Kirk-Othmer Encyclopedia of Chemical Technology.

ELECTROPHOTOGRAPHY

The first xerographic copy was made in 1938 (1). Triboelectricity, the charging of solids by friction, was first reported by the Greeks. Not until the early twentieth century were there serious efforts to develop what became known as electrography for reproducing images. The production of such images was based on the ability of electrostatically charged insulators to attract triboelectrically charged powders (2). This required the scanning of a document, line by line, using a light-sensitive scanner to produce an analogue voltage that was then used to modulate the output from an ion source. Copies could thus be produced by the displacement of a document-size, insulating layer beneath a stationary ion source and then rendering the resultant charged image visible (developed) by dusting with a triboelectrically charged powder.

The combination of electrostatic charging and development using the phenomenon of photoconductivity, first discovered in selenium crystals in the 1870s, led to the invention of electrophotography (3, 4). Photoconductivity, the enhancement of the electrical conductivity of a material by illumination with light, allows the image of an entire document to be copied by simply projecting its optical image onto a page-size photoconductive layer, known as the photoreceptor, uniformly charged with ions. Reflected light from the document then produces selective photodischarge in the photoreceptor proportional to the incident light intensity. The resultant image, consisting of the remaining surface charge, replicates the information content of the document. This latent electrostatic image can then be developed by utilizing its electrostatic attraction for charged powder. The highly photosensitive amorphous form of selenium [7782-49-2] was discovered in the mid-1940s. Other improvements involving ion charging processes, electrostatic transfer, and dry-ink or toner materials followed. Commercialization became feasible and the Greek words for dry, xeros, and writing or drawing, graphein, were combined to give the name xerography and XeroX as a trade name.

The XeroX Copier Machine Model A was announced in 1949, and involved complicated manual operation. Copies of acceptable quality were operator dependent. The Copyflo printer, introduced in 1955, was the first automated xerographic machine and enabled the production of copies on a continuous web of ordinary paper. Early electrophotographic products used paper coated with dye-sensitized zinc oxide Electrofax which had met market resistance in terms of aesthetics and cost, so that in 1958 the total market was only about $100 million (1–3, 5).

The Xerox 914 copier, first shown in September 1959, was a fully automatic machine requiring no special skills to operate. It produced seven copies per minute on plain paper using a reusable photoreceptor. The image, composed of a carbon-black impregnated polymer toner, was impervious to degradation by light or chemicals and thus compatible with archival storage. In contrast to market predictions of 3,000, over 200,000 were sold over the life of the product. By 1992 the total copier and printing business worldwide for all companies had grown to over $50 billion and the annual total number of copies was numbered in trillions. Developments in materials and process, including silicon integrated circuit technology (see Integrated circuits), software, digital transmission networks, and light sources, such as lasers (qv) and light-emitting diodes (LED) (see Light generation), have extended the capability of xerography beyond making copies to creating new documents based on the synthesis and manipulation of electronic images.

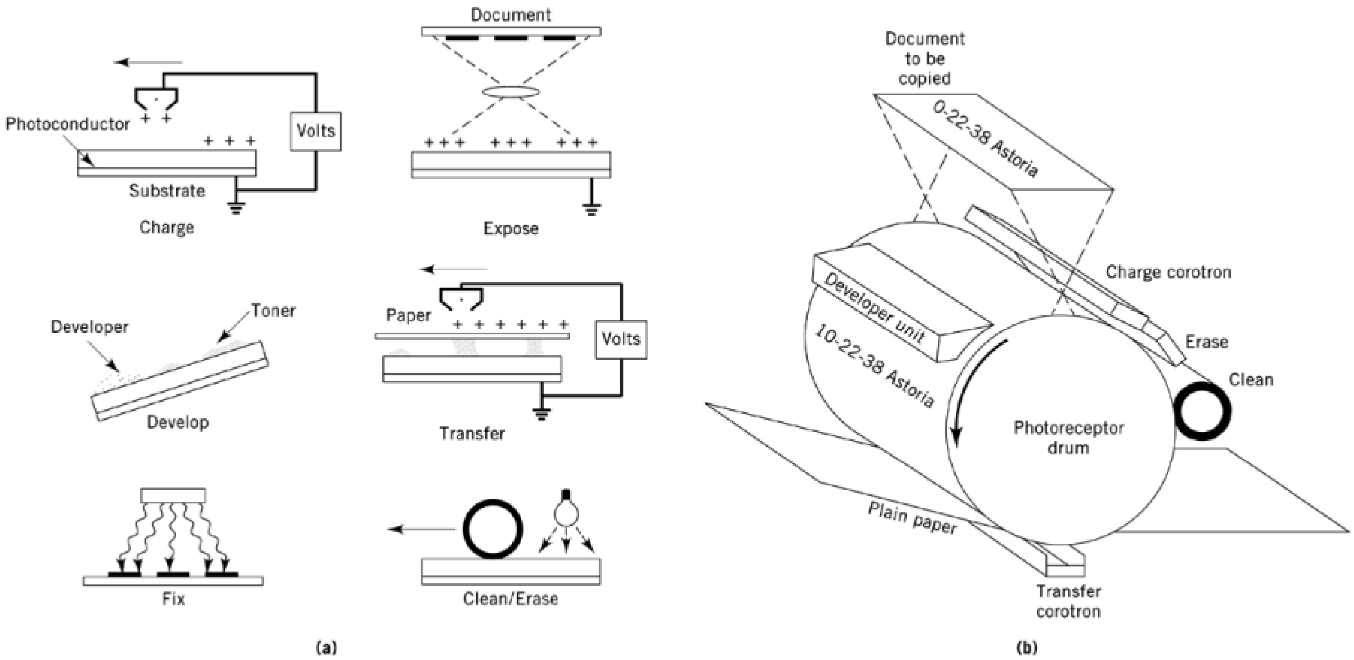

Fig. 1. (**a**) Steps of the xerographic process; (**b**) schematic arrangements of hardware.

The features of the integrated xerographic process are indicated in Figure 1 (3). The heart of a xerographic machine is the photoreceptor which consists of a thin film, 20 to 50 μm thick, coated onto a grounded aluminum drum or metallized belt (see Thin films). The film material must have a high ($> 10^{12}\Omega{\cdot}\mathrm{cm}$) resistivity in the dark and yet be photosensitive on exposure to visible light. The photoreceptor drum or belt is mechanically rotated with respect to the other necessary subsystems. The first of these is a corona charging device, such as a corotron, which produces either positive or negatively charged air ions depending on the polarity of a high voltage applied to a wire. These ions are accelerated by the applied voltage and deposited on the surface of the photoreceptor, which thus charges as a parallel plate capacitor. The resultant voltage across the film is proportional to the number of ions deposited per unit surface area and to the inverse of the material's dielectric constant. Typically, voltages of a few hundred volts are used to provide the necessary development fields. This surface potential, divided by the film thickness, determines the applied electric field within the photoreceptor. The charged area of the photoreceptor then rotates, with minimal loss in the initial voltage because of its high resistivity in the dark, into the exposure position.

In the exposure position an optical image, produced by scanning the document to be copied with a slit light source, is focused by lenses onto the photoreceptor surface. Where light reflected from white areas of the document strikes the photoreceptor, photogeneration of free electrons and holes occurs within the absorption depth of the light, which is typically much less than the film thickness. The dark characters on the original document reflect less light and proportionally fewer photocarriers are created. Assuming the initial voltage is positive, photogenerated holes move across the photoreceptor film and electrons move the shorter distance back to the top surface under the influence of the electric field within the photoreceptor. This causes the initial voltage to selectively discharge to a degree depending on the amount of light locally absorbed by the photoreceptor. In laser printers or digital copiers, the optical image is directly written on the photoreceptor surface by a scanning laser or LED array where the light output is controlled in an on–off fashion using digital electronic signals.

Leaving the exposure zone, the photoreceptor now carries an invisible distribution of surface charge or voltage which replicates the document image. This latent electrostatic image is then developed by cascading charged dry ink or toner, consisting of polymer particles containing carbon black or colored pigment, over the photoreceptor surface. The toner charge which is produced by controlled triboelectric charging is opposite in sign, negative in this example, to the original charge deposited on the photoreceptor. The negatively charged toner particles are attracted by mutual coulomb electrostatic force to the remaining positive surface charges of the latent electrostatic image, and become attached to the photoreceptor surface.

After leaving the development zone, the original document charge image is now a visible toner image. This is next transferred from the photoreceptor to plain paper by using a transfer corotron. This charges the paper with ions of the same polarity as that used to charge the photoreceptor, and toner now moves from the photoreceptor onto the paper. Because only a fraction of the toner is transferred in this step, the remainder must be removed from the photoreceptor surface, for example, by mechanical brushing. Finally, any residual latent-image surface charge must be discharged. This is done by uniformly exposing the entire photoreceptor to light from an intense erase lamp. After the transfer step, the paper moves to a fixing or fusing station where the toner image is softened using either solvent or, more typically, heat. In this way the toner adheres to the paper, the image is fixed, and the copy is ready. At this point the process cycle is completed and can automatically restart. In modern high speed xerographic products, these steps occur automatically to produce over 100 copies or prints per minute.

1. Photoreceptor Materials

The photoreceptor employs photoconductive materials and basically serves the same function as silver halide film in conventional photography (qv). The photoreceptor is designed to transform an optically input image into an electrostatic latent image on the photoconductor surface. The photoconductor remains charged if unilluminated, or even when exposed to unabsorbed wavelengths of light, discharging in the regions where light is absorbed.

The most desirable characteristics of photoreceptors for use in electrophotography are the following:

(1) The ability to accept and hold the electrostatic charge in the darkness. The photoconductive layer should support a surface charge density of approximately $0.5 - 2 \times 10^{-7}$ C/cm^2. The charge also has to be uniformly distributed along the surface, otherwise nonuniformities can print out as spot defects. The applied surface potential should be retained on the photoreceptor until the time when the latent electrostatic image is developed and transferred to paper or, if needed, to an intermediate belt or drum. In other words, the "dark decay" or conductivity in the dark must be very low. The photoconductor materials must be insulators in the dark.

(2) The photoreceptor must lose most of its surface charge upon exposure to the white light reflected from the original or upon exposure to an attenuated laser beam. The residual potential after each exposure must be low, not greater than a very small fraction of the original surface potential. The amount of available light energy is small, typically less than about 1×10^{-6} J/cm^2 (10 ergs/cm^2) for fast duplicators and printers and somewhat more for slower copiers and printers. Thus the device should absorb as much light as possible, and the number of charges generated and transported without a loss per incident photon must be as high as possible. This means high absorptivity of the material designed to generate charges, high charge-carrier generation efficiency, no loss of charge carriers by recombination or from traps when the carriers are transported across interfaces, and essentially trap-free transport.

(3) The photogenerated charge carriers should exit the device in a time shorter than the time between exposure and the development of the latent image. In practical terms, the charge-carrier mobilities μ (velocities ν

per unit electric field E), should be of the order of $10^{-7} - 10^{-6}\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ for slow copiers and printers, or $10^{-6} - 10^{-5}\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ or higher for high volume copiers or printers. It is also important that essentially all charges exit the device in each xerographic cycle, ie, no charges should be accumulated by deep trapping. Deep traps are operationally defined as traps from which the carriers are released in times longer than the time of the experiment, which in this case is the xerographic cycle. This places stringent requirements on the purity of all participating materials, including the solvents used for the deposition, and on the chemical stability of all the photoreceptor components; the presence of as few as 10^{13} trapping defect molecules per cubic centimeter can noticeably affect the residual potential on the photoreceptor.

(4) The photoreceptor must be stable in performance. In order to guarantee that the quality of copies stays the same after hundreds of thousands of produced copies, the photoreceptor should maintain the same charge acceptance. That is, the potential across the photoreceptor should be the same after each charging providing the charging device, the corotron, produces the same number of ions. The rate of the surface charge decay should not increase with the xerographic cycling. In other words, the photoconductor conductivity in the darkness should not vary with time. Also, the number of charges produced and transported (the sensitivity) per incident photon should remain the same. This means that the device should not undergo any degradation process which would result in an increase of the surface or bulk conductivity, in the development of charge traps, in a change in sensitivity, in a change of the blocking nature of the metal–photoconductor interface, or in a significant change of fatiguing. Fatiguing is a temporary increase in dark conductivity after several successive xerographic exposure cycles, which disappears after a brief rest in the darkness. Charge trapping could be caused by impurities, either inherent or formed during the xerographic process.

