37. Organic Photoconductors

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This Chapter surveys organic photoreceptor devices used in electrophotography. Included in the discussion are the materials (polymers, pigments, charge-transport molecules, etc.), device architecture, fabrication methods, and device electrical characteristics that are critical to the successful functioning of an electrophotographic device (printer).

The Chapter is organized as follows. A brief discussion of the history of xerography and the contributions of Chester Carlson is followed by operational considerations and critical materials properties. The latter includes dark conductivity, photodischarge–charge transport, and photogeneration. Organic photoreceptor characterizations of dark decay, photosensitivity, and electrical–only cycling are discussed in detail. This is followed by discussions of photoreceptor architecture, coating technologies, substrate, conductive layer, and coated layers which carry out specific functions such as smoothing, charge blocking, charge transport, backing, and surface protection.

Organic photoconductors, devices fabricated from organic photoconductors, and the applications of these devices, are the topics which will be covered in this chapter. The term organic is used in the chemical sense to encompass materials with carbon as a major constituent. This includes molecular as well as polymeric materials that are not naturally occurring but are purposefully designed and synthesized in the laboratory for specific physical, chemical, dark-electrical, and photoelectrical characteristics. Organic photoconductors are single, or more commonly, a formulated blend of materials which have photoconductive characteristics. Put simply, these are materials in which the electrical conductivity increases on exposure to light [37.1, 2]. Organic photoreceptors are thin-film devices made from organic photoconductive materials with physical, chemical, dark-electrical, and photoelectrical characteristics designed for optimum performance in specific applications. The most important application is in electrophotography, where organic photoreceptors are utilized in machines for digital printing and copying. In this chapter we will discuss details of organic photoreceptor architecture and their composition and characteristics that have enabled their utilization in electrophotographic printing. In this space it will only be possible to touch briefly on many important aspects of organic photoreceptors but references will be provided for those wishing to delve deeper [37.3–7].

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ganic photoreceptors have received the most attention and development effort as the photosensitive image-creating element in electrophotographic-based printers and copiers. In these machines the photoreceptor is a highly uniform, defect-free, multilayer thin film ($\approx 20-50 \mu m$ photoconductor thickness) coated on a metal drum or a flexible belt, with an active area from 160 to over $12000 cm^2$. Organic photoreceptors for electrophotography were first introduced in the 1960s and, after years of development for improved physical and electrical characteristics, they form the basis of a multi-billion-dollar industry today.

### 37.1 Chester Carlson and Xerography

Electrophotography has an interesting history [37.8–11] and we will briefly tell this story with emphasis on the enabling aspects of organic photoreceptors in this technology. The story begins with Chester F. Carlson, a patent lawyer who saw the need for a method of reproducing documents. In his kitchen laboratory in Queens, New York, he demonstrated that a charged photoconductor could be used to produce an electrostatic latent image which could subsequently be visualized by contact with oppositely charged particles. The first electrophotographic image was on 10.-22.-38 Astoria. The patent application was filed on 4th April 1939 and on 6th October 1942, US patent 2 297 691 was issued [37.12]. Figure 37.1 shows the title page of that patent. In concept, electrophotography is a relatively simple process with six (or seven) steps but it took over 20 years to bring it to fruition and another decade to make it truly practical. The essential steps are all illustrated in the US patent cover page: charging, exposure, developing, transfer and fixing. Not pictured are the final steps, blanket exposure and cleaning, to prepare the photoreceptor for the next electrophotographic cycle.

Carlson had great difficulty finding commercial backing for his invention. He was unable to convince the management at a long list of influential and affluent companies that making copies of documents was an attractive business proposition. In the end the Battelle Development Corporation took on the project and made significant advances towards making it more practical. In Carlson’s invention a coating of photoconductive material such as sulfur or anthracene is prepared on a conductive, grounded, metal substrate. The photoconductor is tribocharged by contact with an appropriate material (silk rabbit’s fur, etc.). The photoconductor is then image-wise exposed with light of a wavelength that causes the photoconductive response. The areas struck by light become conductive and the surface charge is neutralized. Thus, there is now a difference in surface charge density, and hence surface potential, between the exposed and unexposed areas. This difference in surface potential, the so-called electrostatic latent image, was visualized by contacting the surface with small marking particles, such as spores from the lycopodium club moss, with surface charge opposite to the original surface charge. The final copy is produced by transferring the toned image on the photoreceptor to the receiver (Carlson accomplished this with a heated sheet.
of waxed paper). Carlson later dubbed his process xerography, meaning dry writing, based on the use of dry powder as the marking particles. Electrophotography is a more general term encompassing, for example, the use of liquid toners in which the charged marking particles are suspended in an insulating fluid.

Two significant early advances were the use of amorphous selenium as the photoconductive material and the development of a practical method (the corotron) for the generation of an air corona for surface charging the photoconductive material. The corotron is simply a fine wire held at high potential (above the air ionization threshold of \( \approx 7 \) kV) and shielded on the back with a grounded metal plate. Xerography was eventually purchased by the Haloid Corporation of Rochester, New York, (later to become the Xerox Corporation) with Carlson as a consultant. The first xerographic product was the Xerox Copier model A introduced in 1949. This initial product had totally manual operation which required several minutes to produce a copy. The photoreceptor was a selenium plate that measured \( 9 \times 14 \) inches. From these modest beginnings, advances in engineering the various processes and materials progressed in an evolutionary manner leading to the introduction of the automated copy machine, the Xerox 914 in 1959. This utilized a selenium-coated drum photoreceptor. The evolution continues today and new product introductions have rapidly shifted from copiers (reflection of light from a document to expose the photoreceptor) to digital printers (pixel-wise exposure of the photoreceptor based on data from a previously compiled image file) using drum- or flexible-belt-based organic photoreceptors. Early examples of copiers utilizing organic photoreceptors are the IBM copier 1 (1970) and the Kodak Ektaprint 100 (1975). Initially the photoreceptors were single-layer in that the photoconductive materials were all contained in a single layer. For high-speed high-quality applications more complex photoreceptors were introduced. These had multilayer structures with each layer being optimized for a specific function. The single-layer OPC architecture is, on the other hand, what one finds to-day in desktop laser printers. The choice of single versus multilayer OPC hinges on the quality and printing speed requirements of the end use printer, and on the OPC manufacturing cost. The details of photoreceptor architecture and composition will be discussed later.

There are some subtle differences in the electrophotographic process between copiers and digital printers. Since the electrostatic image in a copier is produced by reflection of the exposing light from a document (black text for example), areas of the document which are dark (text) reflect no light and the corresponding area of the photoreceptor retains its surface charge. To produce a final print in which the dark areas correspond to dark areas in the original document one must develop the image with a marking particle (toner) with charge that is opposite to that on the photoreceptor surface. This process is called charged area development. In a digital printer the exposure is controlled by an image file and the image is composed of a microscopic halftone pattern of pixels. Pixel size is determined by the desired resolution such that 600 dpi corresponds to a pixel size of about 40 \( \mu \text{m} \). In a digital process it is possible to expose either those areas which will be developed or undeveloped in the final print. The approach sometimes chosen is to expose only those areas which will be toned since most documents are text-based and text occupies only a small fraction of the total document area. This approach decreases the on-time of the exposing system and lengthens its lifetime. Thus, in this case those areas to be developed have been exposed and have decreased surface potential. This process, discharged area development, is carried out by using toner with a charge polarity that is the same as that of the photoreceptor surface. Factors in OPC design relating to their optimization for digital imaging have been investigated but in practice the OPCs used in today’s copiers and printers differ little [37.13–16]. Discussion of the chemistry, physics, and engineering involved in toners, developers, and development systems is beyond the scope of this chapter [37.17, 18].

In addition to the photoreceptor some of the major subsystems of a modern digital printer are:

- Exposure: Scanning laser or light-emitting diode (LED) arrays.
- Development: Magnetic brush or other technology with black and/or colored marking particles plus magnetic carrier.
- Transfer: Heat, pressure, etc. to remove toner from the photoreceptor and place it on the receiver. In some systems the toner is transferred first to an intermediate drum or web and then to the final receiver.
- Erase: Blanket exposure to return the photoreceptor to a uniform surface-charge state.
- Clean: Blade or brush to remove untransferred toner from the photoreceptor surface.
- Fixing: Melting the toner particles onto the receiver.
- Computers and software: Image capture, rendering, and storage, process control, receiver handling, etc.
- Process control: Software and hardware (sensors, voltmeters, etc.) to maintain image quality.
- Sensors and controls: For receiver handling.

A full listing would be much longer and the modern electrophotographic printer is a highly complex sys-
tem where the hardware, software, and materials have been successfully co-optimized to meet the product aims [37.19–21].

Since the photoreceptor surface is either in physical contact with (development, transfer, cleaning), or exposed to, effluents (fusing, corona charging) from the various subsystems its physical and electrical characteristics must be stable to these interactions throughout its life. Much of the development in OPCs has been to extend the photoreceptor process lifetime. Today the most durable OPCs might be replaced after 100,000 or more imaging cycles.

### 37.2 Operational Considerations and Critical Materials Properties

The steps involved in the electrophotographic process were detailed previously [37.17, 19]. In this section we discuss some of the underlying physics in the formation of the electrostatic latent image. From the point of view of device physics the OPC is a large-area transducer configured as a belt or drum which converts optical information into a latent charge (primary) image. The photoreceptor material is a high-dielectric-strength insulator that is converted to the electrically conducting state with the application of a field and illumination. Phenomenologically, a high field is applied across the thin-film photoconductor (corona charging) and the film is exposed to radiation absorbed by the material. The photon energy is converted into charge carriers at or near the site of absorption and these drift under the influence of the field. Since the charged photoreceptor is an open-circuit device the surface potential decreases as the charges drift through the material and the photoreceptor is discharged.

In this section we focus on some of the key physics and materials issues governing the field-biased motion of electronic charge through the photoreceptor during light-induced xerographic discharge – the process which leads to latent image formation. Work done in optimizing the design and characterization of photoreceptors in order to service an evolving technology operated in a push–pull relationship with the growth in scientific understanding of photoinduced charge generation, injection, transport and trapping first in amorphous semiconductors and then, in what will concern us here, disordered molecular media.

Because the photoreceptor assembly is a sensitized large-area device, the materials which simultaneously optimize all the required properties have always been glassy coatings. (Polycrystalline media are largely unsuitable for a variety of reasons.) The inorganic materials used especially in light-lens copiers were initially amorphous chalcogenides [37.22, 23] and to a much lesser extent hydrogenated amorphous Si [37.24, 25]. Much of the early work was therefore focused on the physics and chemistry of amorphous semiconductors. In this case photogeneration and the subsequent transport of charge occur in precisely the same medium, and design latitude is clearly restricted by the particular combination of optical and transport characteristics of that single layer. In addition these inorganic films are relatively brittle and therefore unsuitable for applications which require a belt architecture, i.e., one in which the photoreceptor is required to bend around small rollers. On the other hand, polymer-based OPCs are inherently flexible and multilayer architectures are readily fabricated such that each layer can be optimized for a particular function such as photogeneration and charge transport [37.26]. In fact, all OPCs for high-end applications have been developed according to this principle with the photoconductor divided into a thin light-absorbing charge-generation layer (CGL) adjacent to the electrode and a thicker charge-transport layer (CTL) which transports holes. With this photoreceptor configuration the surface is negatively charged prior to exposure. The details of OPC architecture and the materials chosen for specific layer functions will be discussed later.

