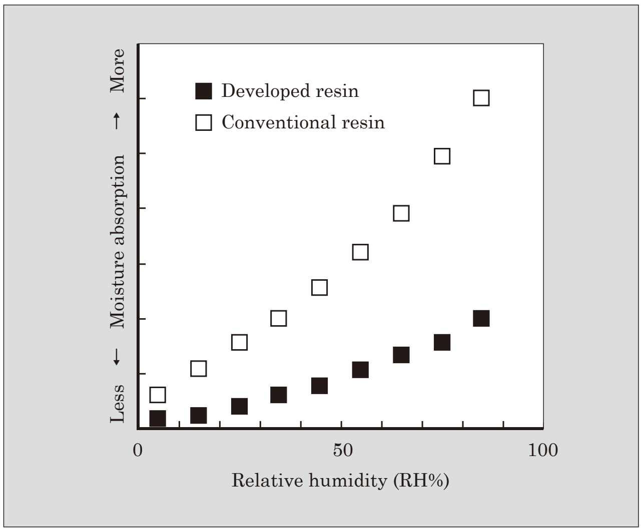
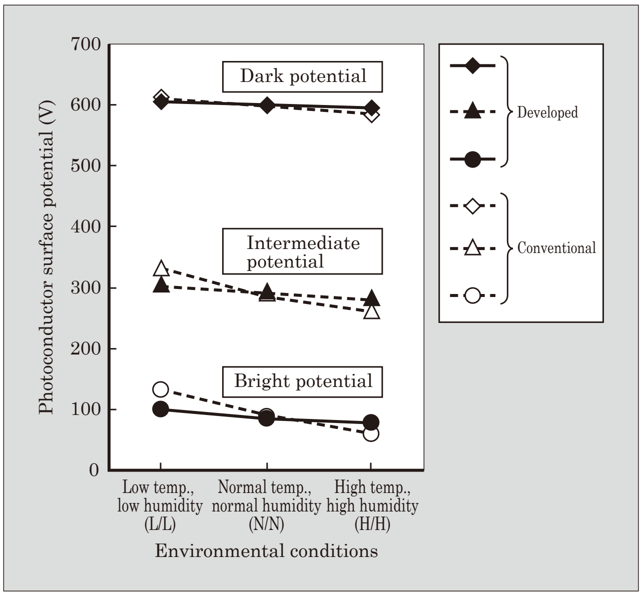


Fig.5 Actual Environmental Properties example of Developed OPC



port of the photosensitive layer as a whole (Fig.5).

The lifetime of the photoconductor was also increased by increasing the resistance to charge leaks from the substrate. A UCL was also applied that reduces reflected light from the substrate surface. This prevents problems with image interference patterns caused by exposure to light reflected from the substrate, while at the same time improving the productivity of the aluminum-substrate machining process.

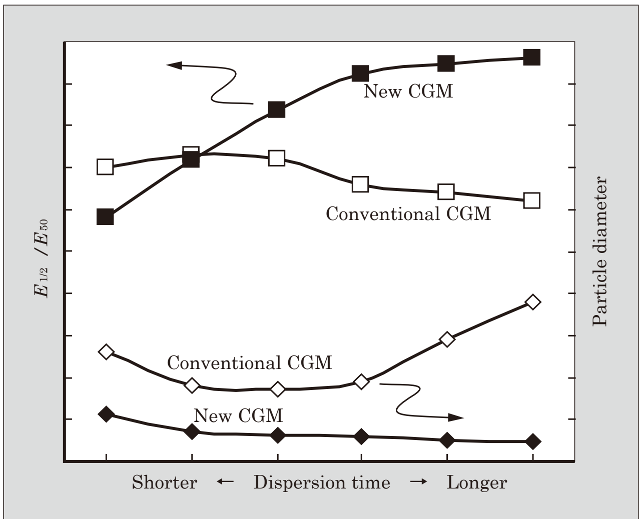
(2) Designing CGL materials

CGL materials must have a wide range of functionality, including adhesion to the UCL, high quantum efficiency in response to exposure to light, charge blocking, easy application of an overcoat layer, and stability of the CGL coating solution. These functions are realized via CGM, film-formation materials, additives, and the like.

Fuji Electric has developed highly-functional and highly stable CGMs via its proprietary synthesis reaction and process-control technologies. It has developed and employs a CGM with appropriate charge generation capacity for laser diode (LD) exposure light sources, and light-emitting diode (LED) exposure light sources, which are effective for making devices more compact. It has developed and employs a CGM with high light sensitivity characteristics: sensitivity E_{100} is at the 0.15 $\mu J/cm^2$ level. It has sufficient light attenuation characteristics even if the exposure energy is reduced, providing OPCs with the potential characteristics desired by its customers. Fuji Electric is thus able to help make devices more energy efficient and reduce their environmental impact.

There is demand for CGMs with greater sensitivity, and gamma characteristics suited to color devices (in this paper, the authors use the ratio of half-decay exposure $E_{1/2}$ to exposure E_{50} for the surface potential-50 V as the gamma property index). Fuji Electric develops CGMs with a wide range of gamma characteristics, and meets its customers' demands for image gradations and other properties. It also develops CGM dispersion techniques and is improving sensitivity characteristics by adjusting the CGM particle diameter (Fig. 6).

Fig.6 Sample CGM Distribution Properties and Gamma Properties



(3) Designing CTL materials

CTL materials must have a wide range of functionality, including adhesion to the CGL, retention of electric charge, charge injection properties, transport of injected charge, printing durability, ozone resistance, oil and grease resistance, and stability of the CTL coating solution. These functions are realized via charge transport materials, film-formation materials, additives, and the like.

Fuji Electric has developed and employs additives that, for example, suppress OPC wear and improve printing durability via its proprietary molecular-design technologies. The company continues to develop new materials in order to further improve print durability and image quality.

The fixing temperature of devices is being reduced in order to conserve energy and increase first-printing speed, and toner physical properties have also been developed correspondingly. Photoconductors also must have material properties that match toners with a wide range of physical properties. External additives are used in order to increase toner flow properties, and the surface energy of the CTL is being reduced in order to reduce the effects of these external additives, and improve cleaning properties. The company is also helping to reduce environmental impact through technologies to extend photoconductor lifetimes, by developing and employing CTLs with improved film strength.

From the perspectives of smaller size, resource conservation, and recycling, there is demand for support of processes that do not use cleaner and reduce waste toner. Fuji Electric is helping to reduce environmental impact by developing and employing OPCs with ultra-high transfer performance. It does this through CTL molecular-design technologies, and by adjusting the matching between the CGL and UCL.

As devices become more compact and have fewer parts, there is demand for support of no-cleaning devices and devices without exhaust fans. In order to support these smaller devices with fewer parts, Fuji Electric develops and employs additives and anti-oxidizing agents that provide ozone resistance and resistance to gas caused by photoconductor wear. Additives can be combined to adjust the gas transmission of the photosensitive layer film (Fig. 7).

Also, since temperature changes are responded to internally in the device, performance has low dependence on temperature, supporting the application of CTL materials with high temperature resistance.

(4) Designing positive charge OPC materials

Positive-charge materials function both as a charge generation layer and a charge transport layer. When a positive-charge OPC is applied, the devices generate less ozone. Fuji Electric has developed positive-charge OPCs with various sensitivity characteristics through its proprietary molecular-design technologies, helping to reduce the generation of ozone during charging, and design more environment-friendly devices.

(5) Material inspection technologies

Various device-analysis technologies are used according to the purpose of the different material inspections. Fuji Electric believes that material-inspection technologies are vital in order to improve OPC performance and make electronics materials with stable quality. It conducts strict inspections, using inspection items that add its unique perspective.

(6) OPC coating solution technologies

Efforts to improve pot-life characteristics of OPC coating solutions must not only take the perspective of reducing waste-fluid cost; it is also vital to reduce environmental impact. Coating solutions are in an environment highly susceptible to wear. They are exposed to or mixed with dust, dust from the substrate and dried coating film, dust from the equipment, water and oxygen in the air, etc.

Fuji Electric has a wide selection of suitable materials in order to suppress wear of OPC materials while in fluid state, by developing technologies to suppress wear to coating solutions. This produces coating solutions that improve OPC performance and provide stable quality. Figure 8 shows an example of a technology to improve the stability of coating solutions through materials technology. It can be confirmed that the additive stabilizes the residual potential.

Environmental impact is also reduced by collecting the solution used in the coating solution using solution-recovery device technology, and reusing this solution.

Fig.7 Gas Transmission Evaluation via Additives

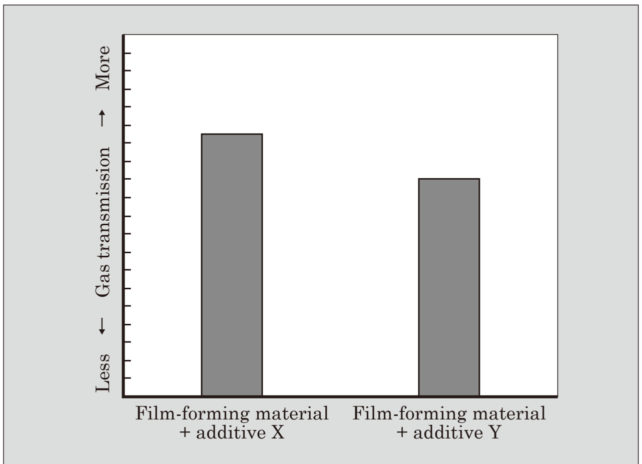
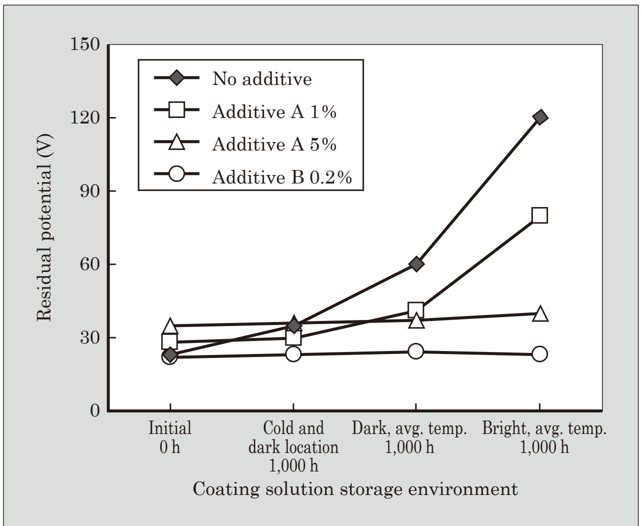


Fig.8 Sample Technology for Improving Coating solution Stability



3.3 Technologies for Evaluating Photoconductors

Fuji Electric has technologies for evaluating various photoconductor properties, including electrical properties, image properties, temperature and humidity properties, and durability since selenium photoconductors era. It has also established evaluation technologies with low environmental impact: it uses fewer actual parts and less actual material by means of its independently developed process simulator and printing-resistance evaluation simulator. It has also made advances in development combining materials technology with photoconductor technology[3].

