Material Technology for Organic Photoconductors

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1. Introduction

With advances in the digitization, coloration and network connectivity of photoconductor-equipped devices such as printers, copiers, facsimile machines, variable printing presses, and the like, more and more corporate and personal documents that contain higher densities and greater amounts of information are being handled.

These market trends request 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 of material technology and chemical technology, which are the fundamental to such organic photoconductors.

2. Organic Photoconductors

Organic photoconductors (OPCs) use the potential difference created on their photosensitive 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 known as a positive charge OPC, and if negative, is known as a negative charge OPC. Figure 1 shows a negative charge multi-layer type OPC, and Fig. 2 shows the layer structure and operating principle of a positive charge mono-layer type OPC.

The negative charge multi-layer type OPC is fabricated by first forming an under coat layer (UCL) made of resin or the like on a conductive substrate such as an aluminum tube. Next, a charge generation layer (CGL) formed from charge generation material (CGM) and resin or the like is provided on top of the UCL, and then 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 is provided on the CGL to fabricate a photosensitive functional multi-layered structure.

The positive charge mono-layer type OPC is fabricated by first forming a UCL made of resin or the like on a conductive substrate such as an aluminum tube, and then forming a layer of CGM, HTM, and electron transport material (ETM), which is a type of CTM, to fabricate a photosensitive mono-layer structure.

Fig.1 Layer structure and operating principles of negative charge multi-layer type OPC

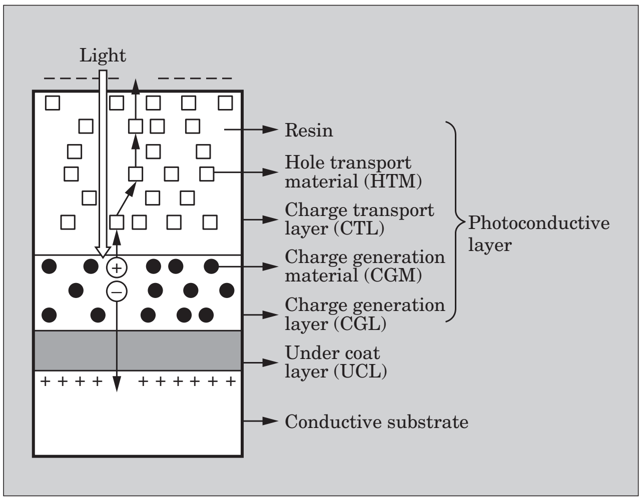
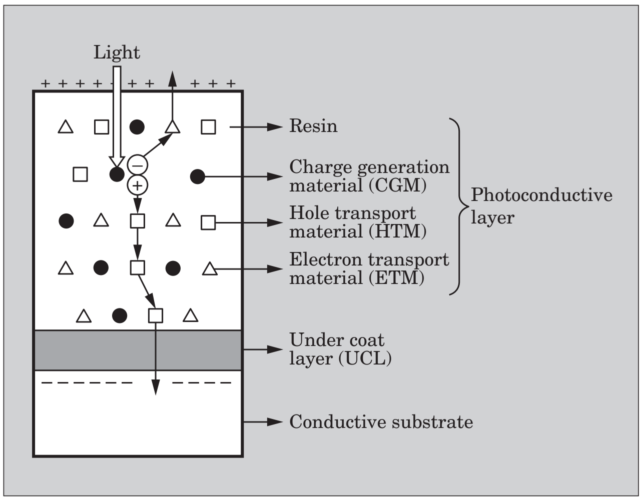


Fig.2 Layer structure and operating principles of positive charge mono-layer type OPC



When the surface of a photoconductive layer is charged and then exposed, both positive and negative charges are generated at the CGM. The positive charges travel in the HTM, and in the case of a negative charge type OPC, arrive at a photoconductive layer, while in the case of a positive charge type OPC, the positive charges pass through the 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 in the ETM and arrive at a photoconductive layer. Thus, charge on a photosensitive surface is neutralized, and the potential difference with surrounding areas causes an electrostatic latent image to be formed. Then, visualization of the latent image by the toner (colored resin ink powder) and the transfer, heating, melting and fixing of the toner to paper complete the printing process.

3. Material Technology and Chemical Technology

3.1 OPC materials

Table 1 lists the main materials used in an OPC. Functional materials of the UCL, CGM, HTM, ETM and the like consist of film formation material, such as various resins, and high-performance additives.

For OPCs to be widely accepted into the marketplace, the performance of each material, i.e., functional material, film formation material, additives, etc., must be designed for optimal balance. This is one of the complex aspects of OPC material technology, and Fuji Electric provides materials with market-leading new performance capabilities by applying its proprietary materials technology to meet market needs.