#### 37.2.1 Dark Conductivity

The electrophotographic imaging process begins by applying a surface charge to the photoreceptor. A parallel-plate-capacitor model is appropriate and the surface potential and surface charge density are related through the capacitance per unit area as,

\[
Q/A = (C/A)V = \left(\frac{\varepsilon \varepsilon_0}{L}\right)V,
\]

where \(Q/A\) is the surface charge density (C/cm²), \(C/A\) is the capacitance per unit area (F/cm²), \(V\) is the surface potential (V), \(\varepsilon\) is the dielectric constant, \(\varepsilon_0\) is the permittivity of free space, and \(L\) is the photoreceptor thickness. For a typical organic photoreceptor \((L = 25 \mu m, \varepsilon = 3,\) and \(V = -500 V\)) \(C/A\) is \(3.2 \times 10^{-10} F/cm²\), corresponding to \(10^{12}\) charges/cm². Assuming the surface is composed of molecules with an area of \(100 \AA^2\) \((10^{-14} cm²/molecule)\) only \(\approx 1\%\) of the surface molecules are associated with the surface charge. The applied field \((V/L)\) is \(2 \times 10^{5} V/cm\).

Electrophotographic imaging is enabled by a difference in surface potential between exposed and unexposed areas when the imaged area enters the development subsystem. Generally a potential difference of
at least 300 V is desired. The materials comprising the bulk of the OPC must be highly insulating. A resistivity of $10^{13} \ \Omega \text{cm}$ at a field of $2 \times 10^5 \ \text{V/cm}$ will give rise to a dark decay rate of nearly 200 V/s. Since development typically occurs at a fraction of a second to one second after charging, the photoconductor resistivity needs to be $> 10^{13} \ \Omega \text{cm}$. Organic polymers such as bisphenol-A polycarbonate meet this requirement and are the major component in OPCs.

There are other sources of dark conductivity such as electrode and/or surface charge injection, bulk charge generation, and/or charge detrapping [37.27–30]. Electrode injection is prevented with the interposition of a charge-injection blocking layer between the electrode and the photoreceptive material. Surface injection is prevented by the chemical composition of the surface layer (which is typically a hole-transporting CTL). Detrapping can be a significant source of dark decay in OPCs and must be controlled by a balance between the process and the materials (the charge-generation material in particular).

### 37.2.2 Photodischarge—Charge Transport

The photoreceptor must retain charge in the dark and also be photosensitive enough to discharge exposed areas to half their initial charge potential when irradiated with (nominally for a mid-volume laser printer engine) $4–10 \ \text{erg/cm}^2$. The xerographic gain or quantum efficiency of supply describes the fractional number of surface charges neutralized per absorbed photon. For a dual-layer OPC it is a complicated convolution of the quantum efficiency of generation in the charge-generation layer, CGL, the efficiency of carrier injection from the CGL to the CTL and the transport parameters of the CTL. For this discussion we will for the moment ignore issues of charge generation and focus on transport. In dual-layer OPCs the majority of photodischarge occurs via charge transport through the CTL with the CGL playing a minor role. In the transport lexicon [37.26, 31] there are essentially two parameters that constitute the figures of merit to characterize charge motion through the polymeric CTL. These are (1) the drift mobility $\mu$, the measure of how fast the carrier moves per unit applied field, and (2) the normalized carrier range $\mu t_r$ ($t_r$ is the free-carrier lifetime against deep trapping), which is how far the injected carrier moves per unit field before becoming immobilized in a deep trap. The time for a photoinjected carrier to traverse the CTL is called the transit time. The transit time $t_r$, and mobility $\mu$ are related to the specimen thickness $L$ according to $t_r = L/(\mu E)$. The importance of mobility as a critical parameter in the electrophotographic process can be understood as follows: for an increase in the exposure intensity $d(F)$, the final decrease in surface potential $d(V)$ is proportional to the number of injected carriers and the distance they travel within the CTL. During xerographic discharge, a charge of $C V_0$ (where $C$ is the CTL capacitance and $V_0$ the initial voltage) traverses the bulk and induces time-dependent variation in the electric field behind the leading edge of the injected carrier front. Thus, as the fastest carriers transit the CTL, the electric field behind them is reduced, and the carriers behind the leading edge transit at a lower field, which in turn makes their velocities lower. Thus during xerographic discharge the transit times of individual photoinjected carriers become dispersed over a wide range, typically about an order of magnitude. For discharge to proceed to completion, even in the complete absence of deep trapping, enough time is required for the slowest carriers in the packet to exit the layer before the photoreceptor reaches the development zone ~ nominally 0.3–1 s after exposure in mid-volume printers. The latter must be allowed for in practice. Thus, carrier mobility in this particular illustration should exceed $10^{-6} \ \text{cm}^2/(\text{V s})$.

For example, consider that a dual-layer photoreceptor with a 25 $\mu$m CTL, in which there are no deep traps, is subjected to a light flash intense enough to ultimately induce complete discharge ($CV_0$ of absorbed photons). Consider further that in this CTL the mobility $\mu = 10^{-6} \ \text{cm}^2/(\text{V s})$ at $E = 10^4 \ \text{V/cm}$ and that the device is initially charged to 1000 V. It can be calculated that under these conditions the device will have a residual voltage of 20 V after 0.3 s or 7 V after 1 s. Incomplete discharge, unless compensated for, might result in an inadequate toning potential and a toned density less than desired. Note further that, if the mobility is even lower, the results can become totally unacceptable. For example when the mobility is $\mu = 10^{-7} \ \text{cm}^2/(\text{V s})$ under the conditions just described, the residual voltage a full second after exposure is 60 V, even in a completely trap-free CTL. In light of the foregoing illustration for the trap-free case, which sets the mobility benchmark, the effect of traps in the polymeric CTL must be of paramount concern. More precisely, we are concerned with traps whose release time at ambient temperature discernibly exceeds the period of a complete electrophotographic cycle. In the present context we take the latter as the operational definition of a deep trap. With such traps present it is clearly the case that, after repeated charge-expose cycling, some quantity of image degrading charge would remain immobilized in the bulk for times now exceeding the period of a complete xerographic cycle. If $\rho$ is the density of uniformly trapped space charge in a CTL of thickness $L$ and relative dielectric constant $\varepsilon$ then there is an associated residual potential $V_R$, where $V_R = \varepsilon \rho L^2/(2\varepsilon \varepsilon_0)$. Here
$e$ is the electronic charge and $\varepsilon_0$ is the free-space permittivity. In a nonpolar dielectric medium ($\varepsilon = 3$) with a layer thickness of 25 $\mu$m, as few as $10^{10}$ electronic charges trapped per cm$^2$ already give rise to a residual of 19 V. Unless process control utilizing electronic feedback correction can be employed, bulk-trapping-induced space-charge buildup during cycling can result in severe image degradation. Residual potential arising from bulk-trapped space charge is a critical electrophotographic process parameter. A residual potential can be related to the normalized carrier range $\mu R$ in the weak-trapping limit from the physically plausible ansatz that the residual potential corresponds to that applied voltage for which the carrier range is about half the specimen thickness $L$. Thus, $\mu R$ is approximately $L^2/(2V_k)$. On this basis the tolerable trap density is defined by the requirement that the $\mu R$ product in practical devices should typically exceed $10^{-6}$ cm$^2$/V. Even highly purified polymer will typically contain many chemical impurities in the 1–10 ppm range, which the foregoing calculations show is vastly higher than permissible trap levels. However, chemical impurities, even when present at relatively high concentration, can be rendered trap-inactive by employing molecular design principles to guide the overall choice of active materials. Concepts derived from scientific understanding of photogeneration, injection across interfaces, and electronic transport in disordered organic materials, in combination with the unique compositional flexibility characteristic of the organic solid state, were together responsible for making multilayer OPCs the dominant practical receptor technology for electrophotography.

As discussed above, successful electrophotographic imaging requires that charge transport through the CTL occur with little trapping in the time scale of the electrophotographic cycle. Here we discuss how this is accomplished in an impure organic-chemical-based CTL. The CTL is a glassy solid solution of a charge-transport-active moiety dispersed in a polymer binder. The charge-transport moiety can be molecular or a polymer component. The molecular solutions are called molecularly doped polymers (MDP). The transport-active component is typically 40–50% weight fraction of the CTL. Thus, doping in the present context is decidedly different from what doping refers to in conventional semiconductor physics [37.32]. In the latter case the dopant is typically introduced at very low concentration to control the relative proportion of electrons and holes in the bands of a semiconductor crystal leaving optical properties largely unaffected. In a semiconductor crystal at ambient temperature the dominant field driven transport mechanism is scattering perturbed motion of charge carriers in the bands. Under these circumstances, mobility decreases algebraically with increasing temperature, while carrier population in the bands is thermally activated. The convolution of these processes manifests in a thermally activated conductivity. On the other hand, in MDPs under equilibrium conditions the transport-active molecule is in the neutral state, and the glassy films are perfect insulators, that is, there are no free carriers present in thermal equilibrium [37.33]. These systems can nevertheless support relatively efficient charge transport under the action of an applied field when in contact with a charge reservoir. At fixed temperature the drift mobility of extrinsic carriers decreases exponentially with increasing average intersite separation of the active molecule ($\rho$) so the drift mobility of MDPs can be tuned over a broad range by simply adjusting concentration [37.34, 35]. This feature of tunability can readily accommodate a wide range of xerographic process speeds as described above and is therefore advantageous from a technological point of view [37.36]. This is illustrated in Fig. 37.2 for a common hole-transport material, $N,N'\text{-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl)-4,4'-diamine}$ (TPD, Fig. 37.3). The data is in conformity with a simple tunneling model where $\rho_0$ is the wavefunction localization radius and the transport states are sited on the TPD molecules. At $40–50$ wt% doping approximately $10^{4}$ hops are required for the hole to transit a 20 $\mu$m photoreceptor.