(5) The photoreceptor should be mechanically robust. This term was coined to reflect the combined mechanical durability, high scratch- and abrasion-(wear) resistance, high flexibility, resistance to cracking and crazing if the photoreceptor is used as a flexible belt or scroll, smoothness, which is believed to enable efficient cleaning of residual toner particles, as well as a chemical resistance to corotron effluents containing ozone, oxides of nitrogen, and other corrosive elements, compounds, or ions.

(6) Lastly, the photoreceptors must be inexpensive and easy to fabricate into defect-free, large-area thin films with uniform thickness of all layers.

1.1. Photoconductors

Only the most recently developed organic photoconductors (OPC) approach optimum behavior (see Photoconductive polymers).

The early xerographic photoreceptors were single-layer devices, 20–100 μm thick, comprised of a photoconductive material deposited on a conductive ground, a drum or a plate, as illustrated in Figure 2**a**. Because most photoconductive materials have high absorption coefficients, the incident photons are absorbed and, consequently, most of the charge-carrier pairs, holes and electrons, are produced in a very thin surface region. The sign of charge deposited on the photoconductor depends on which sign carrier has the best chance of moving through the bulk of the material without trapping, and which is faster. Thus amorphous selenium-based photoreceptors are charged positively because selenium transports holes better than electrons. The photogenerated electrons, the role of which is to neutralize the surface charge, may have a limited range but do not have to travel a large distance.

Anthracene and sulfur were used as photoconductors to produce the first xerographic images in the late 1930s (1, 4, 6–9). These elements do not easily form good thin films nor absorb visible light strongly enough.

Amorphous (vitreous) selenium, vacuum-deposited on an aluminum substrate such as a drum or a plate, was the first photoconductor commercially used in xerography (6). It is highly photosensitive, but only to blue light (2). Its light absorption falls off rather rapidly above 550 nm. Because of the lack of photoresponse in the

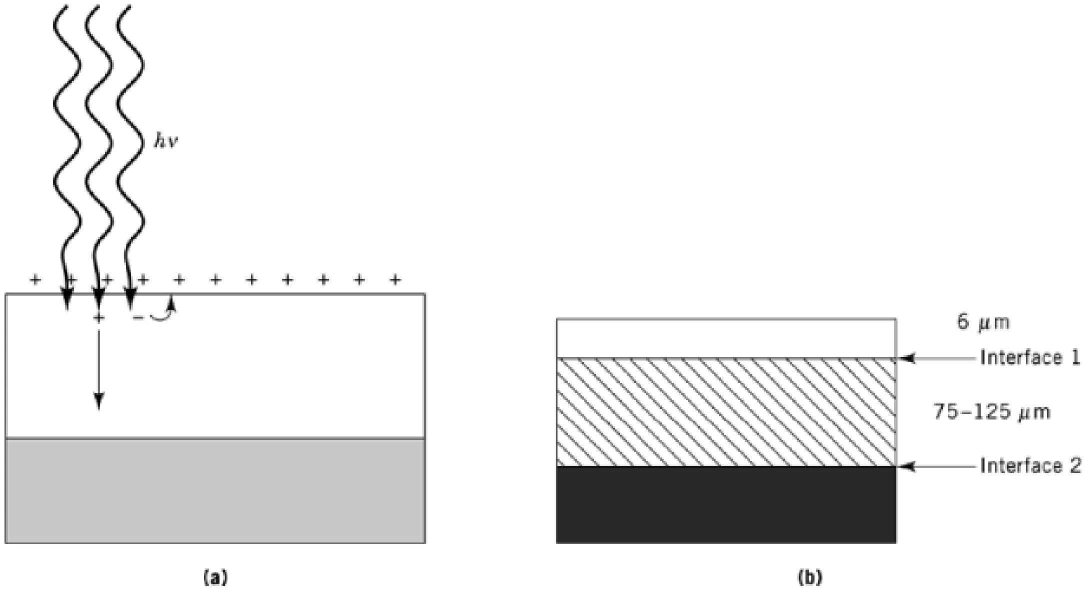

Fig. 2. Schematics of (**a**) single-layer photoreceptor, where the + signs represent the corona-deposited charge, □ the photoconductor, and ○≡▌ the conductive substrate; and (**b**), the CdS_xSe_{1-x} (Katsuragawa) photoreceptor, where □ represents the insulating layer, ▨ the CdS_xSe_{1-x}, and ■ the conductive base.

red or near infrared regions, selenium photoreceptors cannot be used in laser printers having He–Ne lasers (632.8 nm), or solid-state lasers (680–830 nm).

The useful spectral range of selenium can, however, be extended. For example, the addition of substantial amounts of tellurium shifts the absorption tail to the red or eventually to the near infrared (10). Addition of 7.5% of Te extends the spectral response almost throughout the visible region. Further increase of the Te content, however, may lead to compositional instabilities and phase separation, particularly when the alloy is exposed to corona or to an abrasive environment. The localized change in composition results in higher dark conductivity and the localized loss of the surface potential, which can lead to image degradation. One way of minimizing such compositional instabilities is to build a multilayer structure comprising a thick layer of selenium in conjunction with a thin Se–Te layer (11, 12). Se–Te alloys in layered configurations have been used in a number of copiers.

Another disadvantage of selenium is that it crystallizes readily when heated above about 55°C. The crystallized form of selenium is highly conductive and therefore when the photoreceptor is accidentally exposed to higher temperatures, it does not accept charge. Crystallization can be retarded by the addition of small amounts of arsenic (several wt % based on selenium) (13). The addition of larger amounts of As also extends the spectral response into the red region (14). Selenium alloy photoreceptors having about 40 wt % As (nearly stoichiometric As_2Se_3) are highly sensitive throughout the visible region of light and have been used in high speed laser printers in conjunction with the He–Ne lasers. Only holes are mobile in this photoconductor; therefore, these devices must be charged positively. The hole mobility μ in what is essentially arsenic triselenide [1303-36-2], As_2Se_3, is high, and therefore the material is well suited for high speed duplicators or laser printers. For example, at a typical xerographic electric field of 10^5 V/cm at 293 K, the hole mobility μ is 7.5×10^{-5} $cm^2/(V{\cdot}s)$ (15). These photoreceptors are also characterized by unusually high abrasion resistance and environmental stability. The principal drawback, however, is the toxicity of arsenic.

Zinc oxide was also quite successful in xerographic photoreceptors, particularly in Electrofax (5). In this process the image is developed and fixed by fusing directly into a ZnO-sensitized paper. Crystalline ZnO is used as a fine dispersion in a binder host polymer such as poly(vinyl acetate), poly(vinyl butyral), polyacrylics, and the like, in about 5 to 1 weight ratios, close to 1:1 by volume (17). These photoreceptors are usually charged negatively, because the layers do not retain enough positive charge. The ZnO devices have a peak photoresponse between 370 and 390 nm (18). To shift the absorption to the visible range, sensitizers such as Rose Bengal [11121-48-5], $C_{20}H_4Cl_4I_4O_5$; fluorescein [2321-07-5], $C_{20}H_{12}O_5$; Brilliant Green [633-03-4], $C_{27}H_{34}N_2O_4S$; acridine orange [65-61-2], $C_{17}H_{19}N_3{\cdot}HCl$; rhodamine B [81-88-9], $C_{28}H_{31}ClN_2O_3$; bromophenol blue [115-39-9], $C_{19}H_{10}Br_4O_5S$; etc, are added (18, 19). Some of these devices have a respectable quantum efficiency of charge generation and collection, approaching 0.4 (20). The nature of the polymeric binder has a large effect on the device performance (21), and so does the quality and source of the dye (22). Sensitivity to the environment and fabrication methods results in some irreproducibilities and batch-to-batch variances. However, the main advantage of the ZnO-based photoreceptor paper is its very low cost.

Other photoconductive pigments (qv) which found commercial application are cadmium sulfide [1306-23-6], CdS, or the alloy with Se, CdS_xSe_{1-x}. This latter pigment was used in several electrophotographic processes (23, 24) in which the photoreceptors have one feature in common: each contains the powder pigment, ie, the polymer binder matrix, sandwiched between the conductive ground and an insulating overcoat layer (see Fig. 2**a**) (25). These processes differ from the conventional electrophotographic processes using selenium or ZnO. In one of the latter imaging methods (23), the insulating surface is first charged positively, inducing a negative charge in the photoconductive layer at interface 1 of Figure 2**b**. In the second step, the device is charged negatively by corona while it is exposed simultaneously to the projected image. In this step, electron-hole pairs are generated in the photoconductive layer, near interface 1. Because the field is now reversing, holes are trapped in that region, and electrons migrate to the ground. The deposited surface charge in the dark portions of the image is thus reduced to very low levels, whereas in the illuminated portions the negative charge stays on the surface. In the last step, the device is uniformly illuminated. Electrons, which are trapped in the dark portion of the photoconductor layer, are neutralized by photogenerated holes, and newly generated electrons migrate to the ground. The latent electrostatic image on the surface is then developed as in conventional xerography.

The advantage of this process over other xerographic processes using conventional photoconductors is that the most sensitive part of the photoconductor is protected from the corrosive environment. This helps to increase the useful life of the device. The process itself, however, is rather complicated.

A highly sensitive CdS pigment was also developed for a conventional xerographic application. Optimum xerographic properties were obtained using copper doping at Cu concentrations of 200–300 ppm (26).

1.2. Amorphous Silicon

Significant effort has been expended in the development of an amorphous silicon photoreceptor (see Silicon and silicon alloys). For xerographic application, the α-Si:H must be insulating, the permissible conductivity σ no greater than about $10^{-10}(\Omega{\cdot}\mathrm{cm})^{-1}$. Pure amorphous silicon without hydrogen is too conductive because of the presence of large numbers of dangling bonds. Hydrogen, incorporated into the structure, when prepared by glow discharge of silane gas, tends to saturate the dangling bonds, but even with 10–35% hydrogen atoms, α-Si:H is still too conductive for xerography and must be slightly p-doped with boron, up to ca 10-ppm levels (27, 28). The hole mobility in lightly boron-doped α-Si:H is ca $10^{-3}\mathrm{cm}^2/(\mathrm{V{\cdot}s})$, which is more than sufficient for even the fastest duplicators and printers (see Fig. 3). Boron doping is accomplished by adding diborane [19287-45-7], B_2H_6, to the reacting gas (see Boron compounds). The discharge is excited in a capacitively or inductively coupled reactor using d-c, r-f, or microwave power sources.

The main advantage of α-Si:H is the long mechanical life and sensitivity in the whole visible spectrum. However, the primary failure mode of the unprotected α-Si:H photoreceptors is not the reduction of thickness

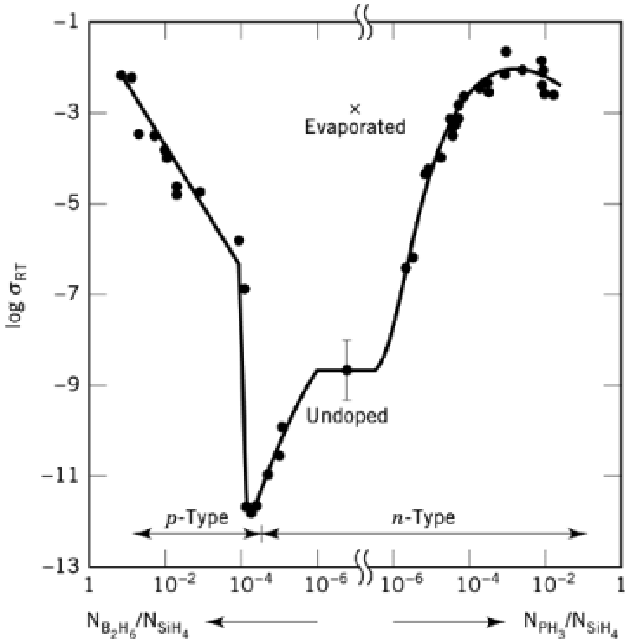

Fig. 3. Logarithm of room temperature electrical conductivity of α-Si:H as a function of doping with diborane, B_2H_6, and phosphine [7803-51-2], PH_3, where $N_{B_2}H_6H_{SiH_4}$ is the ratio of the number of diborane to silane molecules; N_{PH_3}/N_{SiH_4} is the ratio of phosphine to silane molecules. Both ratios refer to the gas mixtures used for sample preparation.

by wear and abrasion, but a catastrophic failure attributable to microscopic scratches caused by foreign objects, dust, or paper, or to corona damage. Gap states can be introduced easily to α-Si:H either as a result of structural irregularities of the damaged surface or by spontaneous oxidation. These new gap states at the surface are responsible for generation of dark charge carriers, and the microscopic damage thus shows in the xerographic copy. It is necessary to overcoat α-Si:H using a thin hard shell of nonstoichiometric silicon carbide [409-21-2], SiC, or silicon nitride [12033-89-5], Si_3N_4. Also, because the α-Si:H photoreceptors are charged positively, spontaneous dark injection of electrons from the conductive substrate must be prevented because such dark-injected electrons would neutralize the surface charge before the latent image could be developed. Electron injection is blocked by a thin layer of α-Si:H heavily doped with boron. As shown in Figure 4 about 1000 ppm boron is inserted between the electrode and the bulk of α-Si:H. Boron doping reduces the electron range.

