Material Technology for Organic Photoconductors

Yoichi Nakamura †
Seizo Kitagawa †
Shinjiro Suzuki †

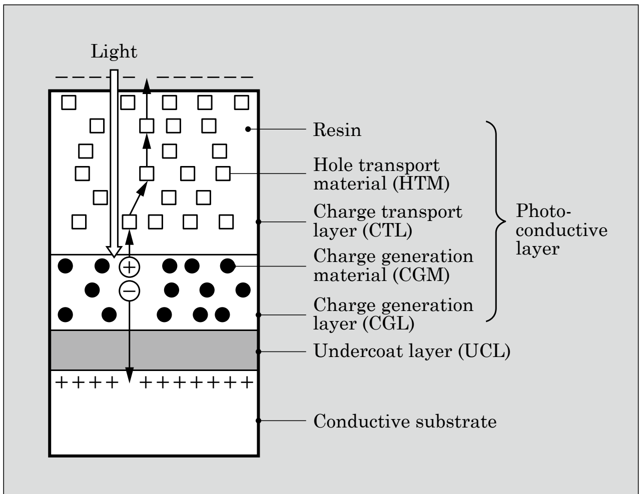
1. Introduction

In recent years, as the trends toward digitization, coloration and network connectivity have advanced for printers, copiers, facsimile machines, printing presses and other electrophotographic equipment equipped with photoconductors, government and business documents as well as personal documents are increasingly highly dense and contain large amounts of information, and the number of pages to be output is also increasing.

Accompanying these market trends are requests for photoconductors to provide higher sensitivity, higher responsiveness, higher resolution and higher stability, and to be smaller in size and have lower cost. In order to satisfy these requests, Fuji Electric is commercializing organic photoconductors having various characteristics.

This paper presents an overview and describes the characteristics and progress of materials technology and chemical technology, which are fundamental technologies for these organic photoconductors.

Fig.1 Layer structure of negative charge multilayer type OPC



† Fuji Electric Device Technology Co., Ltd.

2. Organic Photoconductors

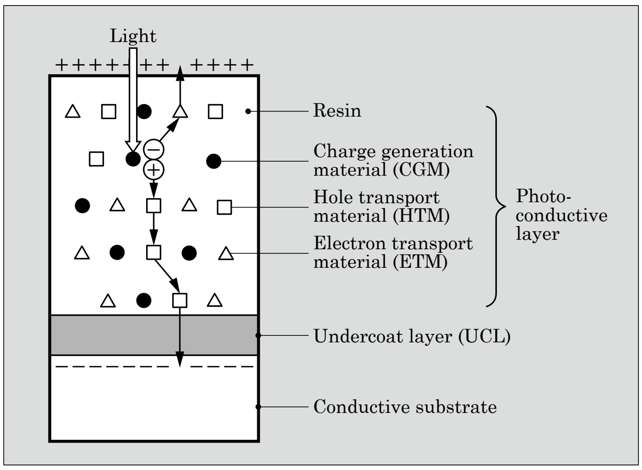
Organic photoconductors (OPCs) utilize the potential difference created on a photoconductive surface to form an image, and in principle, the polarity of the potential, whether positive or negative, makes no difference.

An OPC having an image forming potential that is positive is called a positive charge type OPC, and if negative, is called a negative charge type OPC. Figure 1 shows a negative charge multilayer type OPC, and Fig. 2 shows the layer structure and operating principles of a positive charge monolayer type OPC.

The negative charge multilayer type OPC has a function-separated multilayer structure and is fabricated by first providing an undercoat layer (UCL) made of resin or the like on a conductive substrate such as an aluminum tube, and then providing a charge generation layer (CGL), formed from charge generation material (CGM) and resin or the like, on the UCL, and then providing a charge transport layer (CTL), formed from a hole transport material (HTM), which is a type of charge transport material (CTM), and resin or the like, on the CGL.

The positive charge monolayer type OPC is fabricated by providing, as necessary, a UCL made of resin or the like on a conductive substrate such as an alumi-

Fig.2 Layer structure of positive charge monolayer type OPC



num tube, and then providing a photosensitive monolayer of CGM, HTM, and electron transport material (ETM), which is a type of CTM, on the UCL.