3.2 Molecular design technology

Figure 3 shows an example of the process flow in obtaining a molecular design. OPC material is designed on a molecular level using chemical technology, and in the past, this design work was based largely on prior experience and on a trial and error approach, but there is a need for greater efficiency in order to match the rate of technical innovation in the information technology industry.

Computer-based molecular design technology is becoming feasible for use in practical applications due to improved computational algorithms and high-speed computers.

Fuji Electric is installing molecular design systems, and is configuring proprietary hardware suitable for OPC materials, improving software, and analyzing data to establish computer-based molecular design technology.

Figure 4 shows an example of a molecular orbital of the OPC material. By determining the molecular structure based on computations and consideration of the OPC performance, chemical reactivity during syn-

Table 1 Example of OPC materials

Layer		Constituent material	
Photoconductive layer	Charge transport layer (CTL)	Hole transport material (HTM)	Arylamine, pyrazoline, hydrazone, stilbene, benzidine, etc.
		Electron transport material (ETM)	Azoquinone, etc.
		Film formation material	Polycarbonate, polyester, etc.
		Additive	Photosensitivity enhancing material, film formation ancillary material, coating solution anti-aging material, etc.
	Charge generation layer (CGL)	Charge generation material (CGM)	Phthalocyanine, azo, etc.
		Film formation material	Polyvinylacetate, polyketal, etc.
		Additive	Photosensitivity enhancing material, film formation ancillary material, coating solution anti-aging material, etc.
Under coat layer (UCL)		Conductive material	Metal oxide, etc.
		Film formation material	Polyamide, polyester, melamine, etc.
		Additive	Photosensitivity enhancing material, film formation ancillary material, coating solution anti-aging material, etc.

Fig.3 Example of molecular design process flow

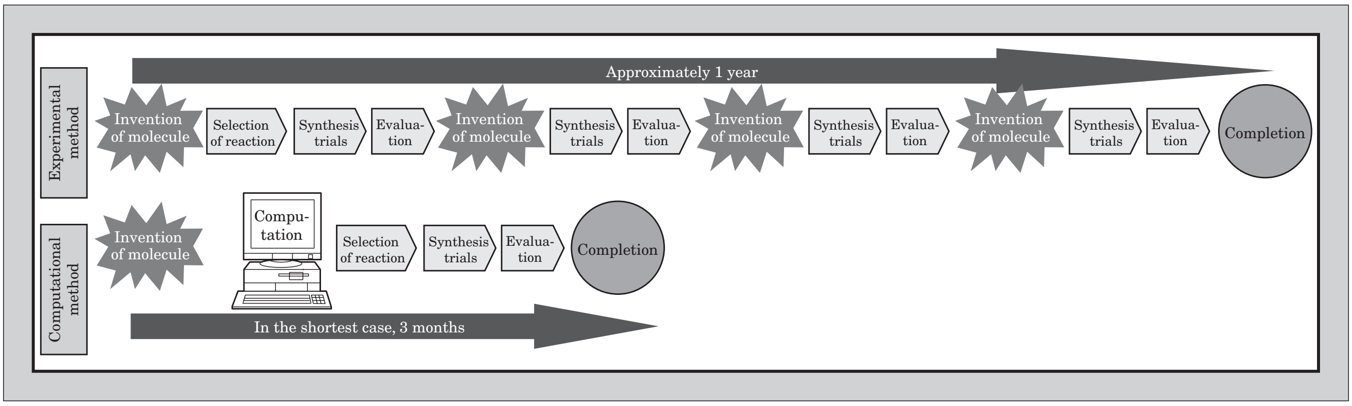
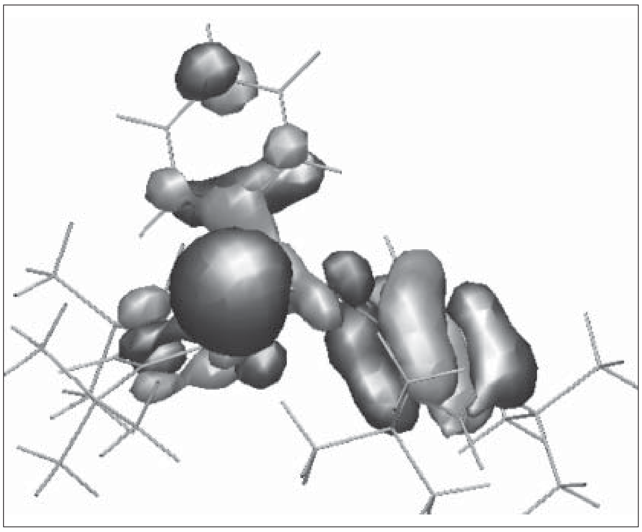


Fig.4 Example molecular orbital of OPC material



thesis, cost of raw materials and so on, the compound can be completed within 3 months of conception and realize the intended design performance.