α-Si:H has sufficient sensitivity to He–Ne lasers (632.8 nm) but lacks the sensitivity to solid-state lasers (780–830 nm) (see Lasers). The spectral response of α-Si:H can be extended to the near ir range by adding germanium. This is accomplished by codeposition of silane in the presence of germane [7782-65-2], GeH_4. Doping with Ge, however, causes an undesirable increase of dark conductivity. This effect is partially mitigated by forming a separate thin layer of α-Si:Ge:H in conjunction with Ge-free α-Si:H, as in the case of alloying selenium, Se, and tellurium, Te.

1.3. Organic Photoconductor-Based Photoreceptors

Organic photoconductor-based photoreceptors (OPCs) appeared in xerographic copiers in the early 1970s. Most modern xerographic copiers, duplicators, and printers use OPCs. The first all-organic photoreceptor was a single-layer device consisting of an electron donor polymer, poly(*N*-vinylcarbazole) [25067-59-8] (PVK), mixed with an electron acceptor, 2,4,7-trinitro-9-fluorenone [129-79-3] (TNF), $C_{13}H_5N_3O_7$, (29). This charge-transfer

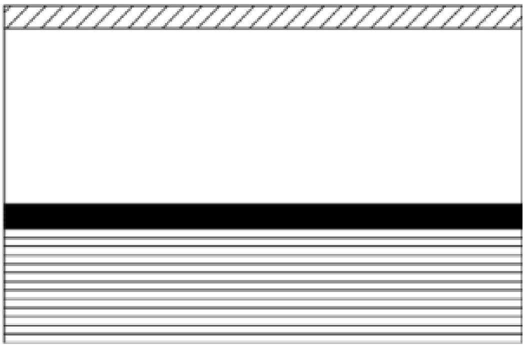

Fig. 4. Structure of an α-Si:H photoreceptor, where ▨ represents SiC_x or SiN_x; □, α-Si:H containing ca 10 ppm B; ■, α-Si:H with ca 1000 ppm B; and ▤, the conductive substrate.

complex absorbs light and photogenerates charge carriers throughout the visible region. The photoconductor is bipolar, which means that it is capable of transporting both holes and electrons and, in principle, can be charged both positively and negatively. In this polymeric charge-transfer complex, holes are transported by a hopping mechanism via the carbazole groups, and electrons migrate via both complexed and uncomplexed TNF molecules (2). The absorptivity varies with the wavelength between 5×10^{-3} cm^{-1} and 10^2 cm^{-1}. At 550 nm, for example, the photogeneration efficiency of PVK–TNF at the optimum ratio is 0.1 for an electric field of about 5×10^5 V/cm (30). The PVK–TNF photoreceptor, considered to be fairly sensitive, was very successful until it was discovered that TNF is a potent carcinogen. Copiers that used the material have been withdrawn from the market.

Another organic photoconductor which found application in copiers and duplicators is a single-layer, two-phase device comprising a hole transporting molecule, bis[4-(diethylamino)-2-methylphenyl]phenylmethane (TPM) (Fig. 5) molecularly dispersed in a host bisphenol A polycarbonate binder. Coincidentally, polycarbonate also forms a unique cocrystalline complex with a thiapyrylium dye (see Fig. 6) (31). The charge carriers are photogenerated in the bisphenol A–dye complex which also supports transport of photogenerated electrons. The charge collection efficiency, near 0.6 upon exposure to white light at an electric field of 10^6 V/cm, is quite high in this photoreceptor. Because both holes and electrons are mobile in this system, in principle, charging of either polarity could have been used; however, in practical applications the device is charged negatively. The only shortcoming of this photoreceptor is the uneven absorption characteristics over the visible spectral range, which leaves the device almost blind at certain wavelengths.

Conceptually similar are single-layer photoreceptors such as PVK filled with a photoconductive pigment, such as *N,N′*-di(3,5-dimethylphenyl)perylene-3,4,9,10-tetracarboxylic acid diimide (32), or a photoconductor containing a bisazo photoconductive pigment, a hole transporting molecule such as an indolinyl hydrazone derivative of carbazole shown in Fig. 5**i**, in a polyester binder (33). In practice, this photoconductor is charged positively even though both holes and electrons are mobile.

All the organic photoconductors discussed are single-layer structures the thickness of which is determined by the desired development field, by the dielectric constant of the material, and the resistivity of the device. Organic photoreceptors are typically capable of withstanding higher electric fields than those based on inorganic materials, with the exception of amorphous silicon. Thus single-layer organic photoreceptors are usually thinner (typically 10–20 μm) than the original α-Se based photoreceptors (40–70 μm).

Most of the currently used OPCs are, however, two-layer photoconductors schematically illustrated in Figure 7. In these devices, the charge-photogeneration function is separated from the charge-transport function (34). This separation enables independent optimization of each layer. The charge-generation layer (CGL) is optimized for the spectral response and the carrier-supply efficiency (sensitivity), and the charge-transport

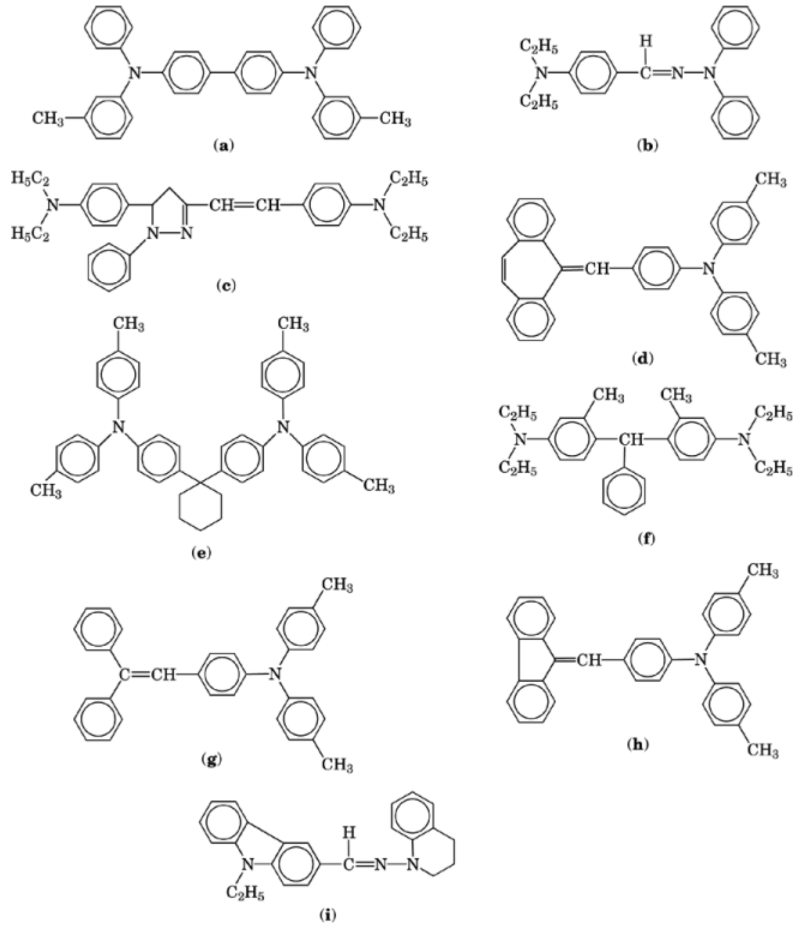

Fig. 5. Charge-transport molecules: (**a**) *N,N′*-bis(3-methylphenyl)-*N,N′*-diphenyl-[1,1′-biphenyl]-4,4′-diamine [65181-78-4]; (**b**) 4-(diethylamino)benzaldehyde diphenylhydrazone [68189-23-1]; (**c**) 4-[2-[5-[4-(diethylamino)phenyl]-4,5-dihydro-1-phenyl-1*H*-pyrazol-3-yl]ethenyl]-*N,N*-diethylbenzenamine [57609-72-0] (5-(*p*-diethylaminophenyl)-1-phenyl-3-(*p*-diethylaminostyryl)pyrazoline); (**d**) 4-(5*H*-dibezo[*a,d*]cyclohepten-5-ylidenemethyl) benzenamine [119344-18-2]; (**e**) 4,4′-cyclohexylidenebis [*N,N*-bis(4-methylphenyl)]benzenamine [58473-78-2] (1,1-bis(di-4-tolyl-aminophenyl)cyclohexane); (**f**) 4,4′-(phenylmethylene)bis[*N,N*-diethyl-3-methyl]benzenamine [15008-36-3]; (**g**) 4-(2,2-diphenylethenyl)-*N,N*-bis(4-methylphenyl)benzenamine [89114-91-0]; (**h**) 4-(9*H*-fluoren-9-ylidenemethyl)-*N,N*-bis(methylphenyl)benzenamine [115838-15-8]; and (**i**) *N*-[(9-ethyl-9*H*-carbazol-3-yl) methylene]-2,3-dihydro-1*H*-indol-1-amine [87866-87-3].

layer (CTL) is optimized for wear resistance, high charge carrier mobility, flexibility, corona resistance, etc. The CGL is usually thin, between 0.3 and ~3 μm, ie, only thick enough to absorb most of the incident light. The CTL is typically 10–25 μm thick. The charge-generation layers are typically sandwiched between the conductive substrate, generally in drum or belt form, and the polymeric charge-transport layer which protects the CGL from the corrosive and abrasive xerographic environment.

Most of the known charge-transport layers are *p*-type or hole transporting. Thus this type of layered photoconductor must be charged negatively.

The CGLs contain highly absorbing photoconductive pigments, either dispersed in binder resins or vapor-deposited (sublimed) directly onto the conductive substrate. Photogenerating pigments and dyes that are most

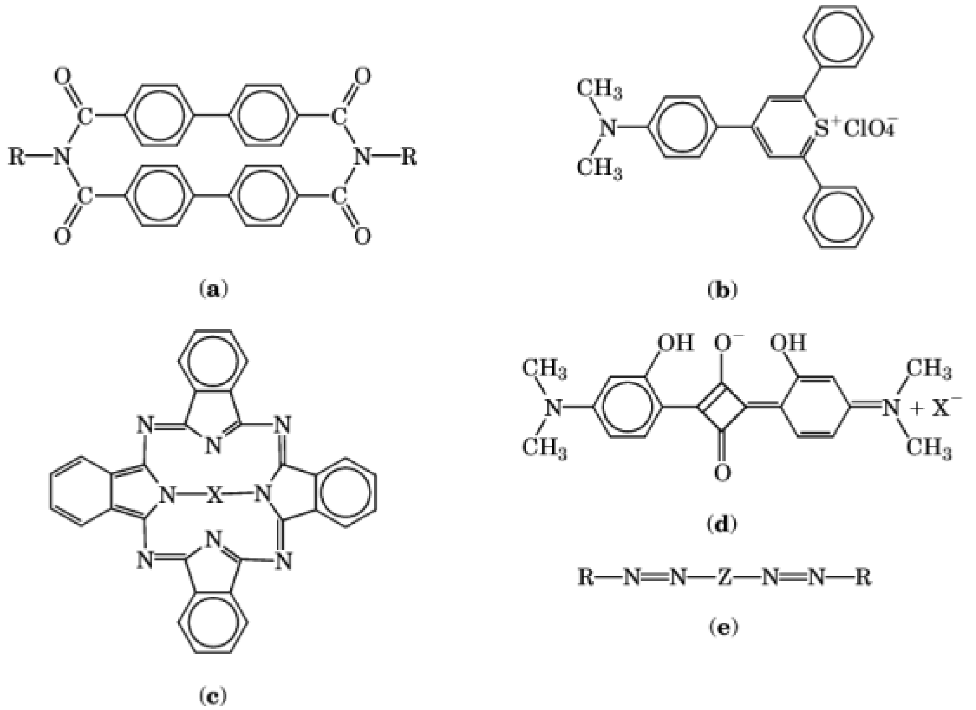

Fig. 6. Classes of charge-generating dyes and pigments: (**a**) perylenes, (**b**) thiapyrylium, (**c**) phthalocyanines, (**d**) squaraines, and (**e**) azo. R and Z are organic groups from small alkyl to very complex; Z is typically aromatic.

frequently mentioned in the literature are the phthalocyanines (35–38), perylenes (39), squaraine and azo-type pigments (40), pyrylium and thiopyrylium dyes (qv) and pigments (41), such as those illustrated in Figure 6, and inorganic pigments such as trigonal selenium in conjunction with an organic CTL (42). A review of the patent literature suggests that, in principle, all dyes and pigments that are known to be photoconductive, are capable of injecting photogenerated charge carriers to typical charge-transporting molecules and polymers. For imaging processes that employ visible, broad-spectrum light sources, the most popular are the bisazo dyes and pigments, primarily because these are relatively easy to synthesize, sufficiently sensitive, and easy to fabricate into photoreceptors. The two-layer photoreceptors may be fabricated by successive solvent coatings of CGL and CTL, although in some cases the CGL pigment is deposited directly by evaporation (see also Azo dyes).