Moreover, positive charge multilayer type OPCs are also being developed, and have a structure, for example, in which a CTL formed from HTM, resin and the like is provided between the UCL and photosensitive layer of the positive charge monolayer type OPC.

When the surface of a photosensitive layer is charged by corona discharge or contact electrification and then exposed, both positive and negative charges are generated at the CGM. The positive charges travel through the HTM, and in the case of a negative charge type OPC, arrive at the photosensitive layer surface, or in the case of a positive charge type OPC, the positive charges pass through the CTL and UCL and arrive at the substrate. On the other hand, negative charges, in a negative charge type OPC, pass through the UCL and arrive at the substrate, while in a positive charge type OPC, the negative charges travel though the ETM and arrive at the photosensitive layer surface. As a result, the surface charge on a photoconductor is neutralized, and the potential differences between exposed and unexposed areas cause the formation of electrostatic latent images. Subsequently, latent images are visualized with the toner (colored resin ink powder), and then processes for transferring, heating, melting and fixing the toner to paper are performed to generate a hard copy.

3. Material Technology, Chemical Technology

3.1 OPC material

Table 1 lists the main materials used in OPCs. Such materials include UCL material, functional materials such as CGM, HTM, ETM and the like, film formation material such as various resins, additives for high-performance, etc.

For OPCs to become widely accepted in the marketplace, the performance of each material, i.e., functional material, film formation material, additives, etc., must be designed for optimal mutual balance, and this is one of the challenges of OPC materials technology. Fuji Electric is able to leverage its proprietary materials technology to not only provide materials that satisfy current market needs, but also to provide new functions that expand the market.

(1) UCL materials

UCL materials are requested to provide such diverse functions as adhesion with 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 with conductive materials, film formation materials, additives, and the like.

Fuji Electric uses proprietary molecular design technology to develop and apply new high-performance film formation materials, and aiming to realize even higher resistance to humidity and higher resistance to dielectric breakdown, continues to advance the development of new materials.

(2) CGL materials

CGL materials are requested to provide such diverse functions as adhesion with the UCL, a large quantum effect in response to the exposure light, charge blocking, easy application of an overcoat layer, and stability of the CGL coating solution. These functions are realized with charge generation materials, film formation materials, additives, and the like.

Fuji Electric uses proprietary synthesis reaction technology and process control technology to develop and apply high-performance and highly stable charge transport materials. Aiming to achieve compatibility with even higher sensitivities and color gamma characteristics, Fuji Electric continues to advance the development of new materials.

(3) CTL materials

CTL materials are requested to provide such diverse functions as adhesion with the CGL, good charge retention, good charge injection performance, good transport of the injected charge, printing durability, resistance to oxidizing gases, resistance to greases and oils, and stability of the CTL coating solution. These

Table 1 Typical OPC materials

Layer		Constituent material	
Photosensitive layer	Charge transport layer (CTL)	Hole transport material (HTM)	Arylamines, hydrazones, stilbenes, benzidines, etc.
		Electron transport material (ETM)	Azoquinones, etc.
		Film formation material	Polycarbonates, polyesters, polystyrenes, etc.
		Additive	Materials for enhancing photoconductor characteristics, ancillary materials for film formation, materials for suppressing deterioration of the coating solution, etc.
	Charge generation layer (CGL)	Charge generation material (CGM)	Phthalocyanines, azos, etc.
		Film formation material	Polyvinylacetates, polyketals, etc.
		Additive	Materials for enhancing photoconductor characteristics, ancillary materials for film formation, materials for suppressing deterioration of the coating solution, etc.
Under coat layer (UCL)		Conductive material	Metal oxides, etc.
		Film formation material	Polyamides, polyesters, melamines, etc.
		Additive	Materials for enhancing photoconductor characteristics, ancillary materials for film formation, materials for suppressing deterioration of the coating solution, etc.

functions are realized with charge transport materials, film formation materials, additives, and the like.

Fuji Electric uses proprietary molecular design technology to develop and apply additives that prevent the deterioration of coating solutions and OPC and additives that enhance durability. Aiming to achieve even higher durability and higher image quality, Fuji Electric continues to advance the development of new materials.