3.4 Material Safety Evaluation and Compliance with Environmental Laws and Regulations

It is essential to confirm the safety of new OPC materials.

Fuji Electric confirms the safety of its materials via third-party institutions at important stages of develop-

Table 2 Examples of Environmental Laws and Regulations

Implementing Country/Authority	Environmental Law/Regulation
Japan	Law Concerning the Examination and Regulation of Manufacture, etc. of Chemical Substances; registry of existing chemical substances
United States	Toxic Substances Control Act (TSCA); TSCA Inventory
European Union (EU)	Council on the Classification, Packaging and Labeling of Dangerous Substances 548/EEC Seventh Revision of Council Directive 92/32/EC; the European Inventory of Existing Commercial Chemical Substances (EINECS)
	The Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS)
China	Provisions on the Environmental Administration of New Chemical Substances; Registry of Existing Valuable Chemical Substances
	Administrative Measure on the Control of Pollution Caused by Electronic Information Products (China RoHS)

ment, according to the laws and regulations of the destination country, and the standards prescribed by Fuji Electric.

Table 2 shows the major environmental laws and regulations. As international interest in the environment increases, it has become necessary to comply with environmental regulations, including new regulations by the European Union (EU) and China, as well as the new designation of organic cyanide compounds as toxic in Japan.

Fuji Electric has advanced environmental technologies as well. Its products is friendly to the global environment and has low environmental impact due to waste and the like, through the development and utilization of materials with low impact on the environment as highlighted here, as well as additives that suppress wear in coating solutions, and devices to recover used solution.

4. Postscript

Fuji Electric develops and produces products and materials combining its proprietary materials technologies, and plant/process control and other chemical technologies, and offers these to customers and markets as products.

Fuji Electric will continue to offer products that meet its customers' needs by improving the performance of OPC materials, and offering photoconductors with leading environmental performance.

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Organic Photoconductors for Printers

Keiichi Morita [†] Yutaka Ikeda [†] Yasushi Tanaka [†]

ABSTRACT

Fuji Electric provides a product line of negatively charged organic photoconductors in three varieties, low sensitivity, medium sensitivity and high sensitivity, for compatibility with various amounts of exposure light. Also, in response to a diversifying range of applications and the desire for more advanced functionality and higher quality, Fuji Electric uses proprietary evaluation technology, analysis technology and material design techniques to realize higher responsiveness, higher resolution, higher durability and higher reliability. For positively charged organic photoconductors, which are environmentally friendly and provide high resolution, in addition to monolayer type that provides low-speed to high-speed and high printing durability, a multilayer type that provides high sensitivity and high-speed response has been fully commercialized for the first time in the world.

1. Introduction

With recent advances in IT, the applications of electrophotographic printers are expanding from personal use to business use. Such devices must have faster printing speeds in order to keep pace with faster information-processing speeds; they must provide color and high definition printing to support increasing diverse information; and they must be more compact, not require maintenance, and have lower printing costs, in order to meet the demands for lower information-processing costs and greater energy efficiency. Electrophotography meets these demands by applying a wide range of technologies, in the charging, developing, transfer, and fusing processes respectively.

Fuji Electric develops negative-charge and positive-charge organic photoconductors (OPCs) in order to comply with the electrophotographic printer specifications of each of its customers, marketing these OPCs while expanding its lineup. This paper presents an overview of these products, and describes their features.

2. Negative Charge OPCs for Printers (Type 8)

2.1 Product overview

Figure 1 shows the layer structure of negative-charge OPCs. Fuji Electric offers three types of product series, with adjusted charge generation layer (CGL) properties in order to support a wide range of light exposures. These are Type 8 A (low sensitivity), Type 8B (medium sensitivity), and Type 8C (high sensitivity). As shown in Table 1, the material and the layer thickners can be controlled to adjust the sensitivity within a range of 0.15 to 0.80 μJ/cm^2, up to light exposure of −100 V.

Figure 2 shows typical spectral sensitivity characteristics for Type 8A (low sensitivity), Type 8B (medium sensitivity), and Type 8C (high sensitivity). All have nearly uniform sensitivity in the wavelength range of 600 to 800 nm, making them suitable for ordinary laser diode (LD) and light-emitting diode (LED) light sources.

These CGLs can be combined with various charge

Fig.1 Layer Structure of Negative Charge OPCs

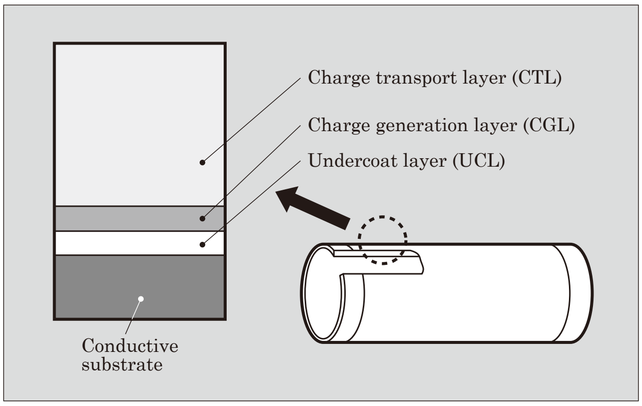


Table 1 Overview of Negative Charge OPC Products for Printers

Type	Sensitivity* (Exposure energy to −100 V)
Type 8 A (low sensitivity)	0.60 to 0.80 μJ/cm^2
Type 8B (medium sensitivity)	0.40 to 0.60 μJ/cm^2
Type 8C (high sensitivity)	0.15 to 0.40 μJ/cm^2

*Sensitivity is the required exposure energy for the surface potential to discharge from −600 V to −100 V

† Semiconductors Group, Fuji Electric Systems Co., Ltd.

transport layers (CTLs) to supply OPCs suited to various processes, from low-speed to high-speed devices.

Using its own unique conductive substrate processing technologies and layer-formation technologies, Fuji Electric is able to produce OPCs with a diameter of 20 to 262 mm, and a length of 236 to 1,000 mm, and markets a wide range of products, from A4-size page printers to A0 plotters.

2.2 Product features

Figure 3 shows the technical challenges for providing the six characteristics required of printer OPCs: high speed, color imaging, high resolution, compact size, maintenance-free operation, and lower printing costs. Each of these features is described below.

(1) High-speed response

In order to make small-diameter OPCs (having a diameter of 20 to 30 mm) suitable for use in high-speed printers capable of printing longitudinally fed A4-size sheets at a rate of 35 ppm or higher, the potential of exposed areas to light must be uniform during the exposure-development time, which is 50 ms or less in a typical processing machine. Accordingly, Fuji Electric has developed a charge transport material (CTM) having mobility of 2×10^{-5} cm^2/(V·s) for use in practical applications. Fuji Electric has further completed the development of a high-mobility material of 8×10^{-5} cm^2/(V·s) to support even higher speeds.

Figure 4 shows the dependency of the surface potential after exposure on the exposure-development time for high-speed response. The potential is stable in any environment, and with an exposure-development time at the 30 ms level, it is commercially viable.

(2) High definition

OPCs for use in color-imaging, high-resolution printers and multi-function printers (MFPs) must have even greater color reproducibility and gradation-reproduction capability for halftone images. Fuji Electric is developing and commercializing OPCs with the optimum light-induced discharge characteristics for various machine processes. Figure 5 shows examples of light-induced discharge characteristics by OPC type. These characteristics are largely dependent on the charge-transfer performance of the CTM and the efficiency of carrier injection between layers. It can therefore be regulated via the combination of the under coat layer (UCL), CGL, and CTL. The requirement for high

Fig.2 Spectral Sensitivity Characteristics of Negative Charge OPCs

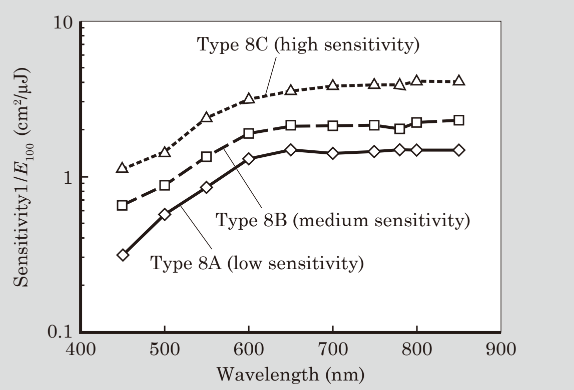


Fig.3 Required Characteristics of OPCs and Technical Challenges

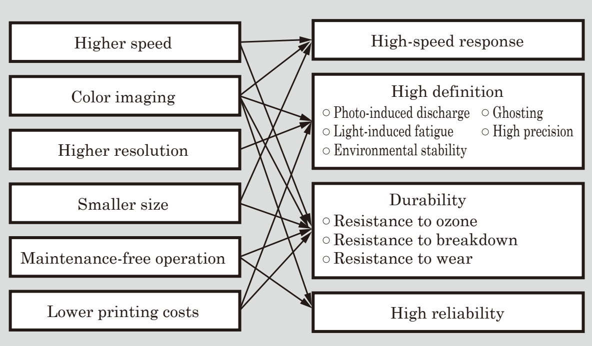


Fig.4 Photoresponsivity of Negative Charge OPCs

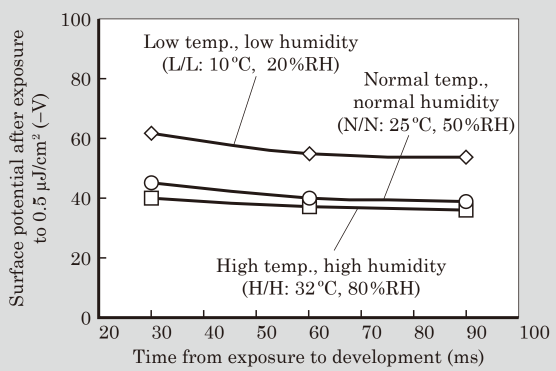
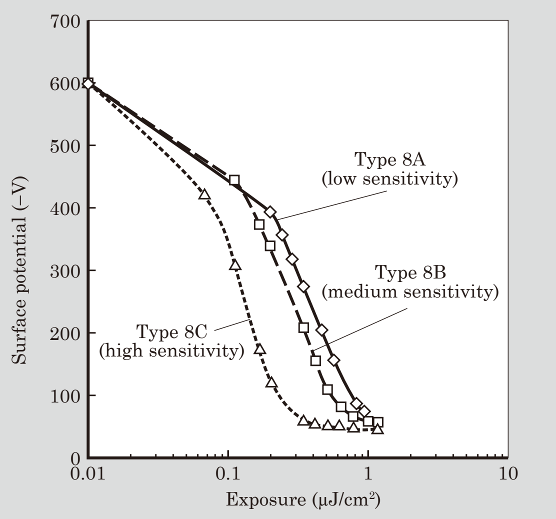


Fig.5 Photo-induced Discharge of Negative Charge OPCs



resolution can be met by developing a CTM with low horizontal charge diffusion. The fine line definition reduces the amount of toner consumed, which reduces printing costs.