![Fig. 37.2 Log ($\mu/\rho^2$) versus average intersite separation $\rho$ of TPD molecules in bisphenol-A polycarbonate ($E = 5 \times 10^4$ V/cm). The triangle symbol is the hole drift mobility in pure TPD film.](image-url)
Drift mobility of holes in CTL films is most conveniently measured by the canonical small-signal time-of-flight (TOF) technique \[37.37, 38\]. However, for a given composition of the CTL, and all other conditions analogous, the same drift motilities can be inferred by analyzing transport-limited xerographic discharge in bilayer photoreceptors \[37.39, 40\]. In TOF, the MDP film is prepared with semitransparent blocking contacts and maintained at a bias which is high enough to insure that the transit time of any excess injected carrier is shorter than the bulk dielectric relaxation time. The sample is exposed to a very short and weak pulse of strongly absorbed light (typically 337 nm from a nitrogen laser) incident on the positive electrode. Under these circumstances photoexcited transport molecules are oxidized at the positive electrode to the radical cation (the \textit{hole} in transport terminology). This process sets up a chain of redox steps where electrons are progressively transferred from neutral molecules to their neighboring radical cation. The concentration of the advancing pulse of holes is low, such that the applied field remains uniform during their transit. In the ideal case the current from the advancing pulse of holes is constant until the leading edge reaches the counter-electrode, after which it rapidly decreases. The transit time can be extracted from the transient current and from this the mobility. For a given MDP composition drift mobilities are determined for films of known thickness as a function of applied field and temperature. The drift mobility in MDPs always has a thermally activated temperature dependence; thus the log of the drift mobility scales with inverse temperature, as illustrated in Fig. 37.4, where earlier measurements \[37.34\] have here \[37.41\] been extended to encompass the characteristic slope change displayed in the glass-transition region \[37.42\]. However, in a significant number of cases cited in the literature \[37.5\] the analogous scaling is with the square of the inverse temperature, (i.e., non-simple activation), as predicted by the disorder

![Chemical structures of representative hole transport materials](image)

**Fig. 37.3** Chemical structures of representative hole transport materials

![Temperature dependence of the drift mobility in a film of 50 wt% TPD in bisphenol-A polycarbonate](image)

**Fig. 37.4** Temperature dependence of the drift mobility in a film of 50 wt% TPD in bisphenol-A polycarbonate ($E = 2.5 \times 10^5$ V/cm). $T_g$ is the glass transition temperature of the film
The field dependence of the hole drift mobility in the polymer PTPB parametric in temperature clearly indicates that electronic transport must involve the field-biased hopping of carriers in an energetically inequivalent manifold of states sited on the transport-active molecules. Apart from their technological importance in electrophotography and light-emitting displays, what has made MDPs a laboratory for the study of hopping transport is that a number of key secondary features in their transport behavior are in fact pervasive in other disordered molecular media. There is then the suggestion of a common underlying mechanism susceptible to theoretical treatment. Thus, the field- and temperature-dependent behavior of molecular dispersions is also observed in polymers with transport-active pendant groups such as poly(N-vinylcarbazole), in polymers in which small molecule moieties are incorporated in a main chain and in certain polyπ-conjugated systems. Figure 37.5 is a plot of the field dependence of the hole drift mobility in the polymer polytetraphenylobenzidine (PTPB) versus field and parametric in temperature over a 60 K range. PTPB is a glassy polymer in which tetr phenylbenzidine (TPD) moieties are covalently bonded into a main chain. The data is replotted in Fig. 37.6 to show the explicit dependence of the log mobility on the square root of the applied field. The field dependence is itself temperature dependent and clearly becomes stronger with decreasing temperature. The two TPD-based hole-transport media are closely related but qualitatively identical results are reproduced in polysilylenes and polygermylenes which have a sigma-conjugated backbone capable of supporting electron delocalization as inferred from analysis of absorption and emission spectra. For example, hole transport in PTPB can be represented in an Arrhenius plot over the temperature range illustrated in Fig. 37.7. In this purely phenomenological description the activation decreases with the square root of the applied field, as displayed in the insert. Precisely the same behavior is exhibited when the same phenomenological description is applied to hole drift mobility data in poly(methylphenylsilylene) (PMPS), as shown in Fig. 37.8. Combining drift mobility and spectroscopic data has in fact suggested that transport in these sigma-conjugated polymers involves the...
hopping of holes among chromophore-like main-chain segments of varying length whose function for transport is therefore analogous to the TPD sites in PTPB. This convoluted pattern of behavior first identified in MDPs and therefore clearly characteristic of hopping among discrete energetically in equivalent molecular sites has been reported in TOF experiments on \( \pi \)-conjugated systems notably the phenylene vinylenes. The sites, like those in polysilylenes, are interpreted to be domain-like backbone segments of varying conjugation length \[37.51, 52\]. These combined results and the recurrent pattern of behavior they reveal in systems of widely varying composition and morphology suggest that a transport theory must be founded on universally shared characteristics \[37.58\]. The theoretical literature stimulated by these observations is in fact extensive and far too detailed to be adequately described here. In the present context it suffices to comment briefly on certain general trends. The activated temperature dependence universal to all these materials systems arises because states in the hopping manifold are energetically inequivalent. Energetic inequivalence can be understood on the basis of site relaxation accompanying polaron formation \[37.59–61\]. Energetic inequivalence of sites is also a common feature of disordered solids resulting from site-to-site fluctuation of the static and dynamic electrostatic potential \[37.43, 62, 63\]. The combination of both effects cannot be excluded. In fact, there is a general need to develop the framework to distinguish the relative contributions of these key processes in the analysis of experimental data \[37.64, 65\]. A particularly challenging issue has been the attempt to account for the special features of the Poole–Frenkel-like field dependence illustrated in Fig. 37.6. Polaron models typically predict that the log mobility should scale linearly with the applied field \[37. 59, 66\]. The disorder model based on analysis of Monte Carlo computer simulation of hopping on a finite lattice as originally proposed by \( \text{Bässler} \) \[37.43\] was in fact able to self-consistently account for a number of key experimental features in terms of a limited set of disorder parameters. On the other hand, it could only model the observed field dependence over a very narrow range. It was later recognized in the formulation of dipole disorder models \[37.67, 68\], that slow site-to-site variation, as distinct from fully random fluctuation, in the effective electrostatic potential could more properly account for the field-dependent behav-
behavior of mobility commonly observed over several orders of magnitude \[37.69–71\]. The more general formulation of the disorder model developed by Dunlap and coworkers, treats the disorder potential as fully correlated and therefore slowly varying, and argues that such a supposition is physically plausible on general grounds in glassy solids. Further advances in the theories of hopping charge transport in organic materials can be found in review articles \[37.72–74\].

If every chemical impurity remaining in even the most scrupulously processed polymer film could act as a trap, organics as a materials class would be completely excluded as a basis for the design of xerographic photoreceptors. Trap-free transport in CTLs was achieved not by entirely eliminating impurities but by properly designing the transport-active moiety \[37.75, 76\]. The associated studies first carried out in this technologically critical context on molecularly doped systems \[37.77\] were instrumental in generally elucidating trap interactions in hopping systems and in first unambiguously illustrating and analyzing the mechanism of trap-controlled hopping transport \[37.78\]. It was already pointed out that hole transport is supported in MDPs when the neutral transport molecule is donor-like. For electrons the corresponding neutral transport molecule is acceptor-like in character. In each case, the CTLs are typically unipolar when analyzed by TOF or xerographic techniques. As it turns out the principle (simple in hindsight) which applies for example to hole-transport CTLs is to make the transport molecule significantly more donor-like than any of the resident impurity species. The limit is that the material must be stable to air oxidation. From an energetic point of view the impurity levels which then lie above the hole transport states are anti-traps. An important class of small molecules which have these desired characteristics are the aromatic amines and TPD is a prime example of a particularly strong donor in this class of molecules. As the trap-free nature of these transport layers is xerographically apparent because there is no buildup of bulk space charge as measured by Kelvin-probe techniques \[37.79\] even after tens of thousands of \((CV_0)\)s of holes are discharged through a photoreceptor with this CTL as a component. The trap-free nature of hole transport can also be independently demonstrated by combining TOF drift mobility and analysis of current–voltage measurements carried out on any transport layer fitted with a semitransparent blocking contact on one surface and an ohmic contact on the opposite face \[37.80–82\]. Figure 37.9 illustrates the result for the polymer PTPB in which TPD is covalently incorporated as the transport active unit \[37.81\]. Semitransparent Al on the films exposed surface is used for the TOF measurements of drift mobility. Dark injection occurs under positive bias from the gold-coated mica substrate \((\text{filled circles})\) with the gold-coated mica substrate onto which the PTPB film had initially been deposited. PTPB is highly insulating so that the bulk dielectric relaxation time is always much longer than the transit time of any excess injected carrier at all applied voltages. With the Al contact under positive bias, hole drift mobility is measured as a function of applied voltage \(V\). From the measured drift mobility the trap-free space-charge-limited current density \((\text{TFSCCLC})\), \(J\), \[37.83\] that would be sustained by an ohmic contact under positive bias can be calculated to a good approximation, even when the drift mobility is itself field dependent \[37.84, 85\] using the expression

\[
J_D = \frac{9\varepsilon_0\mu V^2}{8L^3}
\]

These values are represented by open circles in Fig. 37.9. The electric field in the film is, of course, nonuniform and \(E\) in plots of this sort is simply a shorthand for \(V/L\), where \(V\) is the externally applied voltage. It should be noted that, under the present conditions, the TFSCCLC is in principle the maximum current that the bulk of a transport medium such as PTPB can demand from a contact in the steady state. It should also be noted that the
observation that an injecting contact under test is capable of sustaining a space-charge-limited dark current is a prima facie demonstration of ohmicity [37.26]. Filled circles represent the steady-state current measured when positive bias is applied to the substrate. That these calculated and measured currents coincide demonstrates that the injecting Au contact is ohmic and that the PTPB film is trap-free. Similar results have been obtained for other commonly used CTL MDPs such as TPD in bisphenol-A polycarbonate and in films of poly(methylphenylsilylene).

37.2.3 Photogeneration

The CGL material is designed to strongly absorb light from the exposure system (red to near-infrared LEDs and lasers are typical). In a typical dual-layer OPC the CGL material is a thin (submicron) coating of a dispersed pigment. Simply, the pigment material absorbs a photon and mobile charge is created which is injected into the CTL and then drifts under the influence of the applied field to discharge the device. Charge generation is a very complex topic [37.86]. In general terms, absorption of a photon produces an excited state (exciton) of a correlated hole–electron pair (valence band and conduction band, respectively) which has some mobility. Measured exciton ranges can be on the order of 0.1 μm. The exciton may then undergo recombination, with the release of energy to the environment, or it may be converted into charges. Conversion into charges can occur spontaneously or through chemical (impurities or dopants) or physical (crystal defects or the crystal surface) interactions. With the trapping of one of the charge carriers the other is free to drift under the influence of the applied field and geminate recombination is suppressed. The mobile carrier (assume holes) must drift to where it is in contact with the hole transport moieties of the CTL. In fact, in most cases the CTL penetrates and mixes with the CGL so that, even if the CGL is formulated without transport material, we can assume that these molecules are in molecular contact with the pigment particle surface. Now the hole is available to oxidize or inject into the transport moiety to produce the radical cation. Useful hole-transport materials have relatively low oxidation potentials (≈ 1 V versus the saturated calomel electrode (SCE)). The oxidation potential must be lower than that of the hole at the pigment surface but not so low that the material is unstable to air oxidation. The CTL hole is now transported through the CTL, discharging the photoreceptor, by sequential one-electron redox reactions between adjacent transport molecules as described in the previous section.