Manufacturing processes differ according to the intended use of the photoreceptor. Drum photoreceptors are typically fabricated by a dip-coating technique where the drum blank is immersed in a solution containing the desired components and slowly pulled up from the solution through a concentric ring. The space between the inner circumference of the ring and the drum surface determines the thickness of the solution layer remaining at the surface and thus the dry layer thickness. The excess solution is brought back into the container. An alternative technique successfully used in photoreceptor manufacturing is spray deposition, which is basically the same as conventional spray painting used in car body shops, except for the precision involved. The flexible belt photoreceptors are fabricated by gravure or die casting of the solution or dispersion onto a long web of the metalized polyester substrate which, after extensive drying is sliced into segments that are then ultrasonically welded into continuous loops (see also Coating processes).

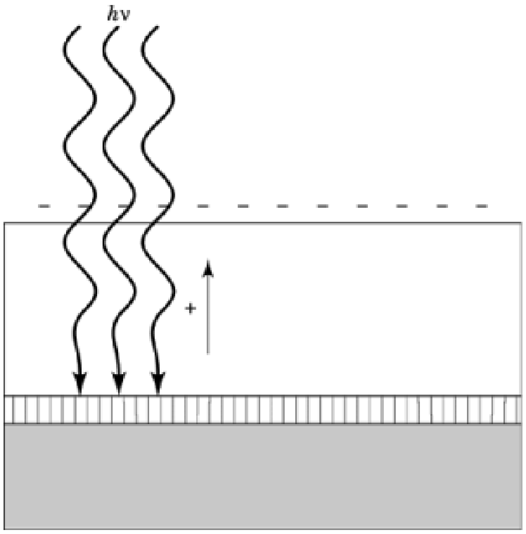

Fig. 7. Schematic of an organic layered photoreceptor, where the – signs represent the corona-deposited charge, which is typically negative; □, the CTL; □≡, the CGL; and ○≡‖, the conductive base. Terms are defined in text.

1.3.1. Charge-Generation Layers

For xerographic laser printers, photoconductors must respond to the wavelengths of coherent light emitted either by He–Ne lasers at 632.8 nm, or by solid-state Ga–As lasers which emit in the near infrared (ir) region, between 800 and 830 nm. Four groups of compounds that show the near infrared response are derivatives of squaraine (43, 44), phthalocyanines (38, 45), bisazo and trisazo pigments (44), and thiapyrylium (46) or pyrylium pigments (47). Among these groups of materials, phthalocyanines are most popular because of high sensitivity. Particularly sensitive appears to be the Phase 3 titanyl phthalocyanine (48) which requires only $\sim$0.25 μJ/cm^2 of light energy at 5.3×10^5 V/cm to discharge the photoreceptor to one-half of the original potential of 800 V. This is roughly the same as the sensitivity of α-Se in white light. The issues plaguing ir-sensitive photoreceptors are not the lack of sensitivity, but rather the thermodynamic stability of the most sensitive form, excessive dark conductivity, and the stability of the xerographic performance in general.

The sensitivity of a photoreceptor depends to a large extent on the method of pigment preparation, however, and factors such as the particle or crystallite size, the nature of the binder polymer, the CGL thickness, the pigment concentration, the method and time of milling the pigment particles, the applied electric field, temperature, and even the nature of the adjacent CTL can come into play. No direct comparison of photoreceptors is possible without specifying all the fabrication and material parameters and the testing conditions. The only meaningful way of comparing various kinds of photogenerating pigments would be a parallel test of fully optimized photoreceptors. Such information is not available.

The design of photogenerating materials is still largely empirical but some tentative design criteria appear to be emerging. The CGL must typically be in an aggregated or crystalline form to have high absorptivity and high photogeneration efficiency; have recognizable donor and acceptor groups separated by a conjugated system of double bonds or an aromatic structure to support polarization of the excited state; have reversible redox for stable operation; and have a broad absorption spectrum for light-lens imaging, or, if near ir-sensitivity is desired, must have extended π-conjugation.

1.3.2. Charge-Transport Layers

The charge-transport layer materials are largely responsible for the overall mechanical characteristics of the photoreceptors. These can be classified into four principal classes: (*1*) polymers having pendent transport-active groups, such as PVK, where the main chain can be vinylic, acrylic, or similar, and the active pendent group is typically a complex aromatic amine or a large polynuclear aromatic group such as anthracene; (*2*) molecularly doped polymers, which are essentially solid solutions of transport-active molecules (20–50 wt %) in tough polymers such as polycarbonate or polyester; (*3*) condensation polymers having transport-active groups acting as building blocks of the polymer chain (49); and (*4*) polymers having a transport-active chain or at least segments of the chain, such as π-conjugated or σ-conjugated polymers represented by polyphenylenevinylene or polysilylenes (50). Examples of these classes of hole-transporting organic media are illustrated in Figure 8.

Even though numerous patents describing all four classes have been issued, almost all existing OPCs now in use in copiers and xerographic laser printers employ the molecularly doped polymeric charge-transport layers. The transport-active molecules are typically complex aromatic amines having strong electron-donor character (see Fig. 5). It is commonly accepted that these materials transport charges by a hopping mechanism involving charge transfer among discrete sites. These sites are either discrete molecules, pendent groups on the polymer backbone, or segments of a transport-active chain. The hole-transport process is a sequence of redox exchanges among these neutral, uncharged species and the charged, electron-deficient counterparts or cation-radicals. The primary prerequisite is complete reversibility of the redox process. The oxidation of transport-active specie, ie, transfer of a hole, to form a cation-radical, and its subsequent reduction back to a neutral molecule must be free of any chemical side reaction which would inevitably result in an immobilization of the transiting hole. Aromatic amines are rather special in that typically the redox processes are completely reversible.

Aromatic amine-based transport materials transport only holes; thus the corresponding photoreceptors must be charged negatively, necessitating positively charged toners. Toners are needed to develop the negative latent electrostatic image which remains on the surface after the exposure. Remarkable progress has been made in triboelectrification of toner particles by using special charge-directing additives and by the appropriate selection of the toner resin. When toner charged to one polarity is used to develop the latent image created by the opposite charge on the photoreceptor surface, the process is called charged area development (CAD). The advancement of xerographic laser printing, however, precipitated discharged area development (DAD), a process in which the toner develops only those areas that lose charge. Both processes are shown schematically in Figure 9. The main advantage of the DAD process is that it is less wasteful: only a fraction of a typical copy area is covered by black marks, and it therefore makes sense to discharge only those areas that have to carry the black marks. Also, the sharpness of the image may be improved because the toner, which is charged to the same polarity as the unexposed areas on the surface, cannot easily spill into those areas still containing charge.

There are two ways to enable use of DAD with organic photoreceptors: one is to use negatively charged toners and photoreceptors, the other to use positive toners and positively charged photoreceptors. Positively chargeable photoreceptors would either have to use electron-transport layers, or their structure would have to be inverted, with the sensitive photogeneration layer facing the environment and a hole-transporting layer underneath. A variety of electron-transport materials have been described, some having respectable charge mobilities, but as of this writing none is used in commercial xerographic photoreceptors.

The trend in the xerographic copying and printing industry is to expand the use of organic photoconductors which are typically inexpensive and have a useful life. However, the α-Si:H photoreceptors, even though more expensive to manufacture, may ultimately have an advantage in greater durability.

The art of making photoconductors for electrophotography is fairly mature and the utilization of light energy is almost complete at any wavelength. The quantum efficiency of charge generation and collection approach unity, the charge-transport materials move charge without trapping, the action spectrum can be

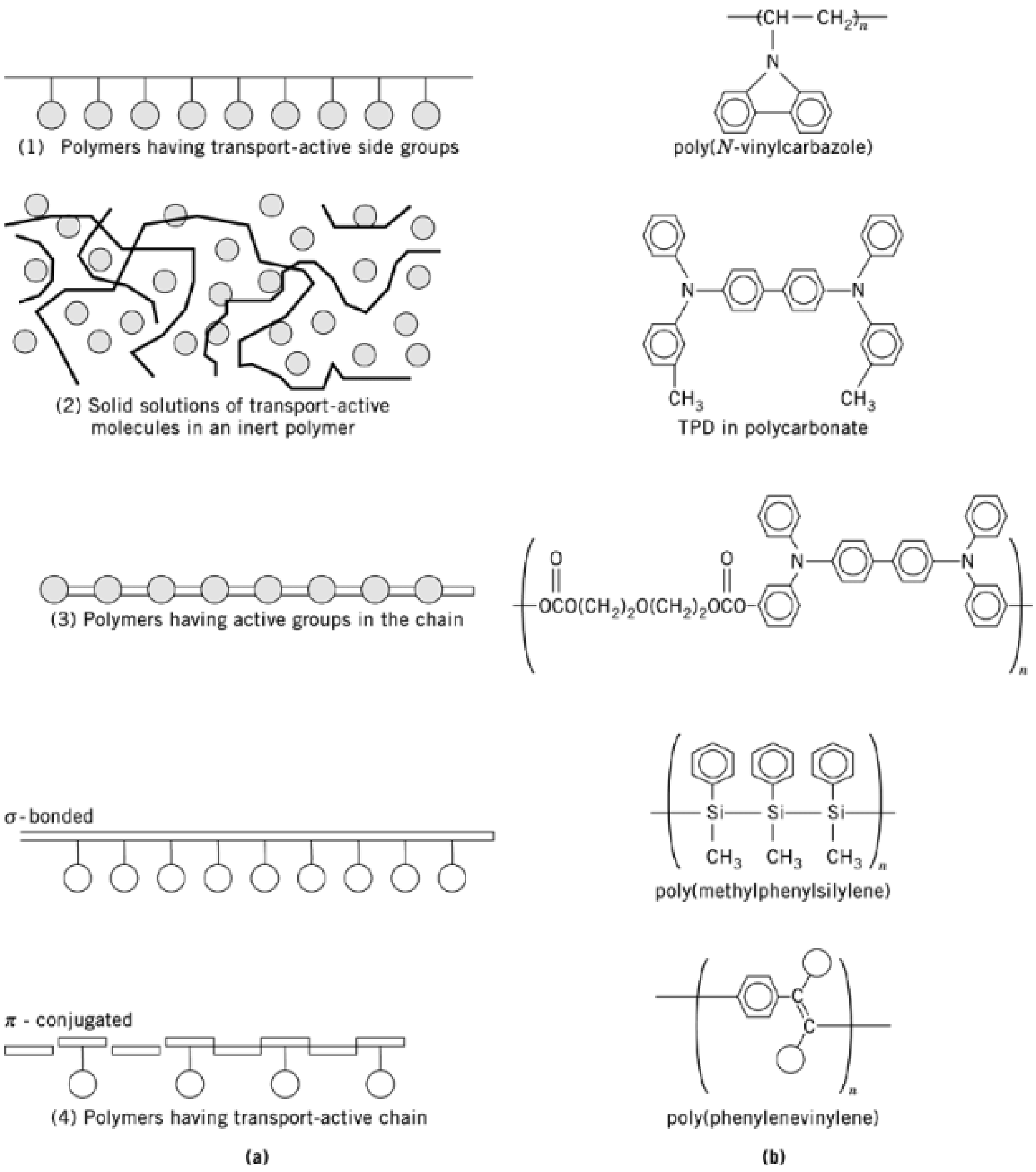

Fig. 8. (**a**) The four basic classes of charge-transporting polymers, and (**b**) corresponding examples. Class *4* polymers may be either σ-bonded or π-conjugated. Only classes *1* and *2* have been used in copiers and printers.

tuned to match the wavelength of the light source, and the materials are mechanically durable. Improvements would involve materials or device designs that retain these properties but produce further reductions in cost of ownership resulting from extension of useful life and alternative, simpler, and ecologically compatible manufacturing processes.