The image quality of printers continues to advance. As a result, minute differences in potential on the OPC surface are more easily reproduced in the image as contrasts in image density. It is therefore preferable for OPCs to have photosensitive layers with uniform thickness, and be relatively unaffected by the application of positive polarity at transfer process, and the increase in residual potential with continuous exposure. Fuji Electric is reducing the potential difference by developing new materials for use in the UCL, CGL, and CTL functional layers, and by optimizing their combination.

In the general market, it is possible that the OPC will be exposed to indoor light or sunlight when cartridges are changed, or when there is a paper jam. The effects of this light exposure on the OPC must therefore be minimized. Fuji Electric has commercialized OPCs whose image quality is largely unaffected by exposure to fluorescent and other forms of indoor lighting, through the appropriate combination of CGL and CTL.

Color printers that print by overlaying four colors require higher dimensional precision than monochrome printers, in order to prevent color drift. Fuji Electric has technologies for processing OPC substrate tubes with a runout of 30 μm or less, and straightness of 20 μm or less, for use in these types of color printers, and it has also established a system for supplying high-precision plastic flanges.

In order to maintain the initial image quality, the characteristics of the OPC should be largely unchanged by changes in the environment or printing durability. A printing test was performed using a commercially available charging laser printer equipped with a 24 mm diameter OPC: 10,000 A4-size longitudinally fed sheets were each printed under the environmental conditions of low temperature and low humidity (L/L: 10 °C and 20% RH), normal temperature and normal humidity (N/N: 25 °C and 50% RH), and high temperature and high humidity (H/H: 32 °C and 80% RH), and the surface potential was measured after every 2,000 sheets. The data is shown in Fig. 6. In all of these environments, favorable characteristics were exhibited without any significant change in potential.

(3) Technology for higher durability

The charging unit in printers generally produce ozone. Various anti-oxidizing materials and other additives are thus used in order to provide the OPC with gas resistance. Ordinarily, using large quantities of additives improves resistance to acidic gases, but has negative effects on electrical characteristics as well, such as increasing the residual potential. Fuji Electric has ensured resistance to acidic gases by developing CTMs with low deterioration and a proprietary additive that does not impact electrical characteristics.

Contact charging is widely used in medium and low-speed printers. There is a strong requirement, however, for improved resistance to dielectric breakdown comparable to scorotron non-contact charging. Since launching a UCL equipped with an interference-suppressing function in 1995, Fuji Electric has been working continuously to develop OPCs with improved resistance to dielectric breakdown and environmental characteristics. Fuji Electric is presently developing UCL products that exhibit excellent environmental stability, and the same degree of resistance to dielectric breakdown as an anodized layer. It is also working to improve the overall performance of OPCs, including the charge-generation and charge-transport layers.

The useful service life of an OPC is determined by abrasion from such contact parts as the developing system, the paper, and the cleaning blade. Fuji Electric is independently developing resins with excellent abrasion resistance and lubricative resins, and offers OPCs optimized for various processes by selecting the appropriate combination for each process.

In order to improve image quality, the particle diameter of toners is being reduced, and manufacturers are moving from mechanical toner to chemical toner.

Fig.6 Surface Potential Stability of Negative Charge OPCs During Environmental Printing Life Tests

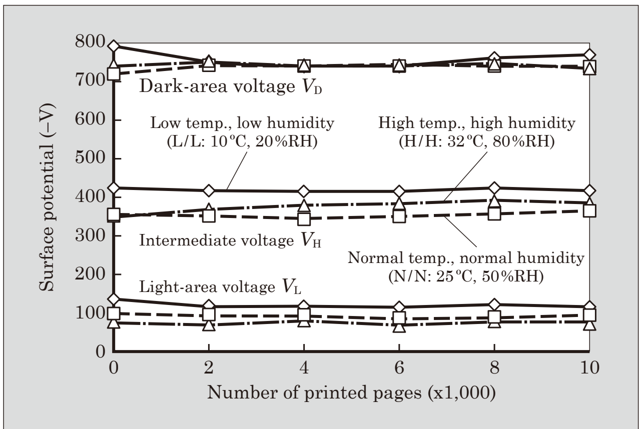
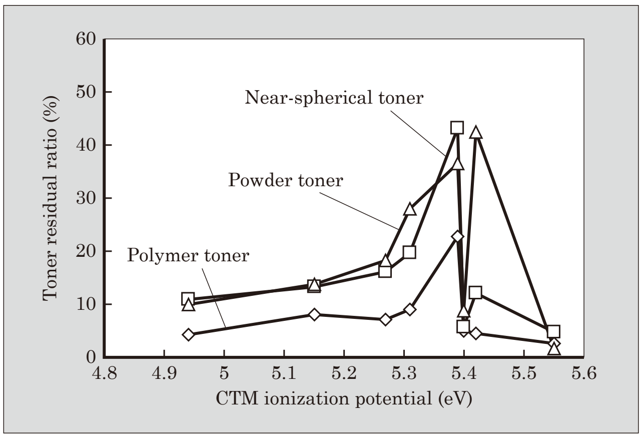


Fig.7 CTM Dependence of Toner Residual Ratio



This makes the toner adhere strongly to the OPC surface (“filming”), and low-filming performance is therefore required. Fuji Electric develops and employs methods to evaluate the adhesive strength of toner using the toner residual ratio[1]. Figure 7 shows the CTM ionization potential and toner residual ratio of each toner. Fuji Electric is developing the optimum OPCs for each type of toner.

(4) High reliability

OPCs should maintain stable characteristics in a variety of environments, and remain stable in response to external mechanical and chemical stresses.

Starting from the stage of materials development, Fuji Electric independently establishes a list of inspection items, and evaluates the reliability of each product, including long-term storage characteristics. This enables it to develop and produce highly reliable OPC products.

3. Positive Charge OPCs for Printers (Type 11 & Type 12)

3.1 Overview of Fuji Electric’s Products

Fuji Electric offers a line of positive-charge OPC products. These products feature higher image resolution than typical negative-charge OPCs, and demand for them is growing. The charged parts also produce less ozone, making it friendlier to the environment as well.

There is also strong demand to increase the sensitivity of OPCs, in order to conserve energy by enabling the energy consumption of the device’s exposure laser to be reduced. However, positive-charge OPCs have less leeway in material design than negative-charge OPCs, in order to provide the required characteristics, and the difficulty in increasing sensitivity is a challenge for this type of OPC. Fuji Electric has developed a positive-charge CTM through the application of its proprietary computational chemistry and organic synthesis techniques, and has commercialized a new type of multilayer OPC, Type 12, by combining this with its photoconductor technologies to increase sensitivity.

Table 2 shows the product series for Type 11 and Type 12 positive-charge OPCs. Figure 8 shows the spectral sensitivity characteristics of the five series from Type 11A to Type 12. All the positive-charge OPCs have nearly uniform sensitivity in the wavelength range of 600 to 800 nm, making them suitable for ordinary LD and LED light sources. As shown in Fig. 9, types are available with a wide range of sensitivities, with a range of half-decay exposure from 0.15 to 0.38 μJ/cm^2, and they are suitable for use with printers from low speed (15 ppm or lower) to high speed (35 ppm or higher). As shown in Table 3, the newly developed type 12 in particular has improved sensitivity through boosts to the performance of the various functional materials. This enables the amount of energy consumed by the laser to be reduced by about 30%. As

Table 2 Overview of Positive Charge OPC Products for Printers

Type	Features	Recommended machine (ppm)*	Printing life (Converted to A4 intermittent printing, 30 mm external diameter)
11 A	Low speed	< 12	20,000
11B	Medium speed	10 to 18	30,000
11C	Medium & high speed	12 to 24	140,000
11D	High-speed & high printing durability	≥ 30	200,000 Converted to 120 mm external diameter & A4 continuous printing; up to 1 million pages can be used
12	High-speed & high printing durability	≥ 35	≥ 200,000

*ppm: page per minute

Fig.8 Spectral Sensitivity Characteristics of Positive Charge OPCs

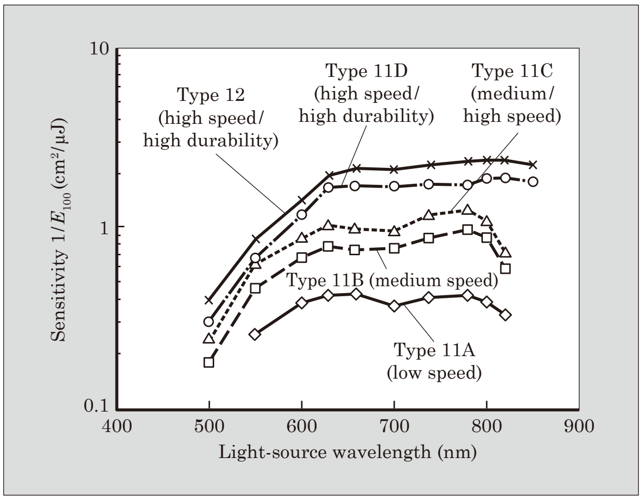
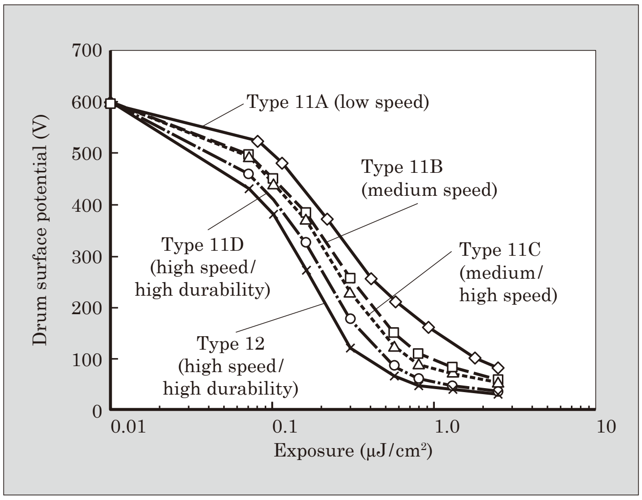


Fig.9 Photo-induced Discharge (PIDC) of Positive Charge OPCs



a result, they are able to meet the demands for higher sensitivity and response speed, while contributing to device design that takes energy efficiency into account.

3.2 Features of Positive Charge OPC Products

Here, the authors describe the features of positive-charge OPC products, with regard to technical challenges common to negative-charge OPCs.