The charge-generation mechanism is characterized as intrinsic when the hole is generated within the pigment particle without the influence of any externally added materials. In this case the hole is injected into the CTL with concomitant oxidation of a transport moiety at the pigment surface. Sensitized generation is said to take place when the photoconductivity is enhanced by an added material (dopant). In this case the dopant is available to react with the pigment exciton at the particle surface. In most cases the dopant is in fact the hole-transport moiety. Dopants may also influence charge generation by forming a (charge-transfer or other) complex which facilitates charge separation. Such complexes may be accessed by direct photoexcitation or via exciton diffusion. Sensitization of the photoconductivity of poly(N-vinyl carbazole) (PVK) by electron acceptors such as 2,4,7-trinitro-9-fluorenone (TNF) (Fig. 37.10) has been extensively studied [37.87–95]. Charge-generation mechanisms in pigment-based CGLs depend on the pigment molecular structure, crystal structure, morphology, and on the transport molecule used in the formulation.

The fundamental quantity of interest in charge generation is the quantum efficiency as a function of field. A strong field dependence is always observed, as shown in the example of Fig. 37.11. Several models have been proposed to explain charge-generation characteristics. These will be summarized here but more complete discussions can be found in Pope and Swenberg [37.86], Popovic [37.97], Law [37.3]; Borsenberger and Weiss [37.5], and Weiss et al. [37.7]. One of the early models to be applied to organic
The quantum efficiency for carrier generation can be defined in several ways, as described above. The efficiency of geminate-pair formation refers to the initially produced charge pair and this is also the efficiency which has been obtained with fluorescence quenching studies. On the other hand, the generation efficiency determined with xerographic discharge always includes some contribution from charge transport because a measured decrease in photoreceptor surface potential is due to charge motion. In addition, very-high-intensity exposures may give rise to (bimolecular) recombination of positive and negative carriers during transport [37.108–112]. Quantum-efficiency determinations from xerographic discharge are carried out with very short, low-light-intensity continuous exposures to minimize the influence of charge transport and recombination (see the following section).

37.3 OPC Characterization

Photoreceptors may be characterized by many techniques. On the one hand one wishes to determine the fundamental characteristics of the materials, while on the other hand one wishes to determine electrophotographic performance-based characteristics of the photoreceptor. The quantum efficiency of charge generation and, depending on the model chosen, the initial separation distance of the charge pair, are common characterizations. Electrophotographic performance characterizations include dark decay, photoinduced discharge sensitivity, and residual potential as well as their stability to electrical-only cycling.
37.3.1 Dark Decay

The quantity of interest is the rate of dark discharge (V/s) as a function of field and environment. However, the dark decay characteristics of a dark-adapted photoreceptor when incrementally corona charged to higher and higher fields will be significantly different from what is observed in the electrophotographic process. This is because OPCs seldom behave as perfect capacitors and there is typically a depletion charging component where previously trapped charges are mobilized and drift in the photoreceptor on the application of the corona charge [37.28–30, 113]. Thus, in addition to field and environment, the observed dark decay characteristics depend on prior exposure history (trapped charges), corona charger characteristics, and timing. Thus, a given photoreceptor will have a higher dark decay rate if the photoreceptor is charged exactly to the desired initial potential ($V_0$) and the dark decay rate determined immediately, as opposed to charging well above the desired potential and measuring when the surface potential decreases to the desired potential. Dark decay measurements which are meaningful to the electrophotographic process must be carried out in an apparatus in which the exposures, charging, and timing elements are fixed. Dark decay is an important characteristic of an OPC because, although process control will attempt to maintain $V_0$, the imaging system in a printer will in general not tolerate a significant $V_0$ drop.

37.3.2 Photosensitivity

Measurements to determine fundamental characteristics (quantum efficiency of generation materials, mobility, etc.) are often carried on photoreceptors that differ from what might be eventually used in a printer. The layer of interest (CGL or CTL) may be isolated or the device may be modified with the application of a vacuum-deposited electrode (Au is common) on the free surface. Common fundamental characteristics include quantum efficiency as a function of field and wavelength, and mobility. Mobility was discussed in Sect. 37.2.2. The quantum efficiency of carrier generation has several definitions as applied to OPCs. On the one hand it can refer to the number of ion pairs generated per incident or absorbed photon. This fundamental characteristic might be determined experimentally by fluorescence quenching, or calculated based on a model such as the Onsager model discussed above. On the other hand a photodischarge efficiency can be determined based on the decrease in surface potential per photon absorbed or incident. The photoinduced discharge (PIDC) method is commonly used to characterize OPCs as a function of field, wavelength, temperature, humidity, exposure intensity, etc. The photoreceptor is corona charged to apply the desired field and is photodischarged. Using the parallel-plate-capacitor model, $Q = CV$ (terms as defined previously), the change in surface charge density can be calculated from the decrease in the surface potential. The change in surface charge density per unit area per photon incident or absorbed is a measure of photosensitivity. This measure includes the efficiency of charge generation, injection into the CTL, and transport through the CTL. Because of carrier bimolecular recombination and range limitations the quantum efficiency determined using this method may depend on the light intensity and the extent of photodischarge. The photodischarge method is carried out with either continuous or flash exposures. With continuous exposures ($J/(cm^2 s)$) the surface potential is monitored as a function of time. One measure of OPC photosensitivity which relates to the electrophotographic process is the exposure required to discharge the photoreceptor a fixed amount, often 50%, from an initial potential. This is typically carried out using exposures (wavelength and duration) relevant to a particular electrophotographic process. The photoreceptor sensitivity is usually reported in terms of $J/cm^2$ (the inverse is often used to report spectral sensitivity). A related method is to determine the initial photodischarge rate ($dV/dr$). This can be related to the decrease in surface charge density through the capacitance, $dQ/dt = C dV/dr$. The light intensity is kept low and the discharge time short to avoid space-charge perturbations during charge transport and to keep the field essentially constant. The ratio of the decrease in surface charge density to the exposure (photons/cm²) is a measure of photodischarge efficiency. In fact the photodischarge per exposure ($V/(J/cm^2)$) is another commonly used metric for OPC photosensitivity. When determined as a function of field, data obtained in this manner can be analyzed in terms of the Onsager models. Because photosensitivity depends on field (surface potential per unit OPC thickness) and the exposure produced decrease in surface charge density (related to the change in surface potential through $\Delta Q = CA V$), meaningful comparisons can only be made between OPCs of similar thickness, charged to similar initial potentials, and exposed to similar discharged potentials.

For a process using a flash exposure the photoreceptor discharge is determined at several exposure levels (with the surface potential determined at a fixed time after the exposure) and the data is plotted as surface potential ($V$) versus log(exposure, J/cm²). An arbitrary
photodischarge point (typically 50%) can be determined from this plot for comparison purposes. The utility of this characterization is that the exposure characteristics and the timing for reading the discharged surface potential directly relate to the printing process. As discussed above, short high-intensity exposures may give rise to Langevan recombination [37.110, 112, 114], resulting in decreased sensitivity (reciprocity failure) relative to low-intensity exposures.

An often overlooked sensitivity factor is that there are more photons per energy unit (J) as the wavelength increases. For example, there are about 30% more photons J at 820 nm relative to 630 nm. Thus, for a photoreceptor with a given quantum efficiency for carrier generation the sensitivity will increase with increasing wavelength of the exposure source.

37.3.3 Electrical-Only Cycling

Electrophotographic performance characterizations are necessarily carried out on the photoreceptor in an apparatus which has the key elements of the electrophotographic process. The most relevant apparatus would of course be the fully configured printer. However, the use of such a complex device is often undesirable, or unnecessarily, for screening purposes. In the laboratory it is common to use electrical-only test fixtures in which the process always includes charge and expose, and may include erase (or unique process elements), with the surface potential being determined after the application of each. With an apparatus such as this it is possible to determine process-relevant characteristics such as: chargeability, dark decay, photosensitivity, and residual potential, all as a function of cycling. Of course large changes in any of these characteristics is generally undesirable and long cycling (10–100 kcycles) is often necessary to adequately determine the electrical stability of the photoreceptor to the electrophotographic process. Such stability is a necessary, but not sufficient, condition for eventual commercialization, and extensive testing in the machine for which the photoreceptor was designed is always the final step in the development process. Other factors, often connected to the device physical characteristics (wear rate, corona chemical sensitivity, layer adhesion, seam strength, etc.) may in fact determine the eventual success or failure of a particular OPC in a printer.

37.4 OPC Architecture and Composition

As we have described, OPCs are large-area thin-film devices that are insulating in the dark and become conductive when exposed to light. A high field is applied by exposure to an air corona (or similar charging method) and the photoreceptor is image-wise exposed to produce an electrostatic latent image. The surface potential in the exposed areas is determined by the exposure intensity and the OPC photosensitivity while the surface potential in the unexposed areas is determined by the dark conductivity. The development system deposits charged marking particles (toner) on the photoreceptor surface according to the difference in surface potential between the exposed and unexposed areas. The key photoelectrical processes which enable latent image formation are photoinduced charge generation and the transport of the generated charge through the device. Organic photoreceptors accomplish this in a multilayer architecture with specific materials (monomers and polymers) designed and optimized for specialized functions: binder, charge generation, charge transport, dark conductivity, etc. In this section we will discuss the architecture and composition of organic photoreceptors with details on the function and composition of each layer.

37.4.1 OPC Architecture

The choice of photoreceptor thickness is a balance between capacitance, surface potential, and internal field. Capacitance relates to surface charge density, which determines the achievable developed toner density for toners with a given surface charge per area. Surface potential, in combination with the development system, provides the potential difference to attract toner to the photoreceptor surface. The internal field enables efficient charge generation and transport. In most electrophotographic printing machines the balance is achieved with an OPC thickness of ≈ 20–30 μm and a surface potential of 500–1000 V.

A schematic cross section of a fully configured modern electrophotographic photoreceptor is shown in Fig. 37.12. In its most simple form the photoreceptor consists of a conductive substrate and a single layer of photoconductive material to accomplish charge generation and transport. The advantage of this structure is in its simplicity, but the disadvantage is that not all characteristics will be optimum. In the modern embodiment the photoreceptor is constructed with separate layers for charge generation (CGL) and charge
transport (CTL). Other layers shown in Fig. 37.12 include: substrate, smoothing layer, charge-injection blocking layer, charge-generation layer (CGL), charge-transport layer (CTL), and protective overcoat layer. Additional layers, such as adhesive interlayers, and a back-side anti-curl layer may also be present. OPCs with separate CGL and CTL are termed dual-layer. Each of these layers may be a complex formulation of materials. The advantage in separating layers is that each layer can be optimized for its specialized function. This adds materials expense and manufacturing complexity but has the advantage of superior performance.