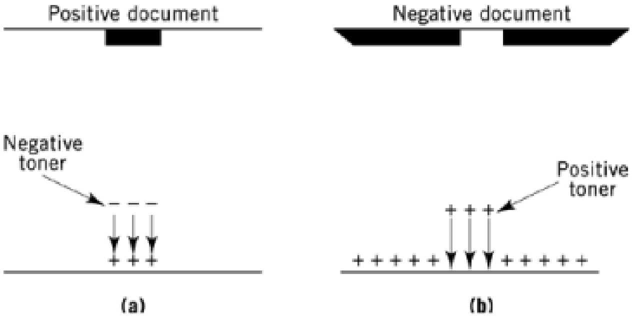

Fig. 9. (**a**) Schematic of charged area development (CAD), using toner charged oppositely to that of the photoreceptor and resulting in a positive document; (**b**) discharged area development (DAD), where the toner and photoreceptor polarity are the same, resulting in a negative document.

2. Developer Materials

2.1. The Development Process

In the original electrophotographic demonstration, development was accomplished by dusting lycopodium powder over an exposed sulfur film. This yielded low density images of poor resolution. Considerable powder settled in the exposed background areas (the white areas of a document), and image transfer to paper could only be achieved by prior coating of the paper with wax or another sticky material. Therefore, the development of organic polymer materials was of critical importance to the success of xerographic technology (51).

The physical basis of development, which may be simple in principle, is complex in practice (3). A uniform surface charge on a photoreceptor of infinite extent produces associated electric fields, the lines of force of which are confined within the photoreceptor, because these lines terminate on the induced charges of opposite sign in the conductive substrate (Fig. 10). This is not true if the photoreceptor has finite dimensions or if a nonuniform distribution of surface charge exists, because discontinuities exist in the surface charge density. At these discontinuities, force lines extend out of the photoreceptor into space. These so-called fringe-fields, associated with nonuniform distribution of surface charge produced by the imagewise exposure of a photoreceptor, though quite strong, are confined to a narrow region at such a boundary. External to the photoreceptor, these fringe-fields determine the development field E_{D} and the electrical force, $F_D = Q \times E_D$, on a toner particle having total charge Q. Because such fields at the center of solid areas are very small, fringe-field development is such that only narrow lines or edges of large-area black images are adequately developed (2–4). This problem was overcome by using a biased-development electrode positioned close to the photoreceptor surface so that the lines of force are pulled out of the photoreceptor, even if the receptor is uniformly charged.

The development fields, which fall off rapidly over distances of micrometers moving away from the photoreceptor surface, exert an electrostatic force on a triboelectrically charged particle of these dimensions. The average toner particle is only 10 μm in diameter, and the challenge is to control and direct large numbers of such particles. The coulombic forces between charged toner and the charges on the photoreceptor surface are used, but to come under the influence of these electrostatic fields the toner must be brought within micrometers of the photoreceptor surface.

A variety of methods can be employed to achieve the required proximity, most involving an intermediary component called a carrier. These different development processes include powder-cloud, cascade, and magnetic-brush development (2, 3). Liquid development, in which an insulating hydrocarbon liquid is used as the carrier, allows the use of much finer toner than can be typically controlled as a dry powder and therefore inherently offers the possibility of much higher resolution development. Powder-cloud or aerosol development

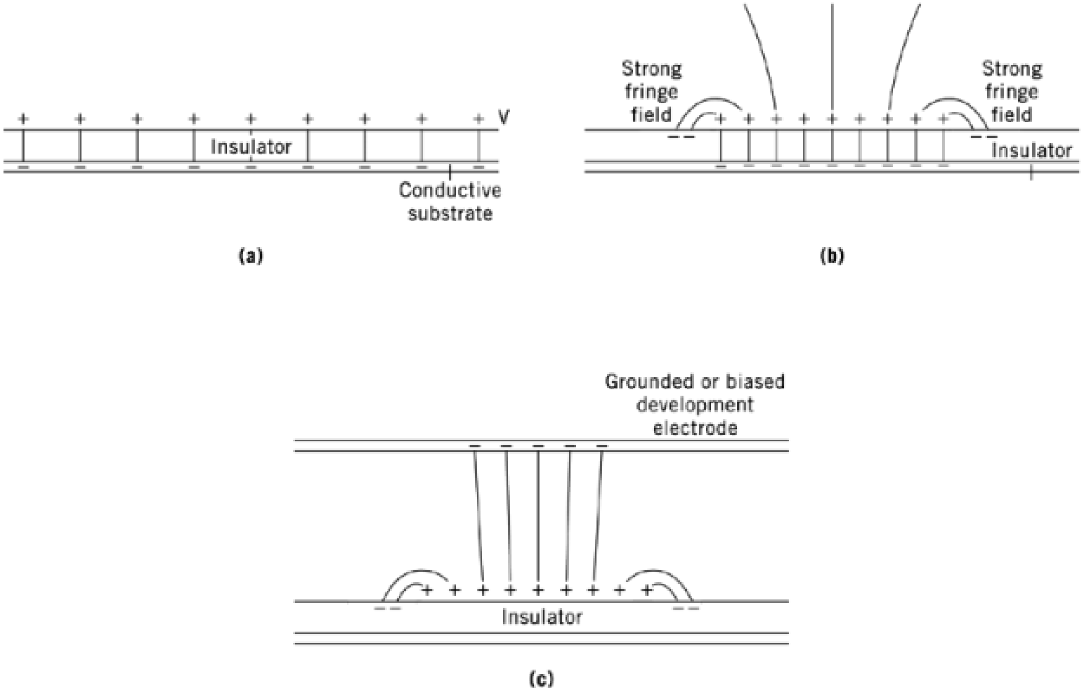

Fig. 10. The lines of force above the photoreceptor for three types of electric fields: (**a**) zero field; (**b**) weak field, where a nonuniform charge pattern is produced by selective photodischarge and the field on charged toner particles is strongest at the edges of the charge distribution, constituting the fringe fields; and (**c**) strong field where an electrode is placed above the charged photoreceptor surface, enhancing the field strength in the center of a broad image.

uses air as the carrier. Shortcomings arise from poor control over the sign and magnitude of the charge on the toner, leading to excessively dark backgrounds. Additionally, in powder-cloud development, as the name implies, a cloud of toner particles is responsive to air movement, inherently leading to a dirty environment in a xerographic machine. There is also the inability to manage the majority of the toner cloud, because it is only the toner within micrometers of the photoreceptor surface that experiences the development fields. For certain specialized applications, however, such development can be the process of choice. One example is in xeroradiography where small changes in transmitted x-ray intensity need to be detected. Without a development electrode the xerographic images give much higher image contrast in edges, as compared to conventional radiology, thus enhancing discontinuities such as fractures. Using a development electrode, high resolution, continuous-tone xeroradiographic images can be obtained that show particular benefits in mammography and provide a sensitive screening technique for breast cancer (2).

Other processes use solid carriers for toner delivery, so that the developer consists of both toner and carrier, and is known as two-component development (2, 3). The process called cascade development is characterized by a dependence on gravitational forces for its operation. In the predominantly used development process known as magnetic-brush development, the carrier is made of a magnetic material such as iron, so that magnetic forces are the dominant delivery force. A single carrier particle or bead, at about 100 micrometers in diameter, is much larger in size than typical toner and delivers the toner to the surface of the photoreceptor. It also controls and determines the sign and magnitude of the toner charge, for which purpose it is usually coated with a thin polymer film. This coating also provides adhesion for the toner particles to the carrier, although

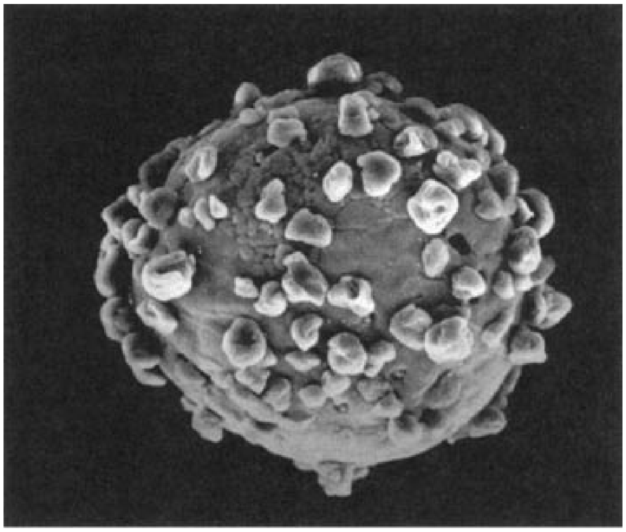

Fig. 11. Magnified photograph of a single carrier bead, 100 micrometers in diameter, showing smaller, attached toner particles.Courtesy of Xerox Corp.

the adhesive force must not be so large as to cause the adhesion to be permanent (Fig. 11). The competing electrostatic, adhesive, gravitational, or magnetic forces must therefore be delicately balanced.

2.2. Triboelectricity

For development to occur, the toner particles must be reproducibly charged to the correct level and polarity for the specific photoreceptor. The phenomena of triboelectricity, which involves the transfer of charge from one solid to another, are exceedingly complex, involving the surfaces of solids and interaction of the surfaces with each other and with the ambient (52). Consequently, the specific experimental observations are highly sensitive to the nature and purity of the materials, the physical and chemical state of both surfaces, and the precise details of the experiments performed. No absolute correlations between theoretical predictions and experimental observations exist.

Triboelectricity originates from the Greek word meaning “to rub,” implying that rubbing is essential to the mutual charging of two solids. Rubbing may only serve to provide an area of contact between the solids, however, and the contact may be the true means of charge transfer. Relative roles of rubbing and contact are not easily separated. Whereas some experiments suggest that charging can occur by contact alone, as demonstrated by experiments where one of the materials is liquid mercury (53), it is likely that both contact and frictional rubbing can be important. Empirical correlations between material properties and corresponding triboelectric behavior have allowed a considerable phenomenological base of understanding and operational control of developer materials to exist.

Triboelectricity is a relative phenomenon and, as a result, use is made of ordering the relative charging capabilities of materials. Thus, in the triboelectric series, window glass > polyamide > common salt > wool > silk > cotton > styrene–butadiene copolymer > poly(vinyl butyral) > epoxide resin > natural rubber > sulfur > polyethylene > poly(vinyl chloride) > polytetrafluoroethylene (52–54). Materials at the beginning of this series charge positively with respect to materials near the end. Such a series is used only as a general guide, and the results of any particular combination may deviate from expectations because of contamination, impurities, or humidity variations. A number of efforts have been made to correlate this series with other material parameters. Because the charge exchange may involve the transfer of ions, electrons, or macroscopic amounts of charged material, either separately or in combination, a number of relationships have been claimed. For example, it has been claimed that materials of higher dielectric constant become positively charged when contacted with those of lower dielectric constant (54). Such a correlation is consistent with a charge transfer of weakly bonded ions between solids, because the relative binding forces of these ions to their respective surfaces are reduced through the dielectric constant. Another correlation involves the differential work function, ie, the relative difference in electron energy levels in materials, because charge transfer requires the movement of electrons from one material to another.

2.3. Development Process Parameters

If a photoreceptor 50 μm thick is charged uniformly to a surface potential of 1000 V, assuming a typical dielectric constant of 5, the amount of charge per square centimeter of the photoreceptor is 100 nC. One electronic charge amounts to 1.6×10^{-19} C; thus 6×10^{11} singly charged ions would reside on each square centimeter of surface. To achieve complete photodischarge, therefore, 6×10^{11} electronic carriers must be generated for each square centimeter and for a photogeneration efficiency of unity this requires an exposure of 1 μJ/cm^2 (10 erg/cm^2).