(1) High-speed response

Table 3 Relationship between Characteristics and Material for Type 12

Feature	Characteristics of material
Higher sensitivity	CGM→increased quantum efficiency
High-speed response	HTM→increased hole mobility ETM→increased electron mobility Optimized balance between hole and electron transport
Higher strength	Resin binder→higher glass transition temperature →increased surface hardness
Resistance to breakdown	UCL→thicker layer (electrical conductivity control)

Fig.10 Photoresponsivity of Positive Charge OPCs

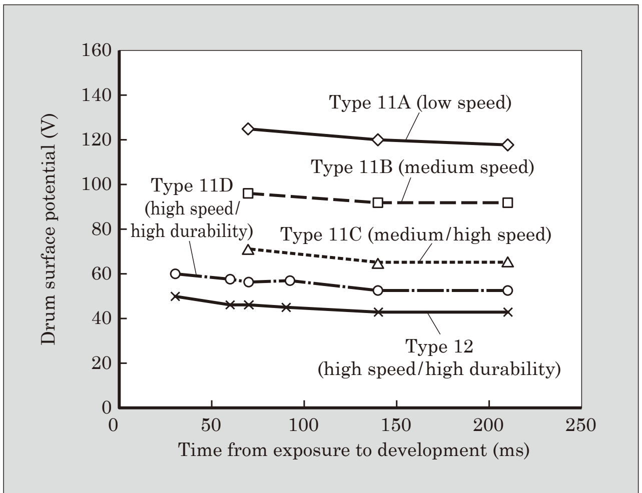


Fig.11 Comparison of 1-dot Latent Images of Positive and Negative Charge OPCs

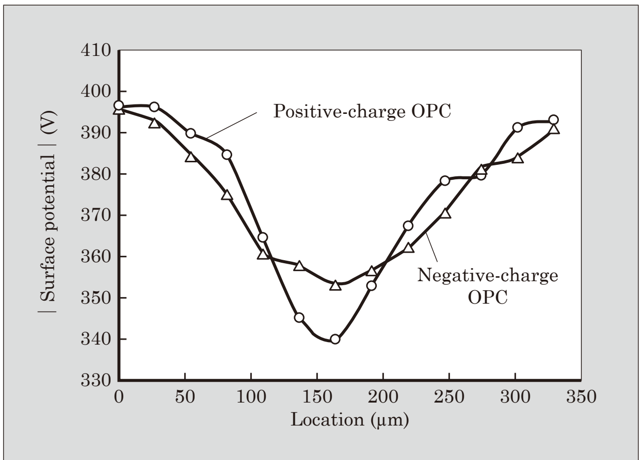


Figure 10 shows the photoresponsivity of positive-charge OPCs. All of the positive-charge OPCs are suited to devices with times from exposure to development of 75 ms or greater. Type 12 in particular has little increase in exposed-area voltage even after 30 ms of exposure, making it suited to compact, high-speed devices with shorter times from exposure to development.

(2) High definition

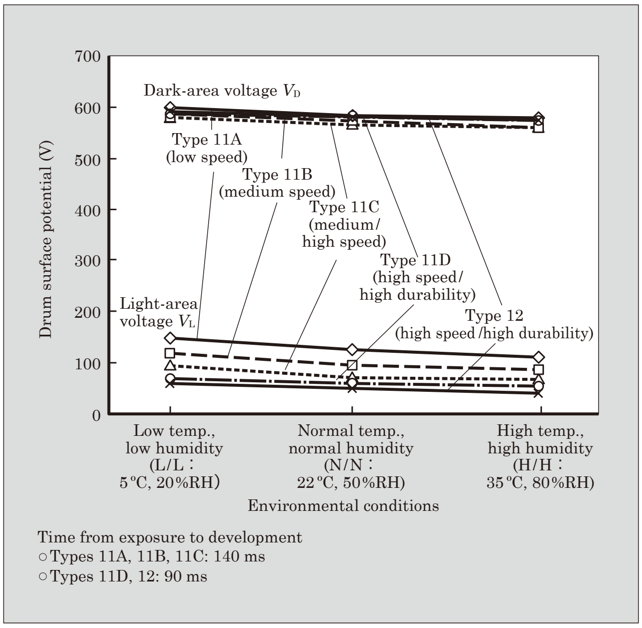
Positive-charge OPCs are well suited for use in high-resolution applications, since the absorption of exposure light and the subsequent generation of charge occurs near the OPC surface, because there is little scattering or diffusion of exposure light and charge within the photosensitive layer. Figure 11 shows the results of measuring the electrostatic latent-image width at the area of 1-dot exposure writing[2]. Spreading of the latent image can be observed in the negative-charge OPC, and indicates the extent of the high resolution performance of the positive-charge OPC.

The optimal regulation of the UCL and GTL, even during durability testing, enables better uniformity of the halftone image quality and suppresses the phenomenon of residual images. All types had favorable light-induced fatigue characteristics. Exposure to light at 1,000 lx for 10 minutes caused little change in the dark-area voltage in any of the types, and the recovery time after the light exposure was short.

Figure 12 shows the environmental characteristics of light-area voltage V_L and dark-area voltage V_D. All of the positive-charge OPCs have stable dark-area voltage and light-area voltage, and exhibit little environmental fluctuations with the range of low temperature and low humidity (L/L: 5 °C, 20% RH) to high temperature and high humidity (H/H: 35 °C, 80% RH).

(3) High printing durability

Fig.12 Environmental Dependence of Exposed-area Voltage V_L and Dark-area Voltage V_D of Positive Charge OPCs



Issue : Photoconductor

Table 4 Changes in Characteristics in Reliability Tests

Test item	Test conditions	Change in characteristics before and after test	
		Dark-area voltage fluctuation	Exposed-area voltage fluctuation
Exposure to high temperature	45 °C: 1,000 hours	< ±5%	< ±10%
Exposure to high temp. and high humidity	35 °C, 90% RH: 1,000 hours	< ±5%	< ±10%
Heat cycles 1 to 5 (10 cycles)	(1) –20 °C: 1 hour (2) Normal temp./humidity: 0.5 hours (2) Normal temp./humidity: 0.5 hours (3) 45 °C: 1 hour (4) –20 °C: 1 hour (5) Normal temp./humidity: 0.5 hours	< ±5%	< ±10%
Roller contact test	Roller materials: NBR, polyurethane rubber, silicon rubber; 50 °C, 90% RH: 250 hours	None	None
		No image faults	

As shown in Fig. 13, all of the positive-charge OPCs exhibit a temporary drop in charging potential shortly after exposure to ozone for 30 minutes at a concentration of 5 ppm, but then recover to their initial charging potential after being left to stand at room temperature for 24 hours. OPC types 11A, 11D, and 12 are particularly resistant to ozone, and exhibited only slight drops in charging potential immediately after exposure.

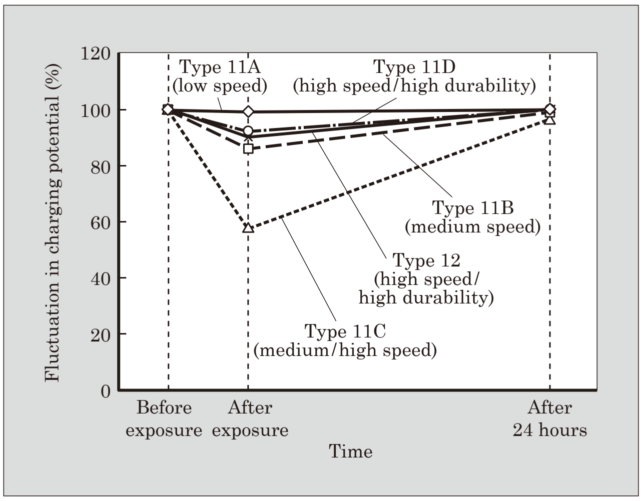
In a printing-duration evaluation using a two-component development printer, the Type 11D OPC exhibited stable light-area voltage and dark-area voltage with no observable image defects, and had a printing life of approximately 200,000 sheets. Type 12 is expected to have an even longer useful service life, and further environmental measures are being advanced as well.

(4) High reliability

Table 4 shows changes in characteristics as a result of various reliability tests. The tested OPCs exhibited high reliability: for all of the test items, fluctuation in dark-area voltage was no more than 5%, and fluctuation in exposed-area voltage was no more than 10%.

In a roller contact test in particular, rollers formed from acrylonitrilebutadiene rubber (NBR), polyurethane rubber, silicon rubber, and the like are pressed against each photoconductor, and even after the OPC was left standing in an environment of 50 °C and 90% RH for 250 hours, cracking did not occur in the photosensitive layer, and the photoconductor characteristics did not change.

Fig.13 Ozone Resistance of Positive Charge OPCs



4. Postscript

The trends toward higher speed, greater functionality, higher image quality, and lower cost will continue to advance for electrophotographic printers, and performance requirements for photoconductors will become more diverse. Fuji Electric will continue to utilize and develop chemical and photoconductor technologies to provide a variety of high-functionality photoconductors, suitable to meet the increasingly diverse needs for information output, and in doing so, to fulfill its social responsibility toward environmental conservation, and to make a positive contribution to society.

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Organic Photoconductors for Digital Plain Paper Copiers

Takahito Miyamoto † Shuichi Hamada † Yuji Nakamura †

ABSTRACT

Fuji Electric provides type 10A (low sensitivity), type 10B (medium sensitivity) and type 10C (high sensitivity) OPCs for digital copiers. The OPCs are sensitive in the 600 to 800 nm wavelength range of laser and LED light used as the light source for copiers. The Charging characteristics of the OPCs have been improved in accordance with the shortening of the first copy time of the copiers. Computer-aided molecular design has been utilized to develop a binder for a highly durable charge transport layer and prevent the charging characteristics from deteriorating. As a result, printing durability has been improved by at least a factor of 2, contributing to a reduction in the running costs of the copier.

1. Introduction

In fiscal 2009, the copier industry's shipment volume plummeted by 10% year on year, due to the effects of the worldwide recession precipitated by the financial crisis. Although it is predicted that major growth will not be seen moving forward either, there is a trend in the industry away from monochrome devices with high added value, and toward color devices. Manufacturers have been acquiring independent distributors, and entering the production market as well.

As a consequence to the abovementioned industry trends, copiers are increasingly becoming faster, supporting color imaging, and providing higher resolution, more stable operation, and maintenance-free operation (being provided as a single unit). The photoconductor is a key component for the image formation of electrophotographic devices. In order to respond to these trends in the copier industry, photoconductors require such improvements as higher sensitivity, better printing durability, better operating stability, and higher reliability.

Fuji Electric is committed to helping to reduce waste, lower running costs, and contribute to the conservation of the global environment by improving the durability of organic photoconductors (OPCs). The focus of this paper is an overview of durable OPCs for copiers.

2. Product Overview

Copiers that use OPCs can be categorized according to their copying speed: low-speed copiers (up to 25 ppm), medium-speed copiers (25 to 50 ppm) and high-speed copiers (50 ppm and above). Fuji Electric continues to develop materials and design photoconductive layers for all speed categories, in order to offer digital copiers that meet the specifications demanded by its customers.

A separated-function multilayer OPC is formed by applying an under coat layer (UCL) to a cylindrical conductive substrate typically made of aluminum or the like, then applying a carrier generation layer (CGL) on top of the UCL, and finally applying a carrier transport layer (CTL) on the top surface.