In a single-layer photoreceptor when exposed with strongly absorbed radiation directed at the free surface, charge generation will occur near the free surface and the photodischarge will be dominated by the transport of positive or negative charge through the bulk of the layer. The polarity of the mobile charge will be the same as the applied surface potential. In most commercial dual-layer photoreceptors the architecture is substrate–CGL–CTL. Because the CTL is formulated for hole transport, dual-layer OPCs are charged with a negative surface potential. Positive corona charging has some advantages over negative (better uniformity and less ozone production). A single-layer OPC can function with either a positive or negative surface charge depending on the exposure direction and the transport characteristics of the materials used in the formulation. Positive-charging dual-layer photoreceptors with the architecture substrate–CTL–CGL have been commercialized but these require a protective overcoat to prevent the CGL from being damaged by contact with the electrophotographic process elements. The typical substrate–CGL–CTL architecture will function with positive charging if the CTL is formulated for electron transport. Electron-transporting CTLs have been widely studied by not yet commercialized.

In a multilayer photoreceptor the principle is that the functions of each layer are optimized. Thus, with separate CGL and CTL the former is designed for strong absorption of the wavelength of light used in the process and efficient charge generation, and the latter is optimized for the injection of photogenerated charge from the CGL and transport of that charge to the free surface. In general, most charge-generation materials efficiently transport only one polarity of charge (electrons or holes depending on the material) so that it is generally desirable to have the CGL as thin as possible while retaining the required optical density at the exposure wavelength. It is also necessary that the CGL be uniform over the entire area of the photoreceptor to maintain consistent sensitivity for the entire photoreceptor surface. Submicron CGLs are typical of the photoreceptors used in most modern digital printers. The CTL determines the device capacitance and a thickness of approximately 25 μm is typical. However, the CTL thickness also influences the ultimate latent-image resolution in a digital printer because holes transiting the CTL experience mutual Coulombic repulsion [37.13, 115]. It has been shown that for optimum resolution the photoreceptor thickness should be about one quarter of the pixel size [37.13, 14]. Thus, for 600 dpi imaging (≈ 40 μm pixel size) the ideal photoreceptor is on the order of 10 μm. Thin OPCs have not yet been introduced into digital printers but one might anticipate that this will occur as toners get smaller and the processes of toner transfer and fusing are refined to minimize image disruption [37.116].

37.4.2 Coating Technologies

Hopper coating of continuous webs and dip coating of drums are the two technologies commonly used to fabricate photoreceptors. As with any large-area photoelectrical device absolute cleanliness is required to prevent artifacts in the coated layers. In a multilayer device one must carefully control the interfaces between the layers. For example, a key interface is that between the CGL and CTL. Here it is important that the two layers adhere but do not mix to such a degree that the desired characteristics of either layer are compromised. Attaining the desired degree of mixing is a process of optimization depending on the materials, solvents, and coating method.

In hopper coating the coating solution is continuously pumped through a slot onto the moving web. Film thickness is controlled by the pumping rate and solids content of the coating solution. Precise control of drying temperature, humidity, and air flow enable optimization of the coated layers. Curing of the coated film involves removal of solvent and annealing of the
polymer binder(s). In a hopper coating process several layers can be coated in a single pass with sequential hoppers as long as the previous layer is adequately cured. Hopper coatings can be carried out at a very high speed (m/s) to produce a roll of many thousands of feet. To coat subsequent layers the previously coated substrate is re-run through the coating machine. Because the hopper coating process involves contact of the coated surfaces, and winding of the coated web, there is the possibility of film damage. Final inspection for film defects must be carried out and damaged, or imperfectly coated, regions must be removed before construction of the final photoreceptor loops.

In a dip coating process the substrate and coated layers are dipped into a solution or dispersion of the next layer to be coated and slowly withdrawn and cured. The coated layer thickness is determined by the rheological characteristics of the coating solution and the rate of withdrawal. Under these conditions there is the opportunity for extensive interaction between the previously coated layer and the solution into which it is dipped. Thus, formulations which are suitable for hopper coating may be inadequate for dip coating even though the chemical compositions of the final coated layers might be identical after curing. Another consideration with dip coating is that components of the previously coated layers which are soluble in the solvent used in the subsequent dip will contaminate the dip reservoir. Low levels of contamination may be insignificant, but since the amount of fluid removed in each coating operation is a small fraction of the total volume one must make sure that such contamination does not degrade performance.

Other processes such as ring coating (a dipped drum is withdrawn through an annulus which acts as a doctor blade to control the wet coating thickness), spray coating, vacuum coating, etc. may be used for specific applications and materials. In all layers coated from solution it is often necessary to add a small quantity of surface-active agent as a coating aid to enable smooth, defect-free coatings.

In recent studies on charge transport in free-standing doped polymer films it has been reported that the surface exposed to the air during drying may have degraded transport characteristics, and a depleted concentration of charge transport material was suggested as the cause [37.117, 118]. This finding demonstrates that solvent coated layers are not necessarily of uniform composition. Inhomogeneous composition of a charge-transport layer could lead to degraded electrophotographic performance. Thus, in analyzing the electrophotographic performance of an OPC one must consider not only the composition of each layer, but also its uniformity both spatially and compositionally particularly at the interface with another layer.

In the following sections we will discuss details around the compositions of each of the layers which might be found in an organic photoreceptor for electrophotographic printing. The order of discussion is in the order in which the typical photoreceptor would be constructed: substrate and ground layer, smoothing layer and charge-blocking layer, charge-generation layer (CGL), charge-transport layer (CTL), and protective overcoat layer.

37.4.3 Substrate and Conductive Layer

A common element to all electrophotographic photoreceptors is a substrate on which all the layers are deposited. In a research environment a small square of glass or quartz is convenient, but in commercial applications the substrate is invariably either a polymer film or a metal drum. Some of the material characteristics which might be considered in the choice of a polymer film are: stiffness, toughness, transparency, core set, and surface friction. Polymeric photoreceptor substrates are often 3–7 mil. A common polymer film material is the polyester poly(ethylene terephthalate) (PET). PET film is very durable, optically transparent, and readily available in a wide range of thickness. Since it is highly insulating it must be coated with a conductive material to act as the ground plane. PET or other polymer films are available in large rolls and the coating operations are usually done on the roll rather than cut-to-size sheets. Although a solution-coated conductive layer is possible, the most common ground layers are metals such as Ni, Al, Cr, and Ti, which are applied in a continuous sputtering or similar vacuum technique. The metallized rolls are subsequently coated with the photoconductive layers. If a metal drum is the chosen substrate it is almost invariably aluminum (1–10 mm wall thickness). The conductive metal serves as the ground layer but typically it receives further treatment before coating the photoconductive layers. The treatment may be chemical such as anodization to form a thin hole-blocking layer, or physical such as turning or sanding. Because these secondary surface treatments add cost, a smoothing layer is often used instead.

The electrical conductivity requirements of the conductive layer are modest. The higher the process speed the greater the conductivity required for adequate surface charge accumulation. Analysis by Chen [37.119] demonstrated that the result of inadequate conductivity in corona charging of a photoreceptor is a nonuniform surface potential. The surface potential is decreased depending on the distance from the actual grounding
contact. For a typical situation the upper limit of the sheet resistance is \( \approx 10^4 \) \( \Omega \) per square.

Alternative approaches such as seamless webs and conductive plastic drums have been developed but have not yet been commercialized.

### 37.4.4 Smoothing Layer and Charge-Blocking Layer

For xerographic applications it is important that the conductive layer does not inject charge into the photoreceptor in the dark. However, the metals used as grounding layers all have the potential to inject holes into the photoreceptor CGL via direct contact with the charge-generation material or the hole-transport material. The injection and transport of charge in the dark would cause a loss of surface potential (dark decay). Since the formation of a latent image relies on a difference between the rate of dark- and light-induced surface potential decrease, a high dark decay rate means that the process must be amenable to a small imaging potential. Another aspect of dark injection from the conductive layer is that such phenomena often occur in small localized charge-deficient spots. In a process where the discharged areas are developed small deposits of toner are found in what should be non-toned background. To counter such processes it is common to interpose a charge- (typically hole-)blocking layer between the ground layer and the CGL. With drum photoreceptors it may be the roughness of the metal surface which initiates the charge injection. In this case it may be necessary to interpose a relatively thick smoothing layer between the metal surface and the CGL.

In principle, any good film-forming insulating material will suffice as a charge-blocking layer as long as adhesion to the ground layer and CGL are adequate. Several types of materials have been used for this purpose including polysiloxanes and nylons. Since these materials are insulating, in an electrophotographic charge/expose cycle there will be a residual potential due to the field remaining across the layer. This will build up with cycling depending on the layer conductivity and the process cycle time. Although residual potentials typically decrease when the photoreceptor is rested in the dark, in practice such relaxation is usually incomplete and in subsequent cycling the residual builds up at a faster rate. The physics and chemistry of such hysteresis is not well understood. At some point the residual potential may cause image degradation and necessitate photoreceptor replacement. Thus, the blocking layer must be thick enough to cover the ground layer uniformly but not so thick as to cause an undesirable residual potential. Generally such a layer is coated at around 1 \( \mu \)m or less. On the other hand, if a thicker layer is required (perhaps combining the functions of both charge blocking and surface smoothing) this can be accomplished with a charge transporting insulating layer. With the conventional multilayer OPC architecture (holes transported through the CTL), this layer must transport electrons injected from the CGL to the electrode and block hole injections from the electrode into the OPC. Such polymer films have been described with naphthalene bisimides as the electron transporting moiety [37.120, 121].

With an aluminum drum, a thin anodized layer is often used to prevent charge injection. However, anodization is relatively expensive, and it has been reported that a simple chemical process (dilute alkali treatment followed by immersion in boiling water) produces an effective blocking layer [37.122]. Making the drum surface smooth on a submicron scale is expensive and an alternative is to use a relatively thick smoothing/blocking layer to cover the surface irregularities. Smoothing layers are typically metal oxides (titanium for example) in a polymer binder. The oxide loading is high to impart sufficient conductivity to prevent a residual potential. If the metal oxide does not inject holes it also serves as the charge-blocking layer. Such layers are up to around 10 \( \mu \)m thick.

Imaging with monochromatic radiation in digital printers has led to a new imaging artifact caused by interference between the incoming and reflected light. In dual-layer OPCs with the CTL uppermost, if the CGL incompletely absorbs the exposing light it can be reflected from the ground layer. The interference pattern that is produced can be visible in the developed image as a wood grain pattern. One way to counter this is to scatter the incoming light before it’s reflected. There are many patents describing techniques for carrying this out including roughening of the surface of the conductive layer.

