Material Technology for Organic Photoconductors

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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

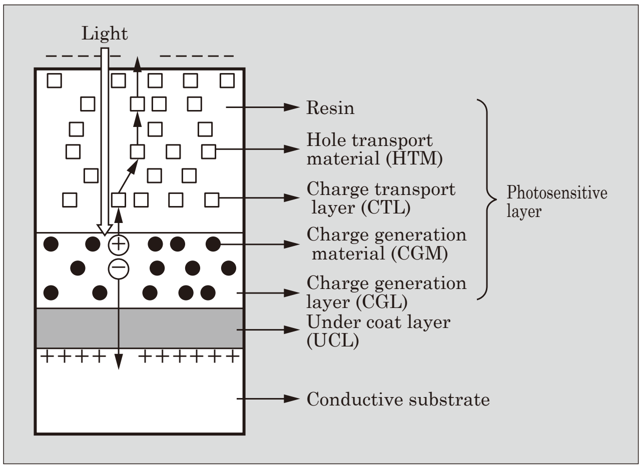
The photoconductor products developed by Fuji Electric are helping to make printers, copiers, and other electrophotographic devices more energy efficient and friendly to the global environment.

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.

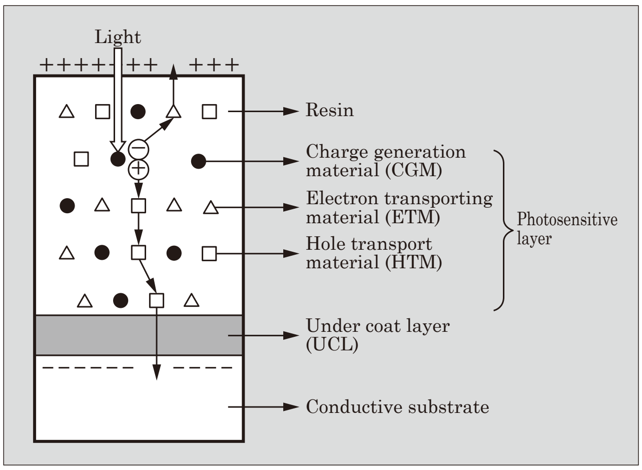
Fig.1 Layer Composition and Materials of Negative Charge Multilayer Organic Photoconductors



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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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

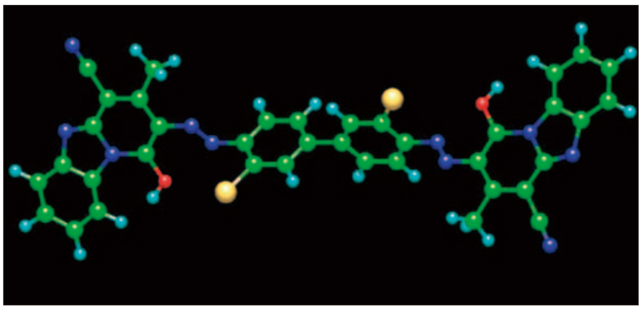


Fig.4 Environmental Dependence of Moisture Absorption

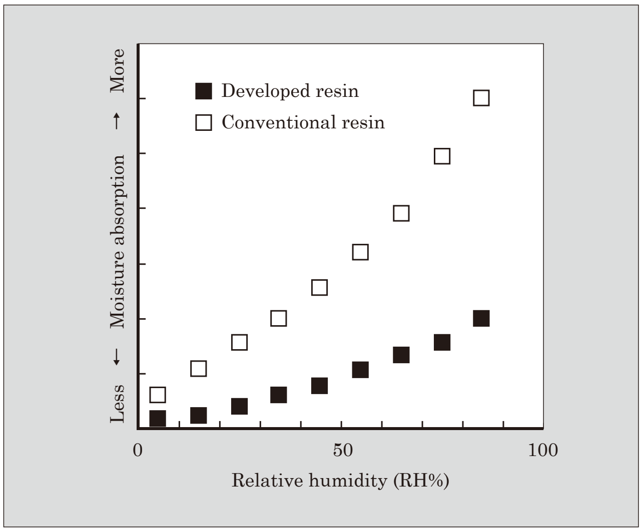
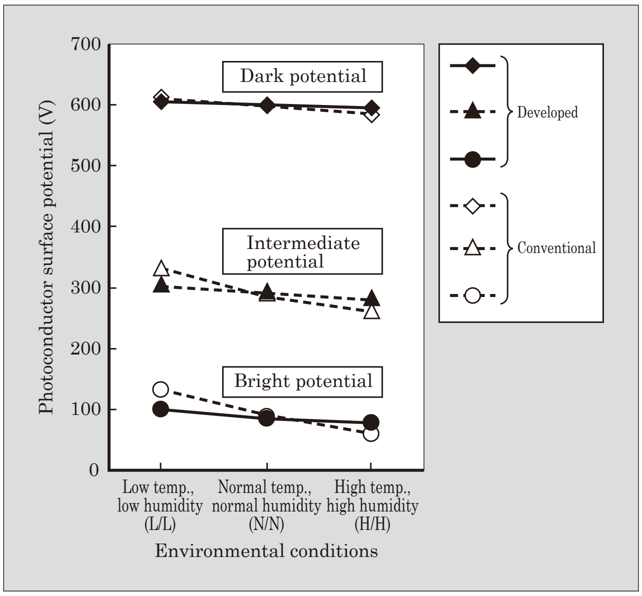