OPCs for digital copiers can use the Type 8 series of materials used in printer OPCs. Fuji Electric also offers a Type 10 series, which applies such proprietary technologies as improved durability for digital copiers.

3. Product Features

As a consequence to advances in electronics, copiers are gaining increased functionality, higher speed, and higher reliability. The characteristics demanded of OPCs have also become quite diverse.

Fuji Electric is developing materials to deliver these required characteristics. Fuji Electric's OPCs for digital copiers can be used in all copiers, from low-speed to medium and high-speed. They include the following features:

(a) High sensitivity
(b) High chargeability
(c) High printing durability
(d) High environmental stability
(e) High reliability

High chargeability and high printing durability are particularly necessary for achieving high durability.

3.1 High sensitivity

Digital copiers use laser diodes (LDs) or light-emitting diodes (LEDs) as exposure sources. Organic pho-

† Semiconductors Group, Fuji Electric Systems Co., Ltd.

toconductors must therefore have high sensitivity to wavelengths in the 600 to 800 nm range. Fuji Electric uses phthalocyanine pigment, which has high sensitivity in this wavelength range. As shown in Table 1, Fuji Electric offers three types of OPC, in accordance with its customers' process design: low sensitivity (Type 10A), medium sensitivity (Type 10B), and high sensitivity (Type 10C). Figure 1 shows the spectral sensitivity of each type.

Table 1 Basic Characteristics

Characteristic / Type	Half-decay exposure in applied sensitivity band ($\mu J/cm^2$)	Half-decay exposure ($\mu J/cm^2$)	Charging retention ratio [after 5 sec] (%)	Residual potential Vr (−V)	Applied range of printing speed (ppm)
Type 10A (low sensitivity)	0.20 to 0.40	0.38	98	50	< 30
Type 10B (medium sensitivity)	0.12 to 0.24	0.18	96	25	20 to 60
Type 10C (high sensitivity)	0.06 to 0.14	0.08	96	10	40 <

Fig.1 Spectral Sensitivity Characteristics of Photoconductors for Digital Copiers

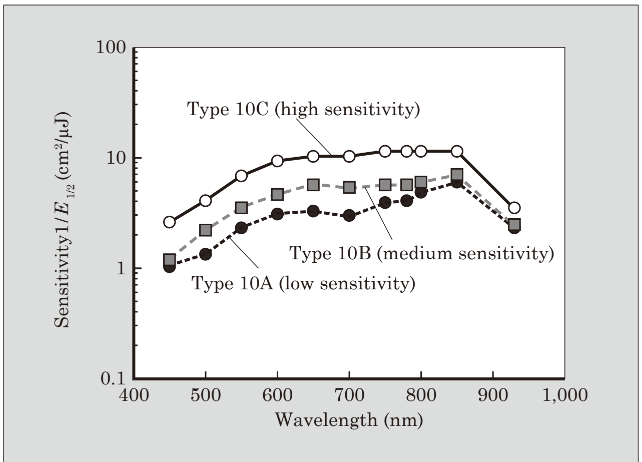


Fig.2 Photo-induced Discharge Characteristics of Photoconductors for Digital Copiers

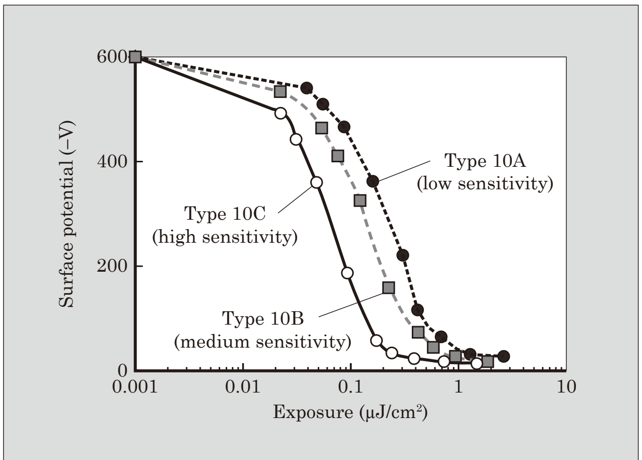


Figure 2 shows the photo-induced discharge characteristics of each type. Type 10C, the high-sensitivity type, has about 50% greater sensitivity than Type 10A, and about 30% greater sensitivity than Type 10B. It also helps improve the energy efficiency of the exposure source.

3.2 High chargeability

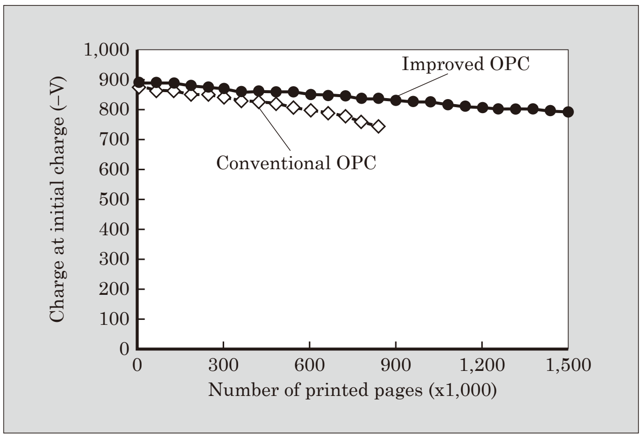
Digital-copier manufacturers offer a wide lineup of digital copiers, from compact, low-speed copiers for small offices/home offices (SOHOs) and personal use, to large, high-speed copiers for office and business use. Manufacturers are working to reduce the first-copy time in their high-speed copiers, in order to provide better on-demand performance. Consequently, OPCs must have high charge performance from the first charge.

The thermally excited carriers in the CGL and carriers resident in each layer and the junctions upon initial charge increase as the number of printed pages increases, and the chargeability decreases correspondingly. Fuji Electric is working to improve the UCL and CTL, in order to improve chargeability, and has sought to optimize the selection and combination ratios of materials with optimum resistance for the UCL. It has developed a charge transport material (CTM) with high charging potential for the CTL, and that optimizes the ionization potential between the CGL and CTL.

As shown in Fig. 3, this greatly improved the charge performance upon initial charge.

Conventionally, a copier would idle for about three to five cycles before beginning the copying process, in order to make up for the lack of charge in the OPC. The improved OPC provides high resolution from the first revolution, which should make it possible to eliminate wasteful idling, improve speed, and conserve energy.

Fig.3 Charge Characteristics of Photoconductors for Digital Copiers upon Initial Charge



3.3 High printing durability

OPCs for digital copiers must have high printing durability; it must be several to ten times higher than that of OPCs for laser printers, in light of the using frequency of copiers and the need for ease of maintenance. Fuji Electric is developing highly durable CTL binders using computational molecular design, in order to commercialize high-durability OPCs that reduce running costs.

(1) Improved electrical characteristics

The repeated exposure of an OPC to corona discharge from the charge-exposure process and to ozone and light generated by that discharge causes chemical changes in the functional materials. This results in deterioration in charging potential or an increase in residual potential, which causes such image defects as low print density and fog.

Fuji Electric has developed a proprietary charge-control agent that suppresses the occurrence of electrical defects in the charge generation layer (CGL) and CTL, in order to reduce the deterioration of charge characteristics and the increase in residual potential. This enables it to offer OPCs that operate stably in a wide range of machine processes.

Figs. 4 and 5 show trends in surface potential and print density when evaluated in typical digital copiers. Fuji Electric has developed OPCs with outstanding operating stability, and less potential fluctuation and fewer changes in image quality than conventional types.

(2) Improved mechanical characteristics

Contact between the OPC and the cleaning blade, charging roller, transfer roller, paper, and toner degrades the mechanical characteristics of the OPCs by causing wear and scratches on the photoconductive layer, and by causing the adherence of toner and paper dust particles. Although the photoconductive layer's susceptibility to degradation varies according to the machine process, it is largely dependent on the performance of the CTL binder, which is a component of the CTL. The performance of the CTL binder is a large factor in determining the useful service life of the OPC. Fuji Electric has introduced equipment for rapidly evaluating the performance of CTL binders, including abrasion and friction testers. With faster evaluation, it has succeeded at greatly improving the performance of its CTL binders.

The binder material in the CTL is molecularly designed to have a polymeric molecular structure and have excellent lubricating properties. This binder material increases the film hardness while reducing the frictional coefficient between the OPC and the cleaning

Fig.4 Printing Characteristics (Surface Potential) of Photoconductors for Digital Copiers

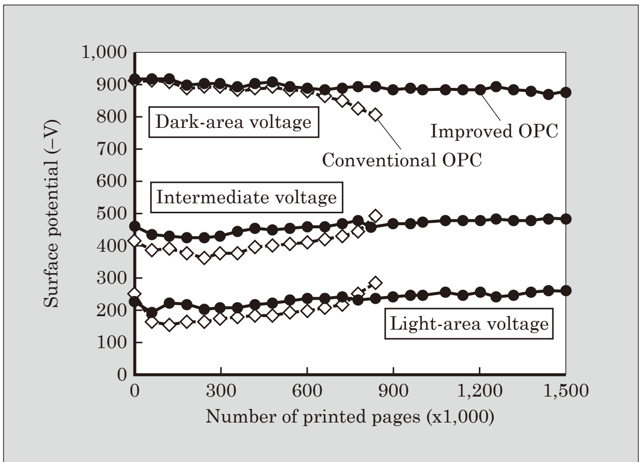


Fig.5 Printing Characteristics (Print Density) of Photoconductors for Digital Copiers