3.2 Molecular design technology

Figure 3 shows an example of the molecular design process flow. In the past, this design work was implemented experimentally and then verified.

In recent years, as a result of improved computational algorithms and higher speed computers, computer-assisted molecular design technology has been utilized in practical applications.[1] Fuji Electric is installing molecular design systems, and is configuring proprietary hardware, improving software, setting parameters, and analyzing data in accordance with OPC materials to establish computer-assisted molecular design technology and to shorten the development time. Aiming to further increase OPC functionality, this computer-assisted molecular design technology is being applied to develop such new materials as functional materials, polymeric materials, additives and the like.

3.3 Synthesis technology

(1) Synthesis reaction technology

Molecularly-designed OPC material is synthesized by chemical techniques, and a synthesis reaction having the highest possible purity and yield must be selected.

For example, high purity and high yield synthesis reactions have evolved using synthesis route design technology such as retrosynthesis[2], which deconstructs a final target material to identify constituent raw materials, and innovative high reactivity reactions such as Suzuki reactions[3] that use new catalysts.

Fuji Electric also uses appropriate catalysts, which are an important element of Suzuki reactions, to establish highly functional, low cost synthesis reactions that are also safe and that restrict sudden increases in the synthesis reaction temperature.

(2) Process control technology

The process control during synthesis requires a shift from the perceived emphasis on chemical material synthesis to that of electronics material synthesis.

Figure 4 shows an example of temperature control during a synthesis reaction. For a set value, OPC material having a certain function could not be synthesized under the condition of a $\pm 0.5\,°C$ temperature allowance during a stable reaction, but under the condition of a $\pm 0.1\,°C$ temperature allowance, a material having the intended function was obtained with a high yield.

Fuji Electric utilizes plant technology and process control technology to manufacture OPC material according to the precise process control for synthesis reactions as used by electrical machinery manufacturers.

3.4 Purification technology

Table 2 lists an example of purification technology. Purification technology is essential for realizing the full functionality of an OPC.