Fig.5 Actual Environmental Properties example of Developed OPC



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.

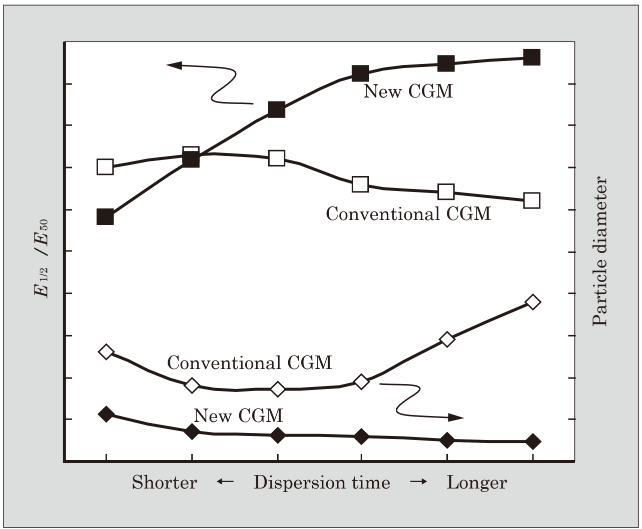
(2) Designing CGL materials

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 μJ/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

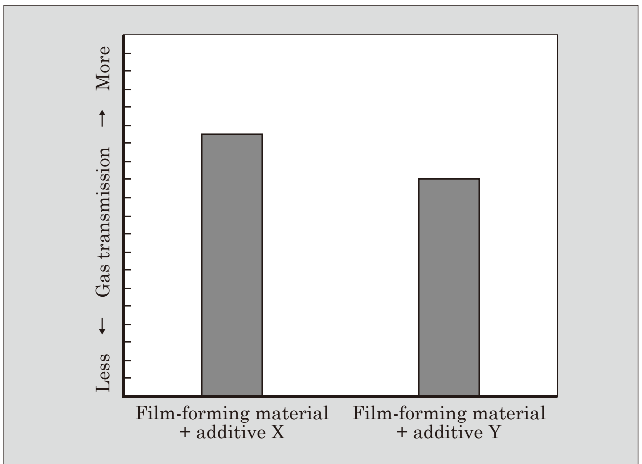
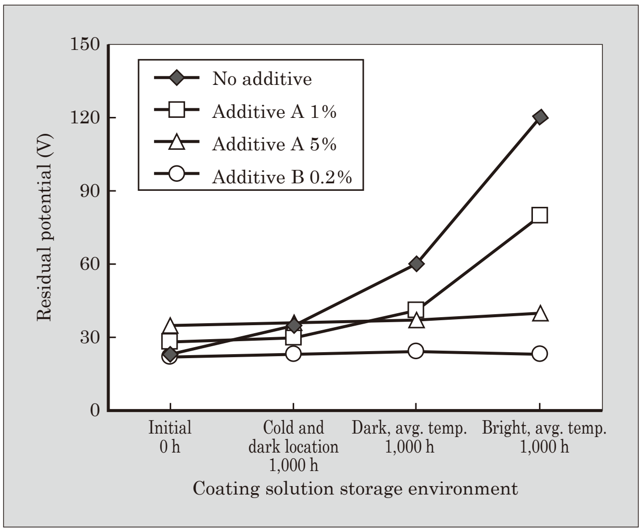


Fig.8 Sample Technology for Improving Coating solution Stability



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.

References

(1) E. J. Corey, Xue-Min Cheng. The Logic of Chemical Synthesis. Wiley, New York, 1995.

(2) Suzuki, A. Organoborane coupling reactions (Suzuki coupling). Series B: Physical and Biological Sciences. 2004, vol. 80, no. 8, pp. 359-371.

(3) Patent Registration Numbers USP5837410, KRP455821.