### 37.4.5 Charge-Generation Layer (CGL)

The CGL is where the imaging light is absorbed and charges are generated. The first major consideration in choice of material is that it strongly absorb the wavelengths of light emitted by the exposure system. In copiers light is reflected from a document onto the charged photoreceptor. Since an original may have colored components the light source must cover the visible range (400–700 nm) and the photoreceptor must have broad sensitivity to visible light. Common light sources in copiers are fluorescent or xenon lamps. Both sources are generally filtered to remove ultraviolet and infrared light. In digital printers the exposing source may be an LED array (680–780 nm) or a scanned laser.
Most modern commercial photoreceptors utilize pigments as charge-generation materials. Pigment-based CGLs comprise submicron crystals of the charge-generation material suspended in a polymer binder. Pigments are milled to the desired size and stabilized with appropriate additives and binders to produce a coating dispersion. Charge-generation materials are generally classified according to their chemical identity. Materials which absorb primarily in the visible region are dye–polymer aggregate, PVK–TNF charge-transfer complex, perylenes, and bisazos. Phthalocyanines, trisazo, and squarylium pigments are utilized for near-infrared absorption. Figures 37.13 and 37.14 show the sensitivity action spectra and Figs. 37.15 and 37.16 the chemical structures of these charge-generation materials. The sensitivity action spectra in these figures are taken from literature data and the sensitivities converted into consistent units (V/cm²/erg) based on information given in the cited publication. Because the data are from OPCs with different thickness, exposure intensity, exposure time, initial potential, and exposed potential, the sensitivities are not directly comparable. However, the wavelength ranges are accurate. When the exposure is through the CTL (in a negative-charging dual-layer OPC) the photosensitivity will be decreased at wavelengths below \( \approx 400 \) nm because of light absorption by the transport material.

Perylenes, azos, and phthalocyanines are best known for their use as colorants and it is because these materials were readily available that they were investigated as charge-generation materials. A complication with pigments is that some exhibit polymorphism. Over many decades the colorant industry has developed technologies for controlling polymorphism to obtain pigments with specific colorant characteristics and similar technologies have been developed to obtain polymorphs with the appropriate absorption as well as charge-generation characteristics for electrophotographic applications. Thus, in many cases to prepare a CGL it is first necessary to convert the pigment-generation material into a dispersion of submicron particles of the desired polymorph. Examples of charge-generation materials are discussed below.

The donor–acceptor charge-transfer (CT) complex between poly(N-vinyl carbazole) (PVK) and 2,4,7-trinitrofluorenone-9-one (TNF) was the first commercialized organic photoreceptor [37.123, 124]. The photoconductivity characteristics have been extensively studied [37.87–89, 92–94] and reviewed [37.125–128]. With the addition of TNF the carrier-generation efficiency of PVK is increased and extended into the region...
of CT complex absorption. Based on field quenching of exciplex fluorescence a mechanism for PVK–acceptor systems was proposed involving carrier generation from a nonrelaxed exciplex which is accessed by either direct absorption into the CT state or via an encounter complex between excited PVK and TNF [37.92–95]. As used in the IBM copiers I and II a 1:1 molar ratio of PVK to TNF was coated as a single 20 μm layer and electron-dominated transport was used to create the latent image (negative surface charge) with a He–Ne laser exposure (632.8 nm) [37.124]. An exposure of 5.5 μJ/cm² was used to decrease the surface potential from −750 to −200 V. The quantum efficiency based on incident photons was ≈0.2 while the maximum efficiency was ≈0.3 at ≈400 nm. The photosensitivity action spectrum for this OPC is shown in Fig. 37.11 [37.123]. Using the photoinduced discharge technique [37.90] the maximum quantum efficiency (charges transported through the device per photon absorbed) was found to be 0.14 at 375 nm and a field of 10⁶ V/cm. The PVK–TNF-based OPC had several drawbacks: low photosensitivity, short lifetime in the electrophotographic process, and concerns about the safety of TNF. It was eventually replaced with dual-layer OPCs with CGL materials based on pigments. Acceptor-doped PVK continues to receive attention particularly with C₆₀ and related molecules as the acceptor [37.129].

The dye–polymer-aggregate based CGL is unique in that the active material is formed in situ during the coating process. A solution of thiapyrylium dye (2,6-di(phenol-3-benzoquinone) diperoxide) was spin-coated onto the OPC surface, and upon exposure to laser light, a charge generation layer (CGL) was formed. The CGL consists of a dye–polymer-aggregate that is created in situ during the coating process, allowing for the formation of a highly localized charge generation layer. This approach offers several advantages over traditional CGL materials, such as improved stability and reduced cost.
chlorate) and bisphenol-A polycarbonate is coated to form a CGL in which the dye and polymer spontaneously aggregate [37.130–132]. The aggregate is a dense filamentary structure which has an absorption spectrum red-shifted from that of the dye. The aggregate filaments transport electrons with high field trapping due to carrier immobilization at filament dead ends. The photosensitivity of the aggregate is several orders of magnitude larger than that of the nonaggregated dye [37.133]. To prepare a CGL the formulation also includes hole-transporting materials. Because the CGL transports both holes and electrons it is possible to use the aggregate as a single layer or as the CGL in a dual-layer photoreceptor. Because the aggregate absorption drops rapidly at wavelengths longer than 700 nm this material is only useful for visible-light exposure systems, Fig. 37.13. In this example the CGL (2 μm) comprised dye and tri-p-tolylamine (TTA) hole-transport material in polycarbonate, and the CTL (13 μm) was a solid solution of 40 wt% tri-p-tolylamine in a polyester binder [37.96]. This was charged to −600 V and exposed with very low-intensity continuous irradiation to obtain the initial rate of photodischarge. At 680 nm the photogeneration efficiency is 0.34 per absorbed photon. The quantum efficiency (Onsager model) was 0.6 and the thermalization distance was dependent on the concentration of hole-transport material ranging from 200 nm (5 wt%) to 600 nm (40 wt%) [37.96], Fig. 37.11.

Azo compounds contain the −N=N− functionality. Bisazo compounds have the general structure R′−N=N=N−R−N=N−R′′. Trisazo compounds have the general structure R(−N=N−R)(−N=N−R)′ (−N=N−R)′′) (−N=N−R′′′). The R substituents generally have extended conjugation to provide the colors which have made bisazo compounds important dyes and pigments for many years. Bisazo CGLs generally absorb in the visible and trisazo into the near-infrared. An early example of a bisazo pigment-based OPC (chlorodiane blue, 4,4′-bis(1′′-azo-2′′-hydroxy-3′′-naphthanilide)-3,3′-dichlorobiphenyl) was used in the IBM 3800 printer. This photoreceptor had over four times the photosensitivity of the PVK–TNF-based OPC [37.134]. Azo charge-generation materials are often synthesized from the reaction of an aromatic amine with an o-hydroxyaromatic carboxylic acid such as naphthol-AS. As CGL materials these materials are used as dispersed pigments. Although bisazo pigments do not generally exhibit polymorphism they can exist as hydroxy-azo or keto-hydrazone tautomers. In some cases, it has been found that the active form is the keto-hydrazone tautomer [37.135]. Because the synthesis of azo compounds is relatively easy there is a considerable literature on the effects of chemical structure on electrophotographic characteristics and carrier-generation efficiency [37.136–140]. In azo pigments charge is generated extrinsically with the pigment exciton oxidizing a hole-transport molecule at the pigment surface [37.140, 141] and it was demonstrated that penetration of the CTL into the CGL occurs during the coating process [37.142]. The photosensitivity action spectrum for a fluorenone bisazo pigment is shown in Fig. 37.13 [37.141]. In this OPC the CGL (0.17 μm) consisted of the pigment in a binder of poly(vinyl butyral) (10 : 4 weight ratio) and the CTL (17.4 μm) a solid solution of hydrazine transport material, p-diethylaminobenzaldehyde diphenylhydrazine (DEH), in polycarbonate (9 : 10 weight ratio). The initial potential was −800 V and the exposure required for a discharge to −400 V determined. The quantum yield of carrier generation from the Onsager model was 0.52 with a thermalization length of 1400 nm. Time-resolved transient absorption spectroscopy has been used to study the formation and decay of the oxidized transport material [37.143]. With a bisazo-based CGL (chlorodiane blue) [37.144] and trisazo-based CGL it was found that the charge-generation efficiency depended on the oxidation potential of the CTL transport materials [37.138]. In the most favorable case the bisazo had a quantum efficiency of 0.25 and the trisazo about 0.5. This was interpreted in terms of the energy gap between the hole at the pigment surface and the transport material. In a study using a series of bisazo pigment CGLs and a common CTL it was found that neither electron donating nor withdrawing substituents favor high photosensitivity [37.139]. Photosensitivity was found to depend inversely on the crystallinity of the pigment, which was interpreted in terms of pigment surface area. The development of high-sensitivity azo-based CGLs has been reviewed by Murayama [37.145]. The trisazo pigment-based OPC has an absorption which extends into the near-infrared, making it suitable for laser exposures. Figure 37.14 shows the photosensitivity action spectrum of an OPC with a trisazo pigment CGL [37.146]. The CGL (0.33 μm) consisted of the pigment in poly(vinyl butyral) binder (10 : 4 weight ratio) and the CTL (18.5 μm) a solid solution of DEH transport material in polycarbonate (9 : 10 weight ratio). The initial surface potential was −700 V and the exposure to discharge to −300 V used to determine the photosensitivity at each wavelength. A photoreceptor with CGL (0.12 μm) and CTL (19.5 μm) had a quantum efficiency for charge generation of 0.46 from 500–800 nm [37.146].

Perylenes used as CGL materials are diimides of perylene-3,4,9,10-tetracarboxylic acid. One example is the N,N′-bis(2-phenethyl)-perylene-3,4,9,10-bis(dicarboximide). In this case the CGL was pre-
pared by vacuum deposition of an amorphous film (0.1 μm). Exposure to dichloromethane (as when over-coating with the charge transport layer) converts the film into a crystalline form with enhanced absorption at 620 nm [37.147]. The mechanism of carrier generation of this pigment in the presence of tri-p-tolylamine has been studied by studying the field dependence of quenching of perylene fluorescence [37.148]. The results were interpreted in terms of both intrinsic (directly from the perylene singlet state) and sensitized (interaction of holes on the pigment surface with the amine) charge generation. A bisbenzimidazole perylene has been developed as a CGL [37.149–151]. Dual-layer OPcs with a CGL of 0.1 μm vacuum-deposited bisbenzimidazole perylene, and a 15 μm CTL of 35 wt% TPD in polycarbonate, exhibit high sensitivity (E1/2 2 erg/cm² for −800 V0) out to 700 nm, Fig. 37.13. Further research has involved the synthesis and study of novel materials such as dimeric perylene pigments [37.152].