The photoreceptor is always charged to a particular polarity using the appropriate sign voltage in the corotron, so the toner particles must be charged to the opposite polarity in order to produce a black-on-white copy of a black-on-white original. If the input were a white on black, ie, a negative, then toner with the same polarity would be required to give a black-on-white copy. The latter is an example of reverse or discharged-area development, DAD (55). Photoreceptors in different products may be either positively or negatively charged, so appropriately charged toner of either sign must be available. In two-component development the charging in both sign and magnitude is controlled by the nature of the toner and carrier through a special coating. Further, the degree and uniformity of triboelectric charging are important to achieve the most efficient development and highest quality images. The blackness or density of the image is related to the amount of toner which deposits on the photoreceptor. Thus the charge-to-mass ratio for the toner is an important parameter. The toner–carrier interactions lead to a mutual charging of from 5–20 nC/cm^2, corresponding to about 10^5 electronic units of charge per toner particle or a charge-to-mass ratio of 10 μC/g of toner. For a typical toner, a deposition of about 1 mg/cm^2 of toner gives the dark image representative of a high quality copy. If the charge-to-mass ratio is 10 μC/g, then the amount of toner needed to give a sufficiently dark image neutralizes 10 nC/cm^2. In the above example 10 nC/cm^2 is only about one-tenth of the charge density on the photoreceptor and sufficient development can take place without substantially perturbing the development field (55).

The very small size toner particles required are produced by a grinding or milling process which involves the continual fracturing of polymeric materials. Although uncharged on the average, fresh toner possesses essentially equal numbers of positive and negative charges, as illustrated by Figure 12. The number of particles having a given charge, mass, or charge-to-mass ratio can be measured by a charge spectrometer, and measurements on freshly made toner show that the charge distribution is indeed symmetrically distributed (56). The situation changes when the toner is mixed with carrier beads. The average charge distribution then becomes nonzero, and the sign of the newly equilibrated developer charge depends on the choice of the materials for the component toner and carrier or any additives. The magnitude of the charge also depends both on the time of mixing and the ratio in the mix of toner to carrier (also termed the toner concentration, C_{T}, and defined as the toner mass divided by the sum of the toner and carrier masses). The average charge grows approximately in an inverse exponential manner with time of mixing and saturates to a value determined by the toner concentration. The inverse exponential growth is consistent with a charging mechanism involving contact in which the fraction of uncharged area on a carrier bead decreases with time. This reflects the fact that the charge density per unit area of a toner particle depends on the probability of finding an uncharged area on the surface of a carrier. This becomes increasingly difficult as C_{T} increases. Based on this intuitive picture, the charge-to-mass ratio of the toner is expected, and found, to decrease with increasing C_{T}.

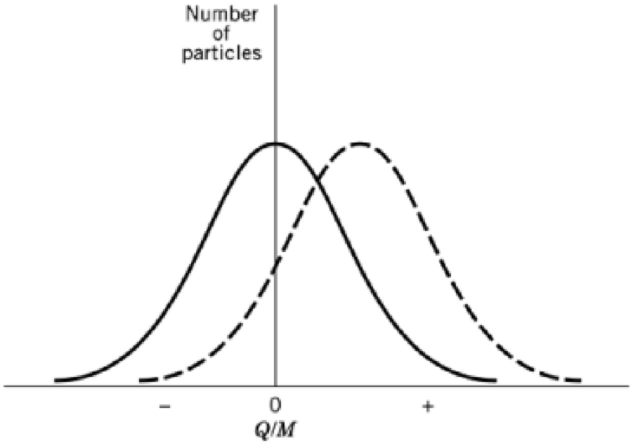

Fig. 12. Charge-to-mass, Q/M, distribution of individual (—) toner and (– –) toner-carrier particles produced by milling. Particles are initially positively or negatively charged and, on balance, the net toner charge is zero.

As a result of carrier-coating abrasion, fracturing of carrier beads, and compression of toner particles, considerable complications can occur (3). Carrier beads are commonly coated with low surface energy polymer coatings for control of charge and adhesive forces. Exposure of the underlying carrier beads which may have relatively high surface energies means that any compressed toner can become permanently bonded to them. In such a case, the carrier now presents a toner surface to the other toner particles, so that on the average no charge exchange can take place at those points. This is but one of many examples of aging phenomena that can occur with developer materials and which reveal themselves in progressive loss of image quality, ultimately requiring replacement of the developer.

Charged toner particles attached to carrier beads come into close proximity to the photoreceptor surface. The toner is bound to the carrier by adhesive forces, an electrostatic force F_{E} and a dispersion force F_{A}, the combined effect of which must be overcome by the development force exerted on the toner by the latent charge pattern on the photoreceptor (Fig. 13). Because the toner acquired its charge from the carrier, the carrier has a charge of opposite sign and the pair is physically bound by the mutual electrostatic attraction, F_{E}; the electrostatic force, F_{E}, binding a spherically shaped toner–carrier pair is proportional to Q^2/r^2, where Q is the assumed uniformly distributed charge on both the toner and the carrier and r is the radius of the toner. A single toner particle typically carries a charge of about 10^{-14} C, and F_{E} is of the order 10^{-8} N, so the electrostatic force on a toner particle is extremely small.

The dispersion force, F_{A}, is a form of van der Waals bonding associated with the interaction of fluctuating dipoles generated by otherwise neutral atoms (3). This force also depends on the separation of the two interacting atoms, but in a way distinctly different from the inverse square relationship of the electrostatic force between two charges. It takes a very short, but finite, time for the electromagnetic signal from one fluctuating dipole to reach a second. In response to the arrival of this signal, the second atom polarizes and emits its own dipole radiation. If the electromagnetic signal from the second atom is felt back at the first atom before the latter changes its original dipole configuration, then the interactive force is said to be in phase and is attractive in nature. The requirement is that the total time involved, the round trip transit of an electromagnetic signal between the two separated atoms, be less than the period of oscillation of the fluctuating atom. For atomic separations less than about 10 nm, this condition can be met and an order of magnitude estimate of the dispersion force, F_{A}, between a typical toner–carrier pair gives a value comparable to or higher than the electrostatic adhesive force. For distances substantially >10 nm, any phase correlation is lost and the attractive character of the dispersion force decreases. Thus the strength of the adhesive force is substantially reduced if

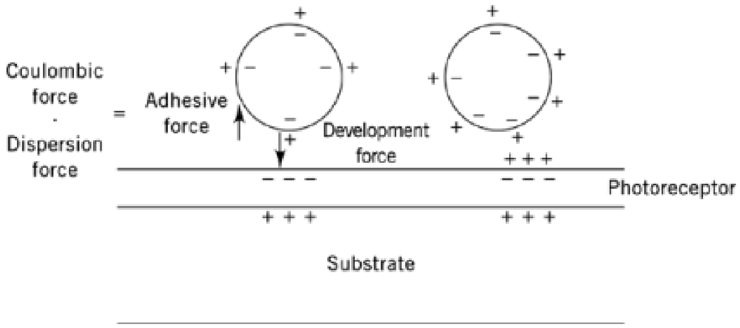

Fig. 13. Two-component development involving competition between electrostatic and adhesive forces, where + outside and beneath the large circles represents the positively charged toner and the large circles containing negative signs represent carrier beads.

the toner particles can be separated or detached, albeit slightly, from the carrier beads. Thus, agitation is a very important factor in the development process (3).

Development therefore depends on whether the development force F_{D} exceeds the forces $F_{\mathrm{A}} + F_{\mathrm{E}}$ which keep the toner attached to the carrier. The electrostatic adhesive force is proportional to Q^2/r^2, whereas the dispersion force F_{A} does not depend on the charge on the toner, and for a given set of materials is constant. Hence for a given development field the charge on the toner may be so small that the development force is less than $F_{\mathrm{A}} + F_{\mathrm{E}}$ and development does not occur. However, as the charge on the toner is increased or the toner radius is made smaller, F_{E} grows faster than the development force and again development does not occur. Thus there is an optimum range of values for F_{E}, and hence for charge-to-mass ratio, for the toner.

2.4. Cascade Development

In cascade development, spherical or near-spherical beads are used to carry finely divided toner powder to the imaging surface (57). Advantage is taken of the gravitational force on the much more massive carrier particle to cascade it, together with the attached toner, over the photoreceptor surface. In the consequent tumbling of the carrier particles across the photoreceptor surface, two effects are significant. In bouncing, the physical impact shakes loose some of the toner which becomes airborne. Because the physical impact has already supplied some of the stripping energy, these particles develop out at relatively low development fields. Toner particles remaining bound to the carrier beads require higher fields for development. Within a few micrometers of the surface, the toner–carrier system feels the effects of the development fields. This force ultimately wins and the toner particle moves toward and becomes attached to the photoreceptor. The retention forces between the toner and carrier in two-component developers give such systems a higher contrast because of a threshold effect. Unless the development fields exceed the forces retaining the toner on the carrier, no deposition occurs. This contributes to clean, dust-free background on nonimage areas.

The earliest copiers used an insulating carrier of sand and had as a principal shortcoming the inability to reproduce solid black areas because development was only by fringe fields. Improvements were achieved by using a closely spaced development electrode or conductive steel shot as the carrier. The conductive carrier itself can serve as a development electrode. However, for a given carrier bead material, the gravitational force (equal to the carrier weight) is proportional to the cube of the bead radius, whereas the carrier charge, related to the charge per unit area, is proportional to the radius squared. Unfortunately, carrier particles have a distribution in sizes so that small carrier particles can be culled out of the cascade flow and become attached to the photoreceptor because the electrostatic forces on them can exceed those resulting from gravity. In addition to possible physical damage to the photoreceptor surface, this limits the achievable flow in cascade

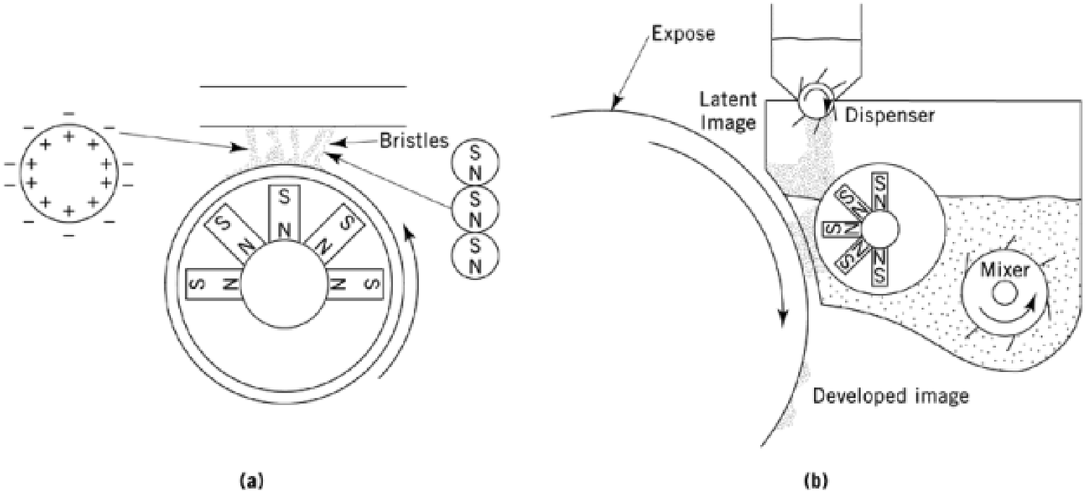

Fig. 14. Two-component magnetic brush development showing (**a**) the magnetic carrier particles (large circles) carrying toner (–), which within the magnetic field of the rotating permanent magnets, behave as individual bar magnets; and (**b**) the production of a developed image. See text.

development and was a constraint for higher machine speeds. To overcome this problem, carriers were made out of magnetic materials (qv) and, by using magnets, the resulting magnetic fields prevailed over gravity. Most modern xerographic machines use magnetic carriers and magnetic-brush development.

2.5. Magnetic-Brush Development

In magnetic-brush development, the carrier is made of beads of ferromagnetic material coated with a thin polymer charge-control film. Ferrite carriers are favored because these are lighter than steel and have a much lower residual magnetic field, allowing ferrites (qv) to mix more readily and flow better in use. The necessary magnetic fields are provided by stationary permanent magnets located within a rotating drum or sleeve which transports the toner–carrier combination to the photoreceptor surface (3). The magnetic fields cause the magnetic cores of the carriers to become individual magnets having north and south poles, as shown in Figure 4. As a result the carrier particles, to which toner is attached, link up to form chains or bristles (hence the name magnetic-brush development), and much higher process speeds can be achieved. The relative speed of the rotating developer drum with respect to the moving photoreceptor plays an important role. At too-high speeds the centrifugal force can result in carrier particles escaping from the constraining magnetic field. If these are stripped of the toner by impacts, then the oppositely charged carrier beads can end up on the nonimage areas of the photoreceptor, an effect known as bead carry-out.