3.3 Synthesis technology

(1) Synthesis reaction technology

Molecularly-designed OPC material is synthesized by chemical technology, and a high purity, high yield reaction must be selected as the synthesis reaction.

In recent years, synthesis route design technology such as retrosynthesis(1) and innovative high reactivity, high purity and high yield reactions such as Suzuki reactions(2) have advanced and are being utilized in accordance with the intended objective.

(2) Process control technology

For the process control during synthesis, it is necessary to change one's viewpoint from that of material synthesis for chemical-use to that of material synthesis for electronics-use.

Table 2 lists an example of temperature control during a synthesis reaction. For a set value, under the conditions of a temperature allowance of ±0.5°C while the reaction is stable, an OPC material having its intended performance was not synthesized, but under the same conditions with a ±0.1°C temperature allowance, material having the intended performance was obtained with a high yield.

Fuji Electric utilizes plant technology and process control technology, and precise synthesis reaction control as used by electrical machinery manufacturers, to manufacture high purity and high yield OPC material.

3.4 Purification technology

Table 3 lists an example of purification technology. Purification technology is an important technology for realizing the OPC performance.

Fuji Electric uses individual purification technologies such as recrystallization, column, distillation, and sublimation according to the intended objective, and pays attention to water and air quality, including the clean room and plant location conditions, to maintain quality.

Table 2 Example of process control technology

OPC material	Temperature control item	Control temperature	Yield (%)
A	Overshoot	Over 1.0°C	0
		0.5°C	12
		0.1°C	95
	Undershoot	Under 0.1°C	91
		0.5°C	43
		1.0°C	24
B	Stable temperature	Allowance ±0.5°C	0
		±0.1°C	94

Table 3 Example of purification technology

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

Table 4 Example of 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 spectrum, UV-VIS absorption spectrum, X-ray diffraction spectrum, atomic absorption spectrum, laser diffusion particle spectrum, etc.
Thermal analysis technology	Melting point, differential scanning calorimetric spectrum, etc.
Mass analysis technology	Mass spectrum, etc.
Other	Various semiconductor characteristics, various photoconductor characteristics, etc.

3.5 Material inspection technology

Table 4 shows an example of material inspection technology. Various technologies, such as chromatography analysis technology, optical analysis technology, thermal analysis technology, mass analysis technology, and the like are used according to the objective.

3.6 Coating liquid technology

Table 5 lists an example of a coating solution technology, which is an anti-aging technology. The coating solution is in an environment that is extremely susceptible to aging due to the inclusion of and exposure to dust, aluminum filings, coating film filings, moisture, oxygen and the like.

Table 5 Example of anti-aging technology

Hole transport agent (HTM)	Aging-suppressing additive for coating solution	Residual voltage change (V) during retention period			
		Initial	After 1 week	After 1 month	After 1 year
C	None	10	55	127	136
	D	10	11	10	11
E	None	10	39	61	85
	D	10	21	44	52
	F	10	11	11	10

* The residual potential is a type of photoconductor characteristic, and preferably does not increase with time.

Table 6 System for verifying safety

Verification phase	Verifying entity	Verification method
Molecular design	Fuji Electric	Exclusion of known dangerous molecular structures
Synthesis design	Fuji Electric	Verification of raw material contaminants, by-products, etc.
Coating solution design	Third party	Ames test, acute toxicity, etc.
Photoconductor design	Third party	Test method conforming to laws of the destination country

With the development of an aging-suppressing additive for the coating solution, Fuji Electric is able to select a wide range of suitable materials to suppress aging of OPC material that has been coated with the coating solution. As a result, the OPC realizes enhanced performance and stabilized quality, and the coating solution is environment-friendly with extremely small scrap loss.

3.7 Safety technology

Table 6 shows the system for verifying safety. Safety verification is essential for new OPC material, and according to the laws of the destination country and Fuji Electric's regulations, safety is verified by third parties at key development sites. Safety verification testing must fully satisfy all criteria of the destination country.

4. Conclusion

Fuji Electric leverages its proprietary materials technology and chemical technology to develop and produce OPC materials, and then to supply those materials as OPC products.

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

To improve the overall performance of OPC materials in the future and, in particular, to contribute to making OPC-equipped devices become maintenance-free, OPC performance tolerances are being reduced and stability is being improved.

Through leveraging these materials and chemical technologies, and expanding their range of use, Fuji Electric intends to continue to contribute to society by supplying OPC products capable of stably reproducing large amounts of color and high-resolution information.

References

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(2) Suzuki, A. ; Brown, H. C. Organic Syntheses via Boranes.Volume 3 Suzuki Coupling, Aldrich Chemical Co., 2003, 314p. (ISBN0-97084-419-0).