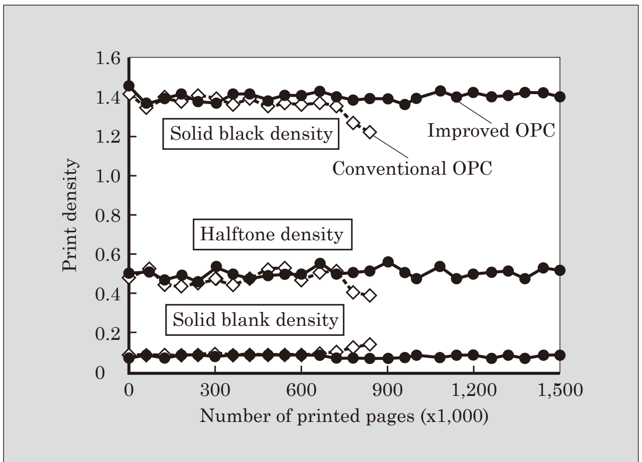


Fig.6 Frictional Coefficient of Photoconductors for Digital Copiers

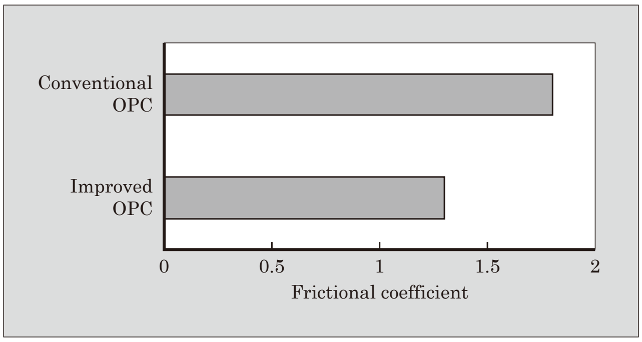


Fig.7 Printing Characteristics (Wear) of Photoconductors for Digital Copiers

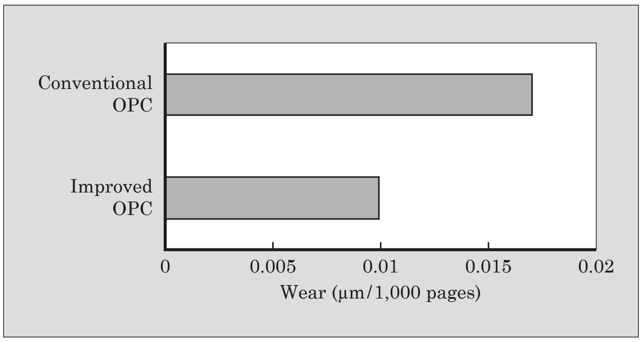
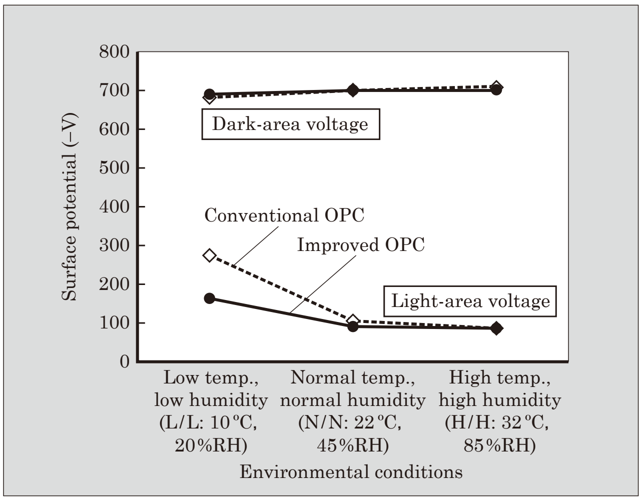


Fig.8 Environmental Dependence of Surface Potential via Process Simulator



blade. As shown in Fig. 6, friction with other contact parts is reduced, thus reducing wear and scratching. As shown in Fig. 7, this OPC has about 40% less abrasion than conventional OPCs. As a result, Fuji Electric's OPCs are suited to the high-speed printing field, as well as light printing.

3.4 High environmental stability

OPCs must have environmental stability in order to support the use of copiers in a wide range of environments.

Fuji Electric optimized the UCL filler performance and binder, and suppressed fluctuations in environment-induced electrical resistance. This ensures that its OPCs remain stable in environments of low temperature and low humidity (L/L), normal temperature and normal humidity (N/N), and high temperature and high humidity (H/H). Figure 8 shows data on the environmental dependency of surface potential from a process simulator. The improved OPC exhibits low fluctuation and favorable characteristics in all environments.

Table 2 Reliability Tests

Test	Description
Electrical characteristics	Ozone exposure test
	Strong light-induced fatigue test
	High-temperature exposure test
	High-humidity exposure test
	Low-temperature exposure test
	Cyclic test of temperature and humidity
Mechanical characteristics	Creep test
	Oil adherence test
	Scratch test

3.5 High reliability

Fuji Electric is performing the reliability testing listed in Table 2 in order to verify the reliability of its OPCs. Each test item conforms to actual copier use. The company develops products after confirming that there are no abnormalities in the characteristics for each test item.

4. Postscript

This paper has described OPCs for digital copiers (Type 10), with a focus on high-durability OPCs developed with the goal of conserving the global environment.

The focus of technical development in the copier market is shifting from monochrome to color copiers, and OPCs must also support color copiers. Additionally, as environmental awareness increases, OPCs are being used that reduce waste through improved durability, and reduce the power consumption of the photographic fixing unit by matching low-melting point toners.

Fuji Electric is committed to accurately assessing the required characteristics, and developing attractive, environment-friendly OPCs that meet the needs of its customers and the market.

Organic Photoconductor Evaluation Technology: Latent Image Evaluation

Koichi Aizawa † **Tomoki Hasegawa** †

ABSTRACT

It is important that printing be made possible at high resolution to make electrophotographic machines faster, color image compatible, and expand the printing field,. Fuji Electric has developed a MASPP (Micro Area Surface Potential Probe) and an EFM (Electrostatic Force Microscope) to understand the mechanism of electrical latent image formation more clearly. The photoconductor surface charge is changed by the irradiation of laser light. MASPP detects the change of the charge as a current induced by it In the case of a high mobility photoconductor, the latent image potential was shown to be spread-out spatially to a greater extent than the potential distribution that corresponds to the exposure. In the case of a low mobility photoconductor, the distribution of surface potential was found to be more precise and similar to the surface potential distribution that closely corresponds to the exposure.

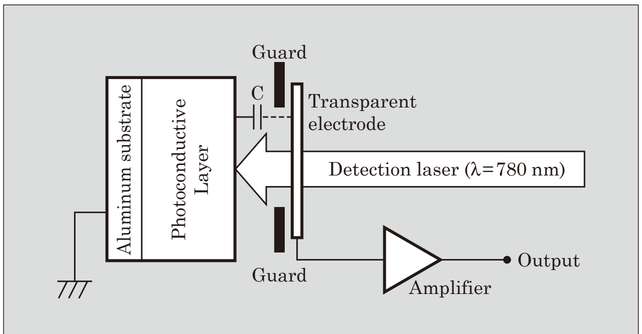
1. Introduction

Electrophotographic devices are increasingly becoming faster and supporting color. It is vital to increase the resolution of electrophotographic devices in order to support photo-quality images in the light-printing field, where growth is expected. The latent-image formation mechanism on photoconductors greatly affects print resolution, and elucidation of this mechanism is vital for improving resolution. Fuji Electric has reported the results of evaluating latent-image formation using a micro area surface potential probe (MASPP)[(1)~(3)], which applies the principle of measuring the changes in the photoconductive surface potential upon illumination with a detection laser as induced current[(4)].

Fuji Electric have improved the exposure system of the MASPP method, and performed measurements with the latent-image formation changed arbitrarily, and triangle-wave exposure applied. Differences between the applied voltage and surface potential on the photoconductor were measured via the surface-potential measurement method using an electrostatic force microscope (EFM), in order to confirm the phenomenon whereby larger the charge mobility causes a larger horizontal spread of surface potential[(1),(2)]. As a result, they confirmed that the surface potential spreads wider than applied voltage in high-mobility photoconductor, and the surface potential is faithful to the applied voltage in low-mobility photoconductors.

This is an important result, showing that it is not possible to rely on higher mobility alone as the direction for designing photoconductors for high-speed machines.

Fig.1 MASPP Principle

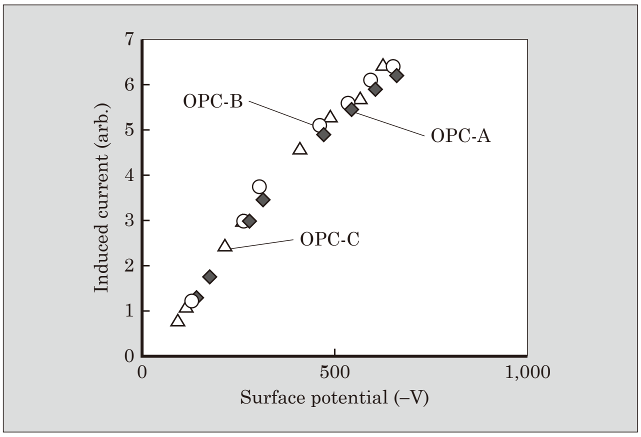


2. The Micro Area Surface Potential Probe (MASPP) Method

2.1 Measuring Equipment and Methods

This section describes the equipment for measuring latent images using the MASPP method.

Fig.2 Relationship between Surface Potential and Induced Current



† MONOTSUKURI Strategy Division Fuji Electric Holdings Co., Ltd.

Figure 1 shows the structure of the probe for measuring the micro area surface potential. A transparent electrode is installed opposite to a charged photoconductive surface forming a capacitor. The surface potential decays, and changes occur, as a result of light exposure (laser with 10 µm diameter and wavelength of 780 nm) passing through the transparent electrode. At this time, the induced current is measured through an amplifier.

Figure 2 shows the relationship between the photoconductive surface potential and the induced current. The surface potential can be detected by measuring the induced current.

For the current research, the source of latent-image exposure light to the photoconductive surface was changed from the laser scanning unit (LSU) of a conventional commercially available laser printer to a line beam with width of 10 µm and length of 4,000 µm. It was possible to create an arbitrary exposure shape by controlling the light power of this beam.

The latent-image potential of a dual-layer negative-charge organic photoconductor when exposed to a triangle waveform was measured, and the changes in the depth and width of the latent image in response to changes to the organic photoconductor's charge transport material (CTM) and the amount of exposure light were investigated.

As shown in Fig. 3, exposure to the triangle waveform was performed, reducing the laser light power linearly from 100% to 0%. At a light power of 100%, the exposure was changed to 100, 133, 166, and 200 µW.

Fig.3 Triangle Waveform Exposure Profile

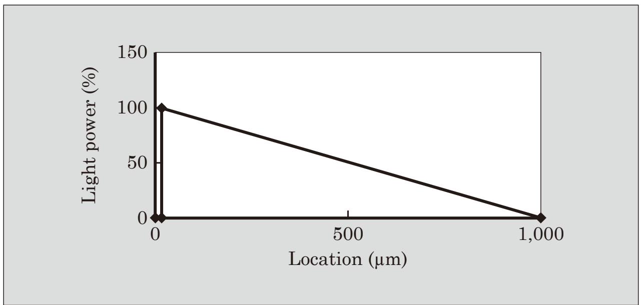


Table 1 Mobility and Photoconductor Properties of Each Sample

CTM	Sample No.	Mobility [10^{-6}cm^2/(V–s)]	E_{300} (mJ/m^2)	E_{100} (mJ/m^2)	V_{r5} (–V)
Low mobility	L-1	1.1	1.70	7.70	31
	L-2	5.4	1.40	2.70	13
	L-3	21.4	1.10	2.20	11
High mobility	H-1	3.1	1.20	3.20	16
	H-2	73.3	1.20	2.50	14
	H-3	106.9	1.20	2.10	10

*E_{300}: Light power required for decay of –600 V to –300 V
E_{100}: Light power required for decay of –600 V to –100 V
V_{r5}: Residual potential after exposure of 50 mJ/m^2

2.2 Measurement Photoconductor

A sample was fabricated, with a structure consisting of a 30 mm diameter aluminum pipe, and the following charge generation layer (CGL) and charge transfer layer (CTL).