Two types of magnetic-brush development, known as insulating and conductive magnetic brush, are employed. The distinction is based on the effective conductivity of the developer and more specifically the assembly of contacting carrier particles (3). These are controlled by the chemical composition and thickness of the polymer coating of the carrier beads. Conductive magnetic brush gives improved solid-area development because of the reduced effective spacing between the photoreceptor and the developer roller caused by the conductive paths within the developer; in essence, the developer itself functions as a development electrode. As in cascade development, the beneficial impact-associated separation of toner and carrier coexists with the deleterious physical impaction and permanent bonding of toner particles to the carrier surface or fracture of the toner or carrier.

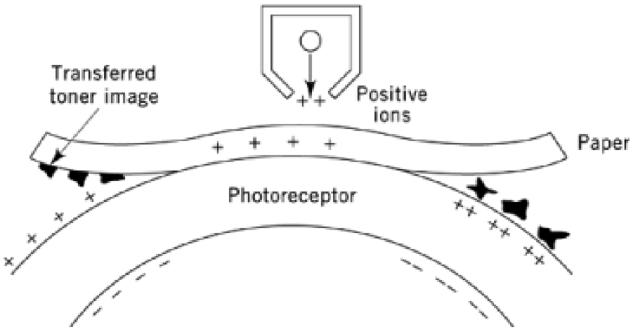

Fig. 15. Transfer of the toned image from the photoreceptor surface to paper is accomplished by charging the paper with a corotron of appropriate polarity.

One drawback of magnetic toners is apparent when colored developers are needed. Materials having the required magnetism are typically brown to black in color and limit the quality of colors achievable. A more recent change in development systems is the use of single- or monocomponent developers. As the name implies, only one kind of particle is used. This particle serves as the toner and can be magnetic or nonmagnetic depending on whether ferromagnetic material is incorporated. No carrier particles are used and the system is simpler, smaller, and avoids some aging effects. There is another material involved in controlling the necessary triboelectric charging of the toner. This charge control is accomplished by coating a roller with the appropriate material, just as carriers are coated in two-component developers, and the roller thus acts to control not only the charging but also the transport and metering of the toner. This, or a similar roller, can also be appropriately biased to function as a development electrode. A particular case of single-component development is jumping-toner development in which triboelectrically charged toner covering a donor roll rotates synchronously with the moving photoreceptor. By use of electric fields between the donor roll and photoreceptor, selective transfer of toner occurs. The simplicity, conciseness, and low cost of this approach enabled the introduction of throwaway copier cartridges.

Once the latent electrostatic image has been developed on the photoreceptor surface, it must be transferred to plain paper with no loss in clarity. Figure 15 illustrates this process. Uncoated paper is brought into contact with the photoreceptor without smudging, followed by corona charging using the same polarity of charge (assumed positive) to that used to originally charge the photoreceptor. Prior to the corona charging, the paper seldom makes intimate contact with the photoreceptor except at a few points; elsewhere an airgap separation of several micrometers is likely to exist. On charging with positive ions, negative charge is induced in the substrate and the top surface of the photoreceptor. Under normal conditions of humidity paper is a good insulator and acquires a potential of several hundred volts during this process. As a result, in unexposed areas an attractive field exceeding 10^5 V/cm exists between the paper and the photoreceptor. The pressure from this force pushes the paper into intimate contact with the photoreceptor and ensures toner adhesion to the paper following separation. The transfer efficiency is maximized by the insulating character of the toner and 80–90% of this can be transferred, even at process speeds of two copies per second.

2.6. Toner

Thousands of metric tons of toner, carbon black, and carrier materials are produced and consumed each year having a retail value of several billion dollars. The most widely used toner manufacturing process uses brittle materials that can be milled or pulverized at a high rate, thus increasing production volume and reducing costs. As well as the important triboelectric characteristics, other properties must also be considered. Additionally, the choice of materials must be compatible with volume manufacturing, reproducibility, and cost. Further, the materials must not be toxic, allergenic, or release unacceptable odors or fumes on heating in the fusing step. These materials must be insensitive to humidity and not clump in storage in a machine under a wide range of ambient conditions. The thermal–rheological properties of the toner polymer are critical in determining the fusing characteristics. Moreover, the important flow properties of the toner in the machine are affected by both particle shape and size distribution. Spherical carrier beads have the advantage of flowing more freely so that fresh toner, which must be added from time to time, is charged faster and with greater uniformity. This also prolongs developer life by allowing more uniform surface coatings and minimizing aging effects caused by impacts.

Almost all black toners consist of a thermoplastic polymer or polymer blend with carbon black as the pigment in a weight ratio of about 85% polymer, 15% carbon black. The earliest toner formulations utilized a polystyrene–carbon black mixture. However the properties of the polystyrene led to unacceptable filming of the photoreceptor. This was solved by blending poly(butyl methacrylate), an acrylic resin, with the polystyrene. Styrene–acrylic, styrene–butadiene and polyester polymers and copolymers are largely used for negatively charged toners for use with positively charged photoreceptors such as amorphous selenium and its alloys; polyamides (qv), polyethylene, and ethylene–vinyl acetate copolymers are used as positively charged toners for polymeric-based photoreceptors, which are typically used with negative charge. The carbon black pigment is produced by the burning of oil in specially designed furnaces, which produces the extremely fine particle sizes (on the order of nanometers) required (see Carbon, carbon black). For color xerography, the three primary colors cyan, magenta, and yellow are needed for process or continuous color (qv) images. A variety of organic pigments exist that provide these colors. However, color is much more subjective than black or white, so that the concentration of the added color calls for particular skill and judgment.

The toner resin and pigment are mixed in either a batchwise or continuous operation using high shear mixers to produce a blend having a taffylike consistency. This is rolled into slabs, cooled, then broken into smaller pieces and fed into a crusher and pulverizer. The resultant powder is then pulverized in a jet mill using high speed air flow in which interparticle collisions and abrasion produces micron-size powder. After screening to remove coarse particles the toner is classified into particular size distribution by a number of techniques. In one of the final processing steps, additives such as metallic stearates, hydrophobic silica, or other materials which enhance flow and cleaning properties are often added. Finally, the toner and developer are comingled so that triboelectic properties such as the charge-per particle and charge-per-mass ratios can be determined. This qualification ensures that the total developer package meets specifications.

2.7. Carrier Materials

Carrier composition includes the core material and various carrier coatings that may be employed. A variety of carrier-core materials have been used such as spherical or nonspherical steel shot, sponge or porous iron, and ferrites (58). Processes used to produce carrier materials include atomizing or electrolytic and chemical reduction methods to produce steel or iron carriers, or spraying techniques for ferrites. The carrier beads are typically coated with a thin polymer film to provide a uniform carrier surface, which also serves as a low surface energy layer to reduce impact adhesion of toner to the carrier, thus extending developer and photoreceptor life. These carrier coatings are also used to control the charging characteristics such as polarity and charge-to-mass ratio.

2.8. Imaging Media

Various physical properties of paper (qv) are critically important not only in the transfer process, but also in its stripping from the photoreceptor surface, high speed transport through the machine, and in the fusing step. Paper, an interpenetrating network of cellulose fibers, possesses a significant amount of free volume occupied by air, whereas xerographic-grade paper also contains fillers to enhance its mechanical strength and smoothness, and to minimize the shedding of fibers. All of these factors are important in minimizing paper jams. The fillers can control the whiteness of paper, important in determining the image-character contrast density, through its reflectivity. Paper's propensity to absorb moisture because of the hydrophilic or water-attracting nature of cellulose, has considerable implications for the transfer and fusing steps. For example, paper in an ambient relative humidity of 50% can contain up to 8 wt % moisture. This moisture can become the controlling factor in the paper's conductance. As a result, ions from the transfer corotron can leak or flow through the paper thereby decreasing toner transfer efficiencies. Thus paper is an active material in the successful practice of xerography.

2.9. Fusing

As the toner image is transferred from the photoreceptor to the paper, the image must be permanently bonded to the paper, rather than attached only by electrostatic and dispersion forces. Otherwise the toner images are easily smudged. In the fusing step, toner particles are made to coalesce with each other, and interpenetrate the paper fibers. The thermoplastic toner may be softened or melted using heat, pressure, or a combination of both. This must happen using minimum energy both for economic reasons and to avoid damaging the paper substrate. The energy needed to soften a thermoplastic is related to rheological properties, specifically the glass-transition temperature, T_g (see Rheological measurements). T_g, the temperature at which the polymer chains of the thermoplastic acquire sufficient thermal molecular motion that it begins to soften, is also characterized by a rapid drop in viscosity through the transition (59). Toners are generally designed to have glass-transition temperatures lying between 50°C and 65°C. Such a narrow window is necessary, because for T_g values less than 50°C unacceptable caking of the developer might occur in storage or the developer housing under ambient conditions. On the other hand, if T_g is too high, excessive amounts of fusing energy are required. The T_g is a function of the polymer molecular weight, and the viscosity of the melted toner is affected by the nature of the polymer or blends, the molecular weight, and the degree of cross-linking within the polymer. Therefore careful consideration has to be given to these thermal and viscoelastic aspects of toner materials. Representative glass-transition temperatures for toners are about 60°C and fusing temperatures are about 130°C. Because the boiling point of water (100°C) is less than the fusing temperature of toner, any water absorbed in the paper is itself vaporized before the fusing temperature is reached. Given the high thermal capacity and latent heat of evaporation of water, a sizable part of the fusing energy can be consumed in the preelimination of moisture (3).

Early fusing systems, such as that used in the Xerox 914, employed radiant heat produced by incandescent lamps. Black toner is an extremely good absorber of the infrared whereas paper is not (60). Water, having absorption in the infrared, competes with the toner particles for this energy. Radiant fusing has the benefit of instant-on warmup and indirect contact with the toner image. However, the small, but real, potential exists for paper to ignite if it becomes stuck in the fuser system. Another disadvantage is that the photoreceptor, particularly if it is sensitive to red light, must be shielded from stray light from the radiant lamps. Modern copier products use hot-roll fusing in which a combination of pressure, shear force, and temperature are used. The hot-roll is typically a metal drum coated with a silicone rubber. Because the drum operates at a lower temperature, it can handle a wider range of paper stock and can fuse effectively and more efficiently at high speeds. There is no associated visible light. One problem with this system is that of offset, which is melted toner build-up on the hot roller. This is minimized by using a silicone oil release agent on the roller (61) (see Release agents).

An alternative fixing process is cold-pressure fixing. This uses steel rollers of high quality surface finish having nip pressures between the rollers that exceed 18 kN/m (100 ppi). The temperature rise associated does not lead to significant softening of the toner so that the fixing is mostly a consequence of cold flow. This means that softer toners than those used in hot-roll fusing must be employed, eg, polyethylene-type polymers. Because the method involves no direct heating, there is no warm-up time and the energy requirements are obviously lower. However, the enormous pressures cause permanent calendering of the paper, in which the thickness of the paper is actually reduced as air is excluded and the fibers compressed. As a result, the toner image typically exhibits an unattractive gloss (60).

2.10. The Cleaning Step

Although toner transfer is a highly efficient process, some toner residue remains on the photoreceptor surface and must be removed prior to the next cycle; otherwise successive corona charging and image exposure would be progressively and adversely affected (3). For such toner can capture further toner, and the absorption of visible light could reduce subsequent exposures of the photoreceptor and degrade achievable image quality. The cleaning process employs direct physical contact with the toner and photoreceptor (2). One approach involves the use of brushes; the second uses a blade. Residual toner is bound to the photoreceptor surface by a combination of dispersive and electrostatic forces and the physical forces exerted by the brush or blade must overcome these (62). Because dispersion forces increase with the area of contact, careful design of the preceding steps of development and transfer to avoid the deformation of toner is important in solving this cleaning problem.

In the case of brush cleaning, a number of design factors have to be considered. Among these are the elastic properties and density of the synthetic bristles. Historically rabbit fur worked very well (3). In the case of blade cleaning, different factors must be taken into account. The blade, which contacts the surface of the photoreceptor, must be conformable, whereas the design must take into account that micrometer-sized toner particles must be removed. This obviously requires exceedingly close tolerances over the full length of the photoreceptor. It is for this reason that conformable elastomers(qv) are typically used, although thin, flexible steel blades can be employed for a hard photoreceptor such as amorphous silicon. In either case, the angle of attack of the blade and the frictional forces between it and the photoreceptor must be carefully considered. As before, efficiency of blade cleaning is determined not only by the toner properties but by those of the photoreceptor. The functionality of blade cleaning is highly dependent on the smoothness of the photoreceptor surface because any roughness lifts the blade, allowing toner to avoid removal. The cleaning step involves direct physical contact and puts additional constraints on the photoreceptor.