Phthalocyanines have received considerable attention as CGL materials for near-infrared exposure systems. Metal-free (H2Pc) [37.153–156], titanyl (TiOPc) [37.157], and hydroxygallium (HOGaPc) [37.158] phthalocyanines have been extensively studied as CGL pigments. Although these materials are relatively easy to synthesize their intractability makes them difficult to purify. Except for halogen substituents on the aromatic rings there has been little research into the effect of chemical structure on performance. Instead, much of the development has been to understand and control polymorphism. Compared with solution absorption spectra, the spectra of many CGL pigments are broadened with enhanced absorption in the red and near-infrared. With specific combinations of milling technique, solvent exposure, and thermal treatment many phthalocyanine polymorphs can be produced [37.159–162]. Polymorphs have been characterized by visible and near-infrared absorption spectroscopy, x-ray diffraction, nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy, and infra-red (IR) absorption spectroscopy. Examples of TiOPc polymorph absorption spectra are shown in Fig. 37.17 [37.157].

Polymorphs may have very different photogeneration characteristics as CGLs in OPcs. The materials shown in Fig. 37.17 were fabricated into OPcs: CGL, 0.4 μm, pigment and poly(vinyl butyral) 1:1 weight ratio; CTL, 20 μm, 43 wt% triarylamine hole-transport material, 4-(4-methylstyryl)-4’4”-dimethoxytriphenylamine, in polycarbonate. The photosensitivity action spectra for OPcs from the Y- and A-forms of TiOPc are shown in Fig. 37.14. The OPC with the Y-form had a photosensitivity for half photodischarge (600–850 nm) of 0.75 erg/cm² (initial potential −600 V) while the A-form was much less sensitive. In another study, photoreceptors formulated with α-, β-, τ-, and X-forms of H2Pc had generation efficiencies as follows (5 ×10⁵ V/cm): r2 ≈ 0.1, X2 ≈ 0.09, X1 ≈ 0.03, β1 ≈ 0.01, α2 ≈ 0.005, and α1 ≈ 0.001 [37.163]. In the preparation of a generation material a common procedure is to prepare the pigment in the amorphous form by acid pasting or with a specific milling technique, and then to convert the pigment to the desired polymorph with a specific solvent treatment. The desired polymorph must of course be stable to all the subsequent operations. In addition to the dominant influence of crystal form on electrophotographic performance, studies have implicated water in carrier generation of Y-form TiOPc [37.157, 164]. A recent paper has reviewed the carrier generation mechanisms in several phthalocyanines [37.165]. In all the pigments studied (x−H2Pc, TiOPc (I) (low sensitivity), TiOPc (IV) (also known as Y, high sensitivity), HOGaPc (V)), fluorescence quenching implicates a neutral excited state (not a charge-transfer state) as the precursor to carrier generation. Studies of the effect of field on fluorescence amplitude and lifetime reveal that with HOGaPc and TiOPc (I and IV) carrier generation comes from a non-relaxed excited state and TiOPc (IV) has an additional generation channel from a trapped state. With x−H2Pc trapped excitons appear to be the major source of charge carriers.

Fig. 37.17 Absorption spectra of polymorphs of TiOPc. (After [37.157])

A-form was much less sensitive. In another study, photoreceptors formulated with α-, β-, τ-, and X-forms of H2Pc had generation efficiencies as follows (5 ×10⁵ V/cm): r2 ≈ 0.1, X2 ≈ 0.09, X1 ≈ 0.03, β1 ≈ 0.01, α2 ≈ 0.005, and α1 ≈ 0.001 [37.163]. In the preparation of a generation material a common procedure is to prepare the pigment in the amorphous form by acid pasting or with a specific milling technique, and then to convert the pigment to the desired polymorph with a specific solvent treatment. The desired polymorph must of course be stable to all the subsequent operations. In addition to the dominant influence of crystal form on electrophotographic performance, studies have implicated water in carrier generation of Y-form TiOPc [37.157, 164]. A recent paper has reviewed the carrier generation mechanisms in several phthalocyanines [37.165]. In all the pigments studied (x−H2Pc, TiOPc (I) (low sensitivity), TiOPc (IV) (also known as Y, high sensitivity), HOGaPc (V)), fluorescence quenching implicates a neutral excited state (not a charge-transfer state) as the precursor to carrier generation. Studies of the effect of field on fluorescence amplitude and lifetime reveal that with HOGaPc and TiOPc (I and IV) carrier generation comes from a non-relaxed excited state and TiOPc (IV) has an additional generation channel from a trapped state. With x−H2Pc trapped excitons appear to be the major source of charge carriers.
Squarylium (squamaine) pigments are a class of materials which were first synthesized in the 1960s. Squaryliums (2,4-di-(o-hydroxy-p-dimethylaminophenyl)cyclobutene and 1,4-bis-(4-dimethylamino-2-methylphenyl diylum-1,3-diolato)) were the first pigments to be utilized as a near-infrared-sensitive CGL in an IBM printer [37.144, 166, 167]. The photoreceptor based on the hydroxy squarylium with a CTL (21 μm, DEH in bisphenol-A polycarbonate) had high photosensitivity from 500–800 nm (≈ 3 erg/cm² for a −700 to −200 V photodischarge), Fig. 37.14 [37.167]. This class of pigment has been extensively investigated for use as pigment-dispersion CGLs for near-infrared exposure systems [37.149, 168–174]. A nonsymmetrical squaraine (UFSq)-based OPC with CGL, 0.4 μm UFSq in poly(vinyl formal) (80 : 20 weight ratio), and CTL 26 μm 40 wt% TPD in bisphenol-A polycarbonate, exhibited an $E_{1/2}$ photosensitivity of 1.9 erg/cm² at 790 nm (−980 V₀) when optimally purified [37.174], Fig. 37.14.

### 37.4.6 Charge–Transport Layer (CTL)

In all current commercial organic photoreceptors holes are the carriers that dominate photodischarge of the device. Hole transport is carried out by aromatic amines which are either doped into, or are incorporated as part of, the binder polymer. The key molecular characteristic is that aromatic amines have relatively low oxidation potentials. The oxidation potential of the transport moiety must be lower than that of the charge-generation material such that photogenerated holes are injected from the generation material into the charge-transport layer. In a chemical sense the key reaction is oxidation of the charge-transport material by the photogenerated hole on the surface of the generation material. If the oxidation potential of the transport material is too low it will undergo air oxidation, if it is too high its oxidation will require an activation energy and will be inefficient. Molecular orbital studies suggest that molecules with little change in geometry with oxidation will be favorable for hole transport [37.175]. Aromatic amines with oxidation potentials between about 0.8–1.2 eV (relative to SCE) are generally useful as hole-transport materials. The synthesis and study of hole-transport molecules is a very active area. Figure 37.3 shows the chemical structures of some common hole-transport materials:

- 1,1-Bis(p-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene (DBP)
- $p$-Diethylaminobenzaldehyde diphenylhydrazone (DEH)
- tri-$p$-Tolylamine (TTA)
- N,N'-Diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD)
- 1,1-Bis(di-4-tolylaminophenyl)cyclohexane (TAPC).

These are often referred to by acronym and classified according to one of their structural functionalities: arylmethane, diarylamine, enamine, triarylamine, heterocyclic, butadiene, and hydrazone. A more complete listing is available in Borsenberger and Weiss [37.5]. A wide variety of new hole transporting materials for electrophotographic photoreceptors have been reported. These include carbazole-containing enamines [37.176], indolo[3,2-b]carbazole derivatives [37.177], and phenyl-1,2,3,4-tetrahydroquinoline [37.178], among many others.

Charge transport was discussed previously (Sect. 37.2.2). Since transport involves orbital overlap between neighboring charge-transport moieties their concentration needs to be as high as possible. In practice, molecular transport materials are doped, singly or as a mixture, at 40–50% by weight into the binder polymer. The purpose of the binder polymer is to provide an inert, robust, substrate for the transport material. The mobility characteristics of a large number of hole-transport materials have been studied and the results interpreted according to a model where the dissolved transport molecules are disordered in energy and position [37.179–181]. Binder effects on hole transport have been observed. It appears that the presence in the CTL of materials with highly polar substituents decrease hole mobility but in general these effects are not well understood [37.182–187].

Since the CTL is typically the surface that is exposed to the various electrophotographic process elements it must be formulated to resist damage and wear. The glass-transition temperature ($T_g$) of the CTL is an important characteristic. Too low and the material will be soft and easily damaged, too high and it will be brittle. Generally a $T_g$ around 60°C is adequate. Polycarbonates and polyesters are two classes of materials commonly used as CTL binder polymers. Exposure of the CTL to the effluents of the corona charging system, UV light, reactive chemicals (ozone and nitrogen oxides), ions, etc., results in surface oxidation and degradation of both the physical and electrical characteristics of the CTL [37.188].

Dual-layer devices in which electron transport dominates have been studied extensively but never commercialized. Examples of commercialized electron-transport-dominated photoreceptors are the single-layer dye–polymer aggregate and the PVK–TNF charge-transfer complex. Electron-transport materials are designed to be easily reduced. The reduction potential
must be lower than that of the photogenerated electron on the charge-generation material so that it is transferred to the transport material. However, it is believed that oxygen may act as an electron trap so the reduction potential of the transport material must be lower than that required to reduce oxygen dissolved in the polymer film. Figure 37.10 shows the chemical structures of some electron-transport materials. As with hole-transport materials acronyms based on molecular functionality are common:

- 1,1-Dioxo-2-(4-methylphenyl)-6-phenyl-4-(dicyanomethylene)thiopyran (PTS),
- n-Butyl 9-dicyanomethylenefluorene-4-carboxylate (BCMF),
- 2,4,7-Trinitro-9-fluorenone (TNF),
- 3,3’-Dimethyl-5,5’-di-t-butyl-4,4’-diphenoquinone and 3,5’-Dimethyl-3,5-di-t-butyl-4,4’-diphenoquinone isomer mixture (DPQ).

A more complete table can be found in Borsenberger and Weiss [37.5]. In general the charge mobilities observed with electron-transport materials are much lower than for hole-transport materials. For this reason dual-layer OPCs with electron-transport-based CTLs have not been commercialized. Analysis of the mobility characteristics of electron transport with the disorder model implicates the highly polar nature of many electron-transport molecules [37.189–192].

Both hole- and electron-transport materials have been prepared with the transport moieties as part of a polymer (main chain or pendant) which would serve as a binder with hole-transport functionality. The advantage of a transport-active polymer is that it is a single material with improved physical characteristics relative to the corresponding molecularly doped polymer. In practice, charge transport is generally not enhanced in these materials and their chemical complexity makes them expensive to synthesize. Also, they are still susceptible to the damaging effects of the charging system in the electrophotographic process. Many polymers have been synthesized utilizing hydrazones [37.193–195] or other hole-transporting functionalities [37.196, 197].