CGL: Thytanil phtalocyanine
Poly-vinyl-Buthyral
CTL: Charge transport material (CTM)
Bisphenol Z type Polycarbonate

Two types of charge transport material were used (high mobility and low mobility), in order to investigate the relationship between the CTL's charge mobility and the latent image. Samples with differing charge mobility were further created by changing the mixing ratio of the charge transport material and polycarbonates.

Table 1 shows the mobility and photoconductor properties of each sample. The property definitions are as follows.

E_{300}: Light power required for decay of −600 V to −300 V
E_{100}: Light power required for decay of −600 V to −100 V
V_{r5}: Residual potential after exposure of 50 mJ/m^2

Fig.4 Light Exposure Dependence

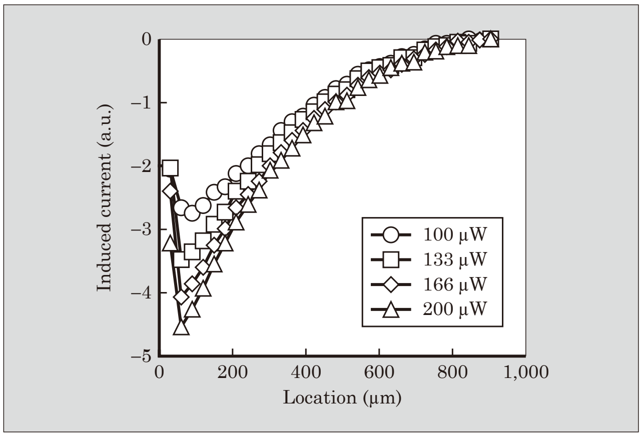
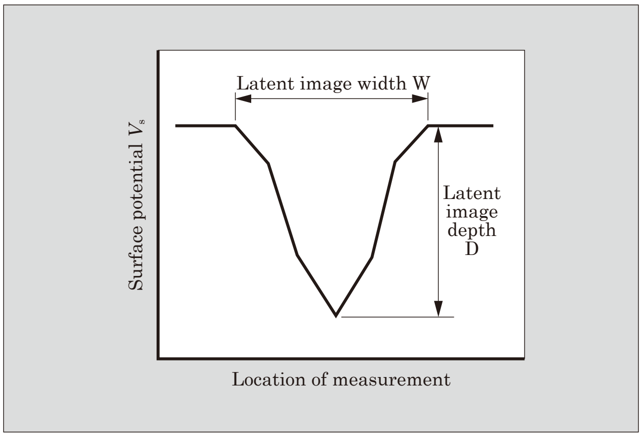


Fig.5 Definitions of Width and Depth in Latent Images



2.3 MASPP Measurement Results and Observations

(1) Light exposure dependence

Figure 4 shows the light-exposure dependence of sample H-3's latent-image potential (∝ induced current). The horizontal axis is the measured location, and the vertical axis is the induced current. A latent image was formed corresponding to the triangle wave. The figure shows that when the light exposure is increased from 100 μW to 200 μW, the induced current increases, and the latent image becomes deeper. At the same time, the width of the latent image also increases in accordance with the light exposure.

The depth and width of the latent image discussed here are as defined in Fig. 5. This is able to explain the decay in surface potential consequent to the increase in light exposure and the increase in density and thickness of the dots or lines in the actual printed image.

Figure 6 shows the latent-image potential (∝ induced current) when the mixing ratio of CTM and resin are changed in the CTL using a low-mobility CTM. At this time, the latent-image formation exposure is 200 μW. The increase in mobility from L-1 to L-3 makes the latent image deeper and wider.

(2) Mobility dependence of latent-image shape

Figs. 7 and 8 show the correlation between the latent-image width and depth of each sample, and the mobility.

Although the width of the latent image increases with the increase in mobility, there is little change in the depth of the latent image. Although the generated carrier in the photoconductive layer may be a large factor in the depth of the latent image, in this experiment, the CGL was kept constant, so it is possible that no difference was noted.

(3) Mobility dependence of latent-image resolution

Next, it was hypothesized that resolution is indicated by the charge level per unit of area, in order to associate the actual printed resolution with the latent-image shape. In order to quantify the resolution, it was defined as follows.

$$\text{Resolution} = \text{depth of latent image} / \text{width of latent image}^2$$

This formula shows that the deeper the latent image, and the smaller its area (proportional to the square of the width), the sharper the latent-image will be rendered. Figure 9 shows the mobility dependence of resolution.

It was shown that as the mobility increases, the resolution decreases.

Fig.6 Changes in Latent Image when Mobility is Changed

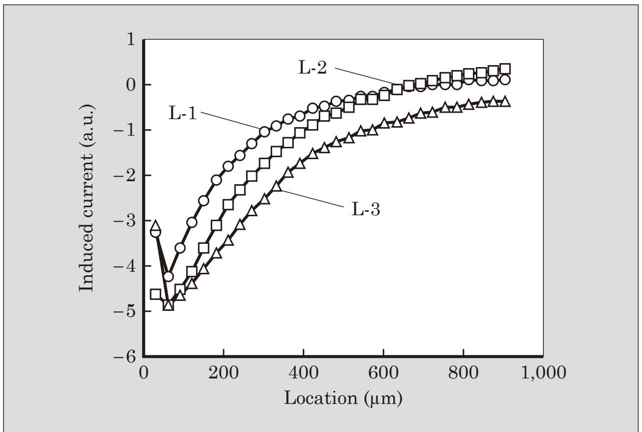


Fig.8 Dependence of Latent Image Width on Mobility

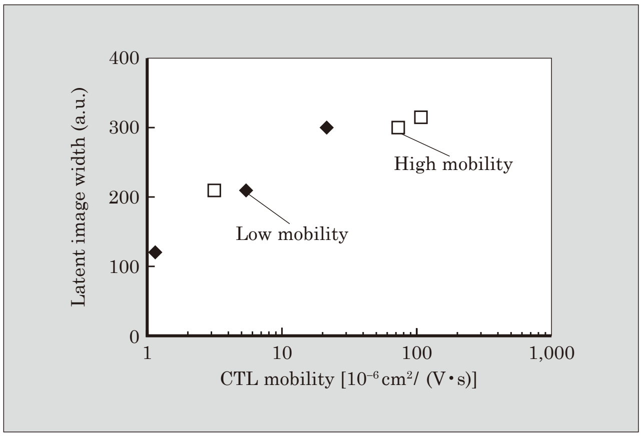


Fig.7 Dependence of Latent Image Depth on Mobility

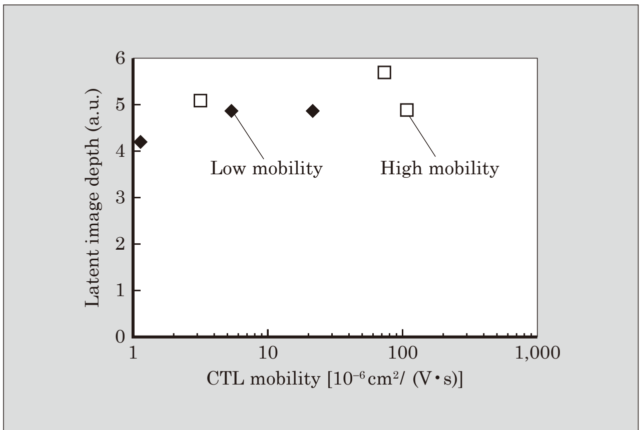
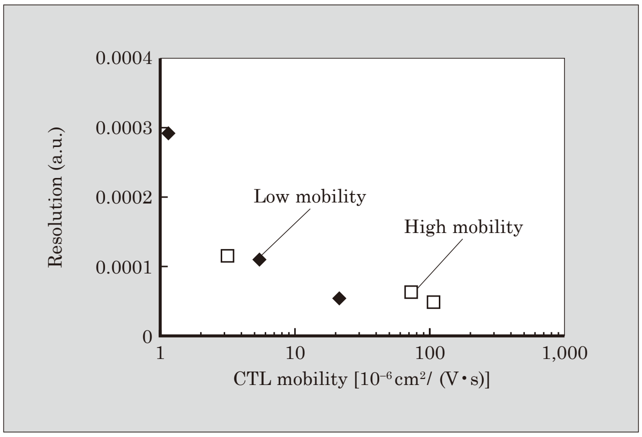


Fig.9 Dependence of Resolution on Mobility



Issue : Photoconductor

3. Electrostatic Force Microscope (EFM) Method

3.1 Principle of EFM Measurement

Figure 10 illustrates the principle of electrostatic force microscopy[(5)~(7)]. Under this method, when a cantilever to which is applied DC bias V_{DC} and AC bias V_{AC} sin ωt approaches a charged sample, the electrostatic induction of the tip generates electrostatic force, which bends the cantilever. The amount of bending is then detected via the optical lever method.

The applied AC bias frequency component $F\omega$ and twice higher frequency component F2ω that act on the cantilever are expressed by the following formula, using the parallel plane model in Fig. 11.

$$F_{\omega}=\frac{V_{DC}-pd_0/\varepsilon_0}{\{d-(1-\varepsilon_0/\varepsilon)d_0\}^2}\varepsilon_0 SV_{AC}\sin\omega t \quad \cdots\cdots (1)$$

$$F_{2\omega}=\frac{1}{4\{d-(1-\varepsilon_0/\varepsilon)d_0\}^2}\varepsilon_0 SV^2_{AC}\cos 2\omega t \quad \cdots\cdots (2)$$

$F\omega$: Applied AC bias frequency component acting on the cantilever
$F2\omega$: Twice higher frequency component acting on the cantilever
V_{DC} : DC bias, tip potential
V_{AC} sinωt : AC bias
d : Distance between tip end and bottom electrode
d_0 : Sample thickness
d-d_0 : Distance between tip and sample
ε : Dielectric permittivity
ε_0 : Vacuum permittivity
$\rho\ d_0/\varepsilon$: Sample potential
S : Surface area of tip end

Fig.10 Principle of EFM Measurement

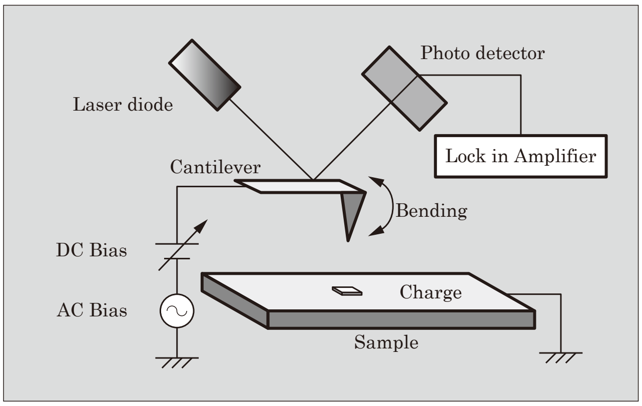
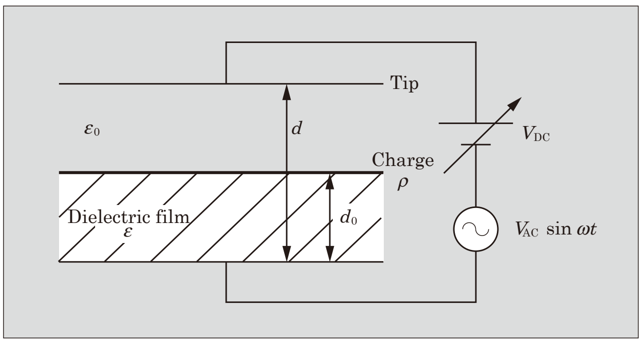


Fig.11 Parallel plane model



If the distance between the tip and sample (d-d_0) and dielectric permittivity ε are known, then it is possible to measure $F\omega$ keeping V_{DC} constant, and calculate sample potential $\rho d_0/\varepsilon$ via formula[(1)].