After the original latent electrostatic image produced by the projection of an optical image on the precharged photoreceptor has been developed by toner, the toner transferred, and residual toner cleaned, there is still some remnant of the original latent electrostatic image. If this remnant is not to interfere with the next image, it must be erased; otherwise the phenomenon of ghosting occurs in which a previous image subsequently prints out. Removal of the latent image is usually achieved by uniformly exposing the photoreceptor to light from an erase lamp which photodischarges the entire surface of the photoreceptor.

3. Summary

Organic photoreceptors predominate in electrophotography because these materials offer a large degree of design flexibility at low cost. The unit manufacturing costs of α-Si:H photoreceptors are significantly higher than those of organic photoreceptors. Plasma-deposited α-Si:H photoreceptors, which have some shortcomings in these respects, have nonetheless entered the commercial marketplace because of demonstrated durability and long life (63). Photoreceptor life is an ill-defined term, unless described within the context of a specific machine design. As an example, in the case of high speed copiers where, in one engineering approach, a flexible belt photoreceptor employs full document exposure using a light pulse, no matter what the advantages of amorphous silicon-based materials, the high internal stress characteristics of the materials are incompatible with production in the form of a flexible device. Thus α-Si:H photoreceptors are constrained to situations where drum configurations are architecturally acceptable and mechanical integrity and stability are inherently maximized. Such requirements are particularly critical in high speed, high volume printers, including digital laser copiers.

In the field of toner materials, the emphasis in the 1990s is on increasing developer life, particularly using color toners. The life of a typical black two-component developer is about 80–100 kilocycles per kilogram, whereas for color toners it is only about 10 kilocycles per kilogram (64). Also, there is a need for better control of triboelectrification of toner particles that would not only allow stable operation under all environmental conditions but also provide consistent, fast, and reproducible contact charging.

The trend in the reprographic business, not only in printing but also in copying and duplicating, is towards the digital processing of information, rather than using analogue light-lens reproductions. Therefore, photoreceptors have to respond to sources of digital input. This can be either radiation emitted by lasers, light emitting diode arrays, or radiation filtered by fast-responding liquid crystals. Because the least expensive and best field-tested lasers are solid-state GaAs lasers that emit in the near ir (680–830 nm) range, photoreceptors must respond to the incident wavelengths. Organic photoreceptors are best suited for this function, and the vast majority of small and medium size xerographic laser printers on the market use OPCs. The possible advancement of either inexpensive solid-state lasers emitting in the visible wavelength range or other sources of digital input such as light-emitting diodes, could diminish the need for such near-ir sensitive photoreceptors (see Light generation).

The main factors that limit the speed of duplicators are paper handling and the input of energy needed to accomplish fusing of toner to paper. In the case of laser printers the main factor is the speed of the rotating polygon, the purpose of which is to deflect the laser beam signals to the appropriate spots on the photoreceptor. The core materials, the photoreceptors and the toners, do not limit the technology. For example, a laser printer operating at speeds greater than three standard 20.35-cm (8-in) wide pages per second having the desired print resolution of 1500 lines per centimeter, with a 16 mirror polygon (a hexadecagon) would have to rotate at 54,000 rpm.

Fusing toner to paper requires a significant amount of energy. The faster the throughput of paper, the more energy needed to heat paper and toner to fusing temperatures that are typically in the neighborhood of 100°C. Enough energy could be supplied and stable fusing temperatures maintained, even at very high throughput speeds, provided the flow of paper through the fuser is steady. However, in real situations, copying and printing jobs come in spurts and the fuser rolls may easily overheat when the flow of paper which cools the rolls is suddenly stopped. The fuser-roll materials, the heat-transfer parameters, and heat capacities of all the materials involved, rather than the photoreceptor performance, thus constitute an important limitation on the printing speeds.

Future development trends in xerographic materials is also dependent on the emergence of color xerography. The triboelectrification of pigmented (color) toner particles has to be improved. In many instances, the colorant itself may direct the triboelectrification in the wrong direction and its effect must be overridden by additives or formulations which do not affect the color of the toner. Then, the average toner particle size of about 9–13 μm, typical of black-only toners, may well have to be reduced to 7–8 μm. Smaller toner particles enable better copy quality, through reduced image pile height and decreased image graininess (64).

BIBLIOGRAPHY

"Reprography" in *ECT* 2nd ed., Vol. 17, pp. 328–378, by J. J. Bulloff, State University of New York at Albany; "Electrophotography" in *ECT* 3rd ed., Vol. 8, pp. 794–826, by N. E. Wolff, Consultant, and J. W. Weigl, Xerox Corp.

Cited Publications

1. J. Mort, *The Anatomy of Xerography*, McFarland & Co., Publishers, Jefferson, N. C., 1989.

2. R. M. Schaffert, *Electrophotography*, Focal Press, New York, 1975.
3. E. M. Williams, *The Physics and Technology of Xerographic Processes*, Wiley-Interscience, New York, 1984.
4. C. F. Carlson, in J. H. Dessauer and H. E. Clark, eds., *History of Electrostatic Recording, in Xerography and Related Processes*, Focal Press, New York, 1965, Chapt. 1.
5. E. C. Giamio, *RCA Rev.* **23**, 96 (1962).
6. U.S. Pat. 2,221,776 (1940), C. Carlson.
7. U.S. Pat. 2,297,691 (1942), C. Carlson.
8. J. H. Dessauer and H. Clark, *Xerography and Related Processes*, Focal Press, London, 1965.
9. U.S. Pat. 2,970,906 (1961), W. E. Bixby (to Xerox Corp.).
10. S. G. Grenishin and I. A. Cherkasov, *Zh. Nauch. Prikl. Fotogr. Kinematogr.* **5**, 433 (1960).
11. J. H. Neyhart, *Photogr. Sci. Eng.* **10**, 126 (1966).
12. K. Kiyota, A. Teshima, and M. Tanaka, *Photogr. Sci. Eng.* **24**, 289 (1980).
13. E. J. Felty, in O. Helwich, ed., *Proceedings of the 2nd International Congress on Reprography, Köln, Germany, 1967*, Verlag O. Helwich, Darmstadt, 1969, p. 40.
14. R. A. Fotland, *J. Appl. Phys.* **31**, 1558 (1960).
15. D. M. Pai and M. Scharfe, *J. Non-Cryst. Solids* **8**, 752 (1972).
16. J. Young and H. G. Grieg, *R.C.A. Rev.* **15**, 471 (1954).
17. Ref. 2, p. 318.
18. W. Eckenbach, in W. F. Berg and K. Kauffe, eds., *Current Problems in Electrophotography*, deGruyter, New York, 1972, 133–138.
19. R. B. Comizzzoli and D. A. Ross, *Photogr. Sci. Eng.* **13**, 265 (1969).
20. P. M. Cassiers, K. Verhille, and J. van Engeland, *Appl. Opt.* Suppl. 3 (Electrophotography), 83 (1969).
21. Ref. 2, p. 336.
22. K. Nakamura, *IEEE Trans. Electr. Dev.* **ED-19**, 405 (1972).
23. M. J. Mitsui, *IEEE Trans. Electr. Dev.* **ED-19**, 396 (1972).
24. P. Mark, *Photogr. Sci. Eng.* **18**, 254 (1974).
25. K. Yoshida, K. Kinoshita, and T. Kawamura, *Appl. Opt.* Suppl. 3 (Electrophotography), 170 (1969).
26. S. Faria and R. E. Karam, *J. Appl. Photogr. Eng.* **7**, 102 (1981).
27. W. Spear and P. G. LeComber, *Solid State Commun.* **17**, 1193 (1975).
28. I. Shimizu, T. Komatsu, K. Santo, and E. Inoue, *J. Non-Cryst. Solids* **35/36**, 773 (1980).
29. W. D. Gill, *J. Appl. Phys.* **43**, 5033 (1972).
30. P. J. Melz, *Photogr. Sci. Eng.* **21**, 73 (1977).
31. W. J. Dulmage and co-workers, *J. Appl. Phys.* **49**, 5543 (1978).
32. Nguyen Chang Khe, S. Yokota, and K. Takahashi, *Photogr. Sci. Eng.* **28**, 191 (1984).
33. Nguyen Chang Khe and co-workers, *Photogr. Sci. Eng.* **28**, 195 (1984).
34. P. J. Regensburger, *Photochem. Photobiol.* **8**, 429 (1968).
35. U.S. Pat. 3,357,989 (1967), J. F. Burne and P. F. Kurtz (to Xerox Corp.).
36. U.S. Pat. 3,816,118 (1974), J. F. Burne (to Xerox Corp.).
37. Brit. Pat. 1,337,228 (1973), M. Smith, R. Radler, and C. Hackett (to Xerox Corp.).
38. R. O. Loutfy, A. M. Hor, and A. Rucklidge, *J. Imag. Sci.* **31**, 31 (1987).
39. E. G. Schlosser, *J. Appl. Photogr. Eng.* **4**, 118 (1978).
40. P. J. Melz and co-workers, *Photogr. Sci. Eng.* **21**, 73 (1977).
41. U.S. Pat. 3,615,414 (1971), W. A. Light (to Eastman Kodak Co.).
42. K. Takeda and M. Nagata, *Photogr. Sci. Eng.* **25**, 268 (1981).
43. A. C. Tam and R. D. Balanson, *IBM Res. Dev.* **26**, 186 (1982).
44. R. E. Wingard, *IEEE Ind. Appl.* **125**, 1 (1982).
45. R. O. Loutfy, A. M. Hor, C. K. Hsiao, and A. R. Melnyk, *Fourth International Conference on Non-Impact Printing*, IS&T, Springfield, Va., 1988, p. 52.
46. K. C. Nguyen and D. S. Weiss, *J. Imaging Tech.* **15**, 158 (1989).
47. J. H. Perlstein in J. H. Perlstein *Electrical Properties of Polymers* Academic Press, New York, 1982, Chapt. 2, p. 59.
48. S. Takano and co-workers, *Imag. Sci. Technol.* **17**, 46 (1991).
49. J. S. Facci and co-workers, *J. Phys. Chem.* **95**, 7908 (1991).

50. M. A. Abkowitz and M. Stolka, in M. Lewin, ed., *Polymers for Advanced Technologies*, VCH, New York, 1988, p. 225.
51. P. J. Flory, *Makromol. Chem.* **1**, 5 (1986).
52. W. R, Harper, *Contact and Frictional Electrification*, Oxford University Press, Oxford, UK, 1967.
53. J. Lowell and A. C. Rose-Innes, *Advan. Phys.* **29**, 947 (1980).
54. L. B. Loeb, *Static Electricity*, Springer-Verlag, Berlin, 1958.
55. R. W. Gundlach, in J. H. Dessauer and H. E. Clark, eds., *Xerography and Related Processes*, Focal Press, New York, 1965, Chapt. IX.
56. R. B. Lewis, E. W. Connors, and R. F. Koehler, *Proceedings of the 4th International Conference on Electrophotogaphy, Washington D.C., 1981*, Society of Photographic Scientists and Engineers, Springfield, Va., 1982; U.S. Pat. 4,375,673 (to Xerox Corp.).
57. A. S. Diamond, *Toner: Black and Powder for an Exploding Market*, Diamond Research Corp., Ventura, Calif., 1979.
58. A. S. Diamond and L. O. Jones, *Copier Powders, Metals Handbook*, Vol. **7**, 9th Ed., American Society for Metals, Menlo Park, Calif., 1984, 580–588.
59. R. B. Prime, *Photogr. Sci. Eng.* **27**, 19 (1983).
60. P. G. Andrus and F. W. Hudson, in J. H. Dessauer and H. E. Clark, eds., *Xerography and Related Processes*, Focal Press, New York 1965, Chapt. XIV.
61. D. A. Seanor, *Photogr. Sci. Eng.* **22**, 240 (1978).
62. L. Nebenzahl and co-workers, *Photogr. Sci. Eng.* **24**, 293 (1980).
63. J. Mort, in Arthur S. Diamond, ed., *Handbook of Imaging Materials*, Marcel Dekker, Inc., New York, 1991, Chapt. 10.
64. D. A. Hays, *J. Imaging Tech.* **17**, 252 (1991).

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