**Backing Layer**

In a web photoreceptor the substrate–photoreceptor may tend to curl due to the residual stress of the coated layers. Such curl can make it difficult to fabricate the web into loops, may degrade loop tracking in the machine, or cause the loop edge to touch other process elements. Any of these attributes would make the photoreceptor unusable. One way to counter film curl is to coat a polymer layer on the back side to compensate for the stresses in the photoreceptor layers. The back-coat polymer must have adequate physical characteristics (friction, wear, etc.) to withstand cycling in the process. The extra coating adds expense but its addition is relatively commonplace. Any suitable polymer, such as a polycarbonate, may be used.

### 37.4.7 Overcoat Layer

Overcoat layers have received increased attention to lengthen the photoreceptor life by preventing wear, minimizing the effects of surface contacts, the effects of corona effluents (ozone and nitrogen oxides), and liquid attack in liquid-toner-based printers. As with the charge-blocking layer, the simplest approach is to coat a thin insulating polymer onto the photoreceptor surface. The thickness cannot be more than a few µm if one wants to avoid large residual potentials. Several approaches have been developed. One approach is to coat a second CTL with a changed composition to maximize polymer toughness (often by lowering the concentration of transport material or adding inorganic filler particles). Other approaches are to overcoat the photoreceptor with a silsesquioxane sol–gel several µm thick [37.198, 199], or with a submicron refractory layer of diamond-like carbon [37.200] or AlZrN [37.201]. However, the thinness of the refractory materials limits their utility for scratch and wear resistance. Furthermore, depending on their chemical make up they may have sensitivity to corona gasses.

Silsesquioxane overcoats applied in a sol–gel process have received attention [37.202, 203]. A commercial application utilized a sol–gel to overcoat a photoconductor with an uppermost CGL (positive-charging OPC). Because the CGL is sensitive to wear and corona chemicals an overcoat was essential to its implementation in a commercial photoreceptor. The sol is prepared and subsequently hopper-coated and cured at elevated temperature to effect crosslinking. To avoid a residual potential some conductivity is necessary but this cannot be so high that the latent image is degraded particularly under high humidity conditions [37.204]. The conductivity can be controlled with an ionic dopant [37.202] or by the incorporation of a hole-transporting functionality into the sol–gel matrix [37.203, 205].

A polyurethane overcoat in a positive-charging dual-layer OPC has been described for use in a liquid-toner-based printer [37.206]. The CGL was based on TiO₂ pigment and, to avoid disruption of the CGL during the overcoat coating operation, an aqueous polyurethane dispersion was used.

A tough, durable, overcoat layer is described in a Konica Minolta Research Report [37.207]. The overcoat is a curable resin chemically bonded to inorganic nanoparticle filler. After one million prints at high
humidity in an electrophotographic printer the OPC thickness decreased by 1.5 μm, but the printed images showed no degradation in quality relative to a new OPC.

### 37.5 Photoreceptor Fabrication

As discussed above the two most common photoreceptor configurations are as a loop or a metal drum. After coating the layers of a drum photoreceptor it is ready to use in the process. Generally the drums are inspected for visible defects and samples are taken for process testing and quality control. Since the substrate is conductive the ground contact is easily made by means of a conductive brush contacting the edge or inside of the drum when it is mounted in the machine. On the other hand, after the appropriate layers are coated on a web several more steps are required for fabrication of the photoreceptor. The web is rolled onto a spool at the end of the coating process and subsequently slit to the desired width and rewound. The coated roll is then inspected for visible defects and defective areas are marked for removal. Defective areas are removed when the photoreceptor is cut to the desired length. The cut sheets are then ultrasonically welded to produce a photoconductor loop. Because the conductive layer is buried between the substrate and the coated layers, making a ground contact is not trivial. It is possible to leave one edge of the ground layer uncoated but, because the thin metal would be readily damaged or worn away with use, one typically finds a conductive stripe coated on one edge of the photoreceptor. The only requirement is that the conductive stripe penetrate the coated layers and contact the metal. The ground contact in the machine is often made with a conductive brush contacting the conductive stripe. The printing machine must keep track of the splice for several reasons: cleaning blade, degraded photoconductivity due to the ultrasonic welding, etc. This is sometimes accomplished by applying marks to the back of the photoreceptor, which are detected by the machine.

Fabricating a photoreceptor loop entails several operations not required in the fabrication of drum photoreceptors (slitting, cutting, conductive striping, welding, backside marking, etc.). Web-coating a photoreceptor is an expensive process but many thousands of feet of photoreceptor can be produced in a single coating event. Furthermore all the loop-processing elements are relatively straightforward and inexpensive. The key factor is that web-coating is a continuous process while drum-coating is a batch process. Photoreceptor loops are generally about ten times less costly to produce than drums.

There are advantages and disadvantages to both seamed loop and drum configurations in a printing machine. Loops can be made small for desktop printers or large for high-speed commercial printers. A large web (current commercial webs are as large as \( \approx 10 \text{ ft} \) in circumference) provides more surface area for imaging (several images per loop cycle) and more space for the various electrophotographic process elements. In addition, exposures through a semitransparent conductive layer are possible. Disadvantages are the presence of a seam which must be tracked and makes some processes, such as cleaning with a blade, problematic. Also, the tendency of a web to flutter or move necessitates both tracking and positioning to achieve adequate print registration. Metal drums are seamless and rigid, making it easier to control drum position. However, drums typically have a diameter of 35–300 mm and have limited imaging area and space for process elements. All things being equal a loop which produces several images per cycle will produce more images over its lifetime than a drum. Ultimately, the choice of loop or drum is a printing system issue.

### 37.6 Summary

Organic photoreceptors have been utilized in electrophotography since 1970. In this chapter we have briefly reviewed the development of organic photoreceptors from the standpoint of the device architecture, materials formulation, and electrical characteristics with emphasis on how the materials used impact on specific device functions.

The use of organic materials has enabled the development of electrophotographic technologies into a multi-billion-dollar business. Today’s organic photoreceptor is a large-area photoelectric device capable of very high spatial resolution in the formation of a large-area image, with pixel resolution as small as 20 μm (1200 dpi), to meet demanding image-quality re-
Organic photoreceptors have to satisfy many diverse requirements to be successfully employed in electrophotography as it is practiced today. These requirements have been met in large part by the principles of: (1) functional separation, and (2) materials design for the enhancement of specific electrical and mechanical characteristics. The concept of functional separation was key to organic photoreceptor development. Rather than try to produce a device with all the desirable characteristics in a single layer it is more productive to have a multilayer architecture with each layer being optimized for a specific characteristic. Not surprisingly these layers are commonly named after those characteristics which are paramount: the charge-generation layer (CGL), the charge-transport layer (CTL), the charge-blocking layer, the protective overcoat layer, etc. In this chapter we have described the characteristics of each of these layers and demonstrated how materials have been chosen and new materials synthesized to optimize their characteristics.

It is worthwhile to take a minute to review the electrophotographic process and consider the characteristics which have been built into the device:

- **Spatial uniformity.** The thickness of each of the coated layers (each varies from submicron to a few tens of μm) and the total thickness (controlled mainly by the CTL) must be very uniform so that the device capacitance (a major factor in determining surface charging characteristics) is uniform (on the order of a few percent variability). The CGL generation characteristics must be uniform, which means that the optical density of the CGL at the exposure wavelength must be uniform, to produce a uniform surface potential after exposure (on the order of a few percent variability). Thickness must be uniform for the smallest pixel (20 μm for 1200 dpi imaging) over the entire area of the device (> 1000 cm²). The ability to coat large areas of such thin layers to this degree of uniformity is a great technological achievement.

- **Chemical resistance.** Photoreceptors must resist chemical attack. Because corona charging is the most common method of applying a surface potential, the photoreceptor must be stable to the acid and oxidizing species produced in the corona. These chemicals (ozone, NO₂, and HNO₃) are highly reactive and the layer that is exposed (usually the CTL) must not be degraded. This is achieved by judicious choice of materials, the addition of stabilizers (antioxidants) to the CTL, or a protective overcoat.

- **Electrical uniformity and stability.** The photoreceptor dark electrical and photoelectrical characteristics (surface potentials with no exposure, imaging exposure, and erase exposure) must be very uniform and stable to prolonged electrophotographic cycling. The initial (dark) and exposed potentials must be the same for each pixel over the entire device area and must remain stable with cycling. If these characteristics drift uniformly with cycling, machine process control must be implemented to maintain image quality. If these characteristics drift nonuniformly the photoreceptor must be discarded when image artifacts (ghosting) appear.

- **Photosensitivity.** The sensitivity of the photoreceptor to light, often expressed as the energy needed to produce a defined decrease in surface potential, must be mated with the exposure used in the process in terms of exposure energy and wavelength. This has been achieved by the synthesis and pigment form manipulation of charge-generation materials. Today’s high-sensitivity photoreceptors can approach a quantum efficiency of unity for charge generation (at a typical applied field of ≈ 20 V/cm). But, most importantly photoreceptors with lower sensitivity can be fabricated depending on the needs of the imaging system.

- **Photodischarge rate (switching time).** The time it takes for photogenerated carriers to transit the device limits the printing process speed. With the synthesis of highly stable hole-transport materials and the principle of molecularly doped polymers it has been possible to prepare devices with hole transit times that permit printing speeds approaching 200 pages/min.

- **Mechanical strength.** The surface of the photoreceptor that is exposed to the abrasive process elements (often the development and cleaning systems), must not wear too rapidly or unevenly and must be stable to crazing or other forms of damage. Typically the CTL is the surface layer, and considering that it is typically a polymer with as much as 50% by weight of charge-transport molecules, it is remarkable that materials can be chosen such that significant wear occurs only after tens of thousands of cycles. Where warranted, very tough protective overcoats have been developed which have little effect on the overall OPC device performance.
Today multilayer organic photoreceptors that meet all of the requirements listed above are made commercially on a huge scale. This success is due in large measure to the skill of the scientists and engineers who design the materials and processes for photoreceptor fabrication, and who then integrate it into the electrophotographic printing system such that acceptable design the materials and processes for photoreceptor measure to the skill of the scientists and engineers who especially on a huge scale. This success is due in large all of the requirements listed above are made commer- imaging cycles, such that the characteristics of a 40 μm pixel area are identical over an area which might be greater than 1000 cm².

Acknowledgments. Martin A. Abkowitz received his Ph.D. in Physics from Syracuse University in 1964. In 1965 he joined the Xerox Corp. Webster Research Center where he was a Principal Scientist until his retirement in 1969. After retirement he was a Visiting Scientist at the University of Rochester. He was a Fellow of the American Physical Society, had 174 publications including 35 U.S. patents, and made over 250 contributed and invited presentations at international conferences. Martin passed away on January 30, 2014. The scientific community has lost an outstanding physicist and I, his co-author, have lost a dear friend.

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