Fuji Electric utilizes individual purification tech-

Fig.4 Relation between process temperature control and yield

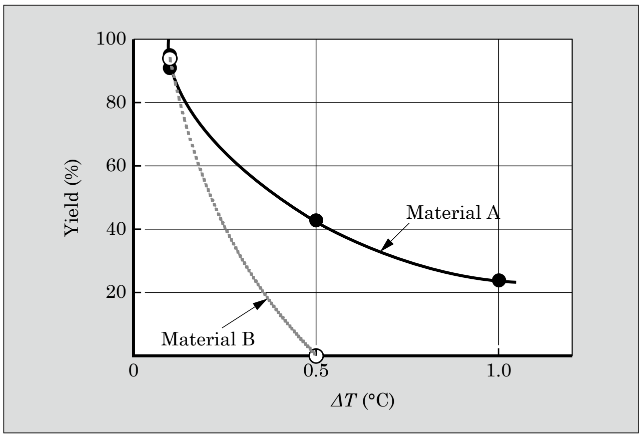


Fig.3 Example of molecular design process flow

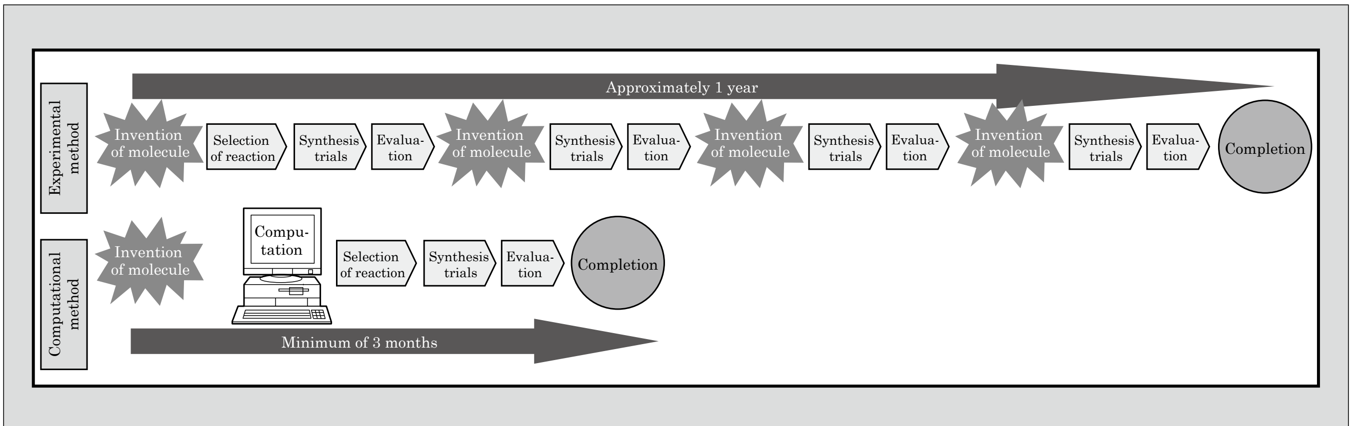


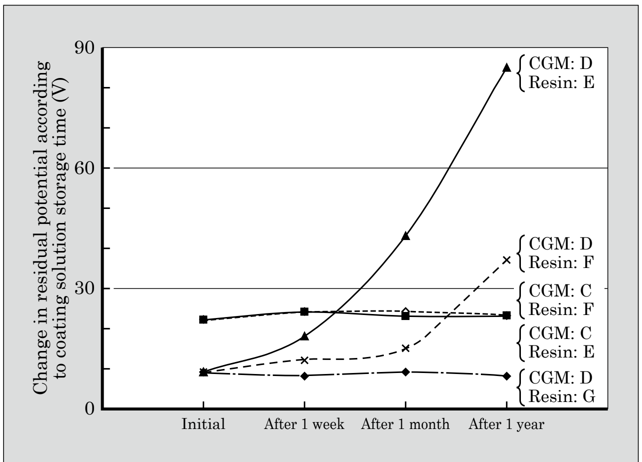
Table 2 Typical purification technology

Purification principle	Purification method
Solubility	Recrystallization, etc.
Distribution of absorption and desorption	Charcoal absorption, alumina absorption, silica gel absorption, zeolite absorption, column chromatography, etc.
Boiling point	Distillation at normal pressure, vacuum distillation, etc.
Sublimation point	Vacuum sublimation, etc.

Table 3 Typical material inspection technology

Inspection-related technology	Inspection method
Separation technology	High performance liquid chromatography, ion chromatography, gel permeation chromatography, etc.
Optical analysis technology	Infrared absorption spectra, UV-VIS absorption spectra, X-ray diffraction spectra, atomic absorption spectra, spectra of laser light scattered by particles, etc.
Thermal analysis technology	Melting point, differential scanning calorimetric spectra, etc.
Mass analysis technology	Mass spectra, time-of-flight mass spectra, etc.

Fig.5 Deterioration-suppressing effect of coating solution



nologies such as recrystallization, column chromatography, distillation, and sublimation according to the intended objective, and carefully monitors clean room and plant site conditions and controls the water and air quality to maintain and improve quality.

3.5 Materials inspection technology

Table 3 shows an example of materials inspection technology. Various technologies, such as chromatographic analysis technology, optical analysis technology, thermal analysis technology, mass analysis technology, and the like are used according to the objective.

Moreover, about petroleum-derived materials, depending on where crude oil for their ingredients was produced, whether in Saudi Arabia, Sumatra, Texas, the North Sea or elsewhere, despite appearing to be the same compounds, they often exhibit different behavior during a synthesis reaction or during OPC production, and therefore the inspection of materials is important.

Fuji Electric believes materials inspection technology to be important in order for electronic materials to realize enhanced functions, stable quality and lower cost in OPCs, and also performs strict inspections according to a list of inspection items.

Table 4 Safety verification system

Verification stage	Verifying organization	Verification method
Molecular design	Fuji Electric	Elimination of known dangerous structures
Synthesis design	Fuji Electric	Verification of raw material impurities, by-products, etc.
Coating solution design	Third party	Ames test, acute toxicity, etc.
Photoconductor design	Third party	Test method suited for laws of destination country

3.6 Coating solution technology

Figure 5 shows an example of a dispersion enhancement technology, which is one type of coating solution technology. The coating solution is placed into an environment in which it is extremely susceptible to deterioration due to contamination by and exposure to dust, aluminum filings, coating film filings, coating applicator filings, moisture, oxygen and the like.