When measuring with the high voltage, there is a large difference in the potentials of the tip V_{DC} and the sample, and there is a risk of discharges. Here, it is possible to perform measurements without causing discharge, by a zero voltage method calculating the V_{DC} at which $F\omega=0$.

The cantilever was made by using the focused ion beam (FIB) method on 5 μm thick nickel foil.

3.2 Details of Sample for EFM Method

Here, in order to discuss the movement of charge in the charge transport layer, a sample was fabricated by coating an aluminum substrate with a charge transport layer (film thickness 5 μm) consisting of CTM and a binder resin (Z type polycarbonate) in a 1-to-1 mixture by mass. The charge mobility of the sample as calculated by the Time of Flight method is as follows.

a-1: 10^{-4} cm^2/(V·s); High-mobility sample
d-1: 10^{-5} cm^2/(V·s); Low-mobility sample

The electrodes were formed via vacuum deposition of aluminum on the charge transport layer. Details are shown in Fig. 12.

Electrodes A, B, and C are all connected to different power sources, and potential can be applied assuming a latent image.

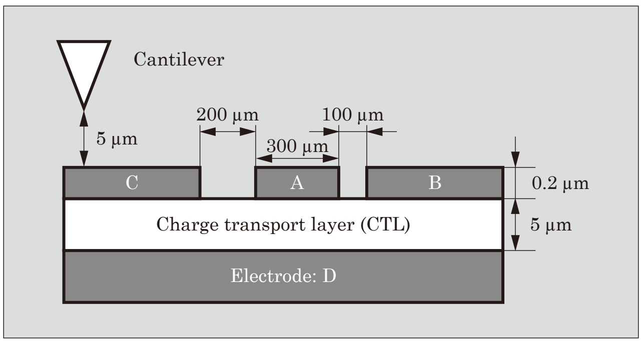
The distance between the cantilever and sample surface was set at 5 μm, and the measurement was performed by moving horizontally at a 2 μm pitch.

3.3 Results of EFM Measurement and Observations[(8)]

(1) Changes in potential in the charged and non-charged areas

A voltage −150 V was applied to electrode A only (equivalent to general OPC voltage boundary of 30 V/μm), and no voltage was applied to electrodes B or C.

Fig.12 Structure of Samples for EFM Measurement



The results are shown in Figs. 13 and 14. The interval between the first and second times is 40 minutes. The low-mobility sample had potential close to the applied voltage, and there was also little difference between the first and second times (Fig. 13).

Meanwhile, for the high-mobility sample, the potential between electrodes A and B, and between electrodes A and C rose starting from the first time, as an effect from electrode A. On the second time, it spread even further in the horizontal direction (Fig. 14).

It is possible that this result suggests that high-mobility samples are susceptible to horizontal charge mobility.

(2) Changes in the charged area and intermediate part of the charged area

Figs. 15 and 16 show the results when −150 V were applied to electrodes A and B, and no voltage was applied to electrode C.

In the low-mobility sample, there is a −30 V valley between electrodes A and B on the first time, and the potential is near to the applied voltage. On the second time, the valley becomes shallower, at −70 V, indicating that the potential contrast may have favorable reproducibility.

This matches the results to date, with high-definition latent images in low-mobility photoconductors.

Meanwhile, with the high-mobility sample, electrodes A and B had the same potential between them on the first measurement, and no valley was noted in the potential. This matches past results in which there is a large horizontal spread in the latent image in high-mobility photoconductors.

These results suggested the possibility that charge is being transported from the charged electrode to the non-charged electrode. Thus voltage (−150 V) was applied to electrodes A and B, making them charged electrodes, and the dependence of the potential of the non-charged area between electrodes A and B on elapsed time was investigated. The results are shown in Fig. 17.

In the low-mobility sample, although the potential was found to gradually rise as voltage was applied to electrodes A and B, it did not reach the applied voltage (−150 V) even after 2,200 seconds.

In the high-mobility sample, a rapid rise in potential was observed, reaching the applied voltage after 136 seconds. It is possible that this was because the charge applied to electrodes A and B is easily transported horizontally on the surface or in the charge transport layer.

These results have shown a way ahead for materials development.

Fig.13 Surface Potential of Low Mobility Sample

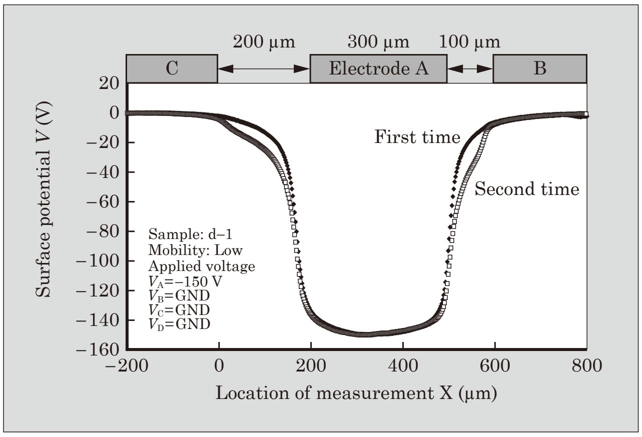


Fig.15 Surface Potential of Low Mobility Sample

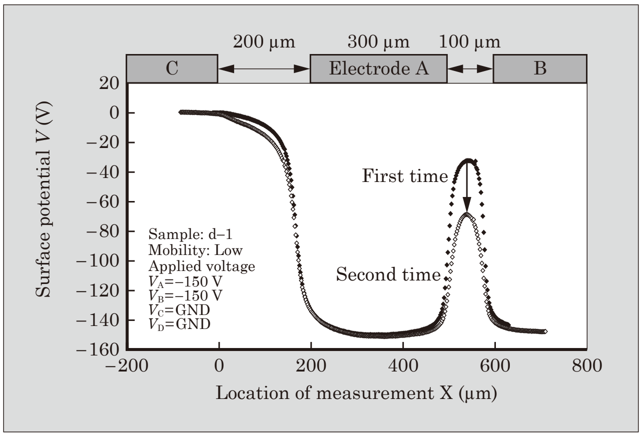


Fig.14 Surface Potential of High Mobility Sample

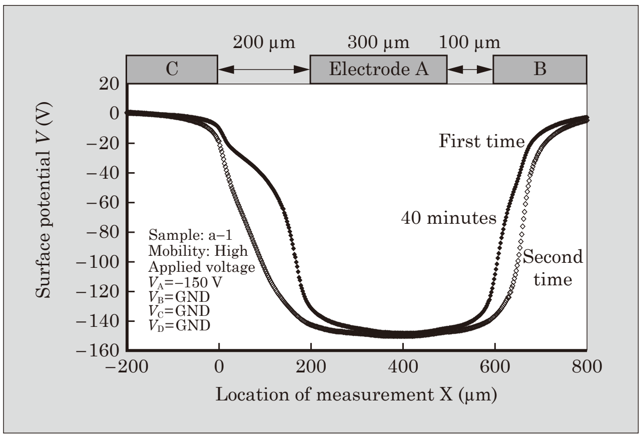


Fig.16 Surface Potential of High Mobility Sample

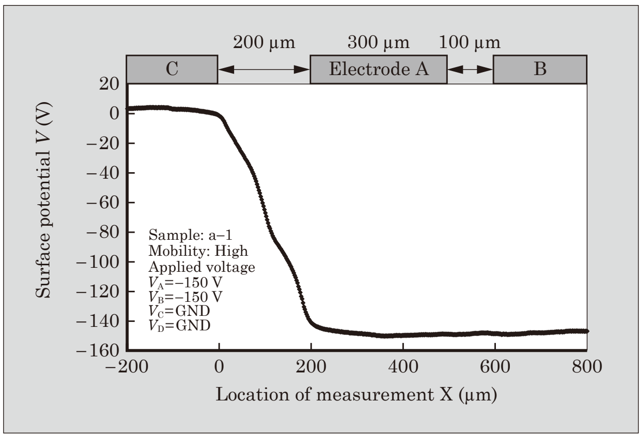
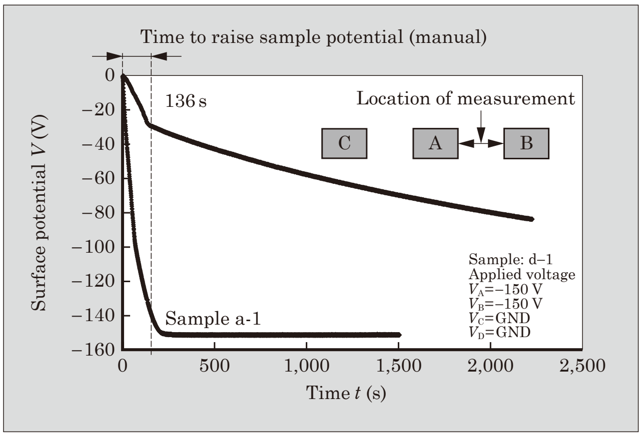


Fig.17 Changes over Time of Surface Potential at Intermediate Point between Electrodes A & B



4. Conclusions

(a) Latent images corresponding to a triangle waveform exposure profile were obtained, enabling arbitrary exposure light shapes to be formed via a 10 µm-wide line beam using the MASPP method. The latent images were found to be dependent on the light exposure power and photoconductor properties.

(b) Increasing the photoconductor charge mobility was found to rapidly increase the latent-image width and slightly increase the latent-image depth, and caused the latent-image resolution to fall.

(c) Using the EFM method, it is possible to measure surface potential with a resolution of 2 µm.

(d) The status of the surface potential on the charge transport layer in response to applied voltage differed according to the charge mobility. With a low-mobility charge transport layer, the surface potential was near to the applied voltage, while with a high-mobility charge transport layer, it spread horizontally beyond the applied voltage.

(e) From these results, the authors conclude that charge has high horizontal mobility in high-mobility photoconductors, causing large widening of the latent image.

5. Postscript

Moving forward, Fuji Electric will work to quantify the charge transport path and level of charge transport, by collecting data on samples with differing mobility, and clarifying the charge-transport mechanism that contributes to changes in surface potential. Fuji Electric further intends to utilize this research to help offer photoconductors that achieve high resolution from the contrast with the latent-image formation mechanism.

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