With the development of a deterioration-suppressing additive for the coating solution, Fuji Electric is able to select a wider range of suitable materials since the deterioration of coated OPC material can be prevented. Accordingly, the coating solution has been perfected for realizing enhanced functionality and stabilized quality in an OPC.

3.7 Safety technology

Table 4 lists the safety verification systems. Safety verification is essential for new OPC material.

Safety, in accordance with the laws of the destination country and Fuji Electric's regulations, is verified by third parties at key development sites.

3.8 Environmental technology

Table 5 lists the major environment-related laws. As interest in the international environment increases, compliance with new laws in the EU (European Union) and China, and with the new toxic material designation of organic cyano compounds in Japan is necessary.

By developing and applying materials having a low environmental impact, a deterioration-suppressing additive for the coating solution, a solvent recovery system, and the like, Fuji Electric has realized a manufacturing system that is sensitive to the global environment, and has a low environmental impact and generates low amounts of waste.

Table 5 Environment-related laws, etc.

Country/ organization	Environment-related laws, etc.
Japan	Law Concerning Examination and Regulation of Manufacture and Handling of Chemical Substances (Chemical Substances Control Law) Existing chemical substance list
USA	TSCA: Toxic substances control act Existing chemicals list (TSCA inventory)
EU (European Union)	Council directive 92/32/EC amending for the seventh time Directive 67/548/EEC relating to the classification, packaging and labeling of dangerous substances EINECS: European Inventory of Existing Commercial Chemical Substances
	RoHS: Restriction of the use of certain Hazardous Substances in electrical and electronic equipment
China	New chemical substance environmental control regulation Name recording of existing chemical substance
	The Administration on the Control of Pollution Caused by Electronic Information Products

3.9 Evaluation technology

Table 6 lists photoconductor evaluation technology. Appropriate evaluation technology is essential for the development of OPC materials.

Fuji Electric possesses technology for evaluating the electrical characteristics, image characteristics, temperature and humidity characteristics, and durability characteristics of photoconductors since selenium photoconductors, and is moving ahead with development that combines materials technology and photoconductor technology.[4]

4. Postscript

Utilizing proprietary materials technology and chemical technology, Fuji Electric develops and produces OPC materials, and then supplies them as OPC products.

These OPC materials are being developed and produced using proprietary computer-assisted molecular design technology and materials technology, and by collectively using the plant technology, process control technology and other chemical technologies of affiliated and partner companies.

In the future, Fuji Electric intends to raise the overall functional level of OPC materials so as to enhance the image quality, ease of use, cost-performance tradeoff and environmental friendliness of equipment that uses OPCs and to increase the level of customer satisfaction.

Table 6 Evaluation technology

Evaluation item	Measuring instrument, etc.
Initial electric characteristics	Photoconductor potential simulator
Photo-induced discharge characteristics	Photoconductor potential simulator
Resistance to oxydizing gases	Photoconductor potential simulator
Strong light fatigue electrical characteristics	Photoconductor potential simulator
Mobility	Charge time-of-flight tester
Electrical characteristics of actual machine	Commercially available printer, etc.
Transfer image characteristics	Photoconductor transfer simulator
Temperature/humidity environment characteristics	Photoconductor potential simulator
Coating solution lifespan characteristics	Photoconductor potential simulator
Durability characteristics	Photoconductor durability simulator
Appearance characterization	Color difference meter, etc.
Surface crack characteristics	Grease and oil tester
Photosensitive layer adhesion characteristics	Cross-cut tester (Japanese Industrial Standard)

References

(1) Cramer, C. J. Essentials of Computational Chemistry, Wiley, Chichester, 2005; Second Edition. (ISBN 0- 470-09181-9)

(2) Corey, E. J. Cheng, X. M. The Logic of Chemical Synthesis, Wiley, New York, 1995. (ISBN 0-47111-594-0)

(3) Suzuki, A. Proceedings of the Japan Academy, Series B: Physical and Biological Sciences. 80 (8), 2004, p.359-371. (ISSN 0386-2208)

(4) Registed patent numbers, USP5837410, KRP455821.