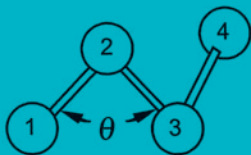


Handbook of Imaging Materials

Second Edition, Revised and Expanded



edited by
Arthur S. Diamond
David S. Weiss

The first edition of this book was edited by Arthur S. Diamond.

ISBN: 0-8247-8903-2

This book is printed on acid-free paper.

Headquarters

Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG
Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
tel: 41-61-261-8482; fax: 41-61-261-8896

World Wide Web

<http://www.dekker.com>

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

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Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface to the Second Edition

Since its publication in 1991, the *Handbook of Imaging Materials* has taken its place on the reference shelf of many leading scientists, engineers, and executives in the imaging industry. It is also well known in the academic world as both a sourcebook and textbook. There is no comparable reference available that is as highly focused or as comprehensive in defining the field of digital imaging technology.

To compile this second edition, we have worked with the authors to expand and update their original chapters while bringing in new contributors to cover the many advances that have occurred over the past decade. This second edition was enlarged and enriched by new ink jet, thermal, and electrophotographic technologies. These technologies, the digital color press, and new thermal dye diffusion methods all promise to challenge silver halide photography in amateur, commercial, and professional applications.

Although the use of diazotype materials is also fading into obsolescence, this process retains a foothold in the marketplace, primarily for wide format engineering and architectural blueprints and drawings. For these reasons and for the excellence of its content, Chapter 3 on diazo papers, films, and chemicals was again included in this volume.

Among the new chapters are: color photographic materials (Chapter 2), electrophotography (Chapter 4), photothermographic and thermographic imaging materials (Chapter 13), and papers and films for ink jet printing (Chapter 15).

In order to incorporate these topics effectively, the chapter on cylithography was excised. Despite major technical advances that have been made in cylith technology since 1991, that process has not had a significant impact in the imaging materials marketplace.

Finally, we are deeply indebted to those who contributed their knowledge, their writing skills, and their patience to this revised edition. We are grateful for their efforts in enabling us to expand the scope of this text and to bring it up-to-date in a field of science that is so rapidly advancing.

Arthur S. Diamond
David S. Weiss

Preface to the First Edition

The field of imaging technology has undergone massive changes over the past 50 years, from the 1940s, when photography served the entire gamut of reprographic applications, to its narrower focus in the imaging industry today. A half-century ago, silver halide-based papers and films performed every task from image capture to document copying.

Diazo processes took on special importance during the war years in the 1940s, growing rapidly in the 1950s to become the predominant method for engineering-drawing reproduction. Electrophotography grabbed the spotlight in the late 1950s and in the 1960s, when it revolutionized office procedures by increasing worker productivity through automation. Exploitation of this technology continues apace in facsimile, in desktop publishing, and in other areas of business communication.

Today, silver halide emulsion is still the primary image-capture medium for visible light, infrared, and x-ray photography. Amateur photographers, carrying some 250 million 35mm cameras worldwide, depend on this technology. In the United States alone, the retail photofinishing market reported revenues of \$5.34 billion in 1989, based on almost 15 billion exposures on silver film.

Although it is now a commercial reality, the digital, electronic camera is not expected to equal the number of photographs taken on silver film until the turn of the century, when an estimated 23 billion exposures will be made in this country.

While silver photography continues to hold onto the most demanding imaging applications—those that depend on its high-speed, high-resolution, and continuous-tone capabilities—it has been essentially abandoned in document copying and largely replaced in many other areas of black-and-white and color reproduction, in microfilm duplicating, and in the graphic arts.

To serve the many markets that comprise the imaging industry, a host of new ink jet, thermal, electrophotographic, electrographic, ion deposition, and microencapsulation processes have emerged. This handbook was compiled for the purpose of sorting out these imaging methods and applications, while describing the materials used in each process, and their properties and performance characteristics. Each chapter has been written by a leading authority in a particular field of imaging technology and contains a discussion of the imaging materials that are being used with an eye toward future technological advances.

Many changes still lie ahead, particularly in the area of color printing and color copying, and in a possible revolution of the printing industry. As the turn of the century draws near, we can expect to be surrounded by color images, at home, at the office, in our shops, airports, and other public places. Digital scanning, image processing, and economical, nonphotographic processes will make large-format color affordable and accessible to everyone. It is likely that our walls will be hung with family portraits, beautiful landscapes, and the world's art treasures, scanned, digitized, and reproduced with breathtaking clarity, colossal in size, and vibrant with color.

Liquid toners, by virtue of their extremely fine particle size, highly saturated colors, and adaptability to digital electrostatic imaging systems, are making large-format color a reality. But the largest potential application for liquid toner is as a replacement for printer's ink in the computer-driven press of tomorrow.

These are some of the forces that are shaping the future for imaging technology, a field that is concerned with the visualization of our knowledge and culture, our literature and art. This text was prepared with the objective of bringing together the latest information in this dynamic field, recognizing that advances in imaging science and technology will inevitably improve the efficiency of our industry and the quality of our lives.

It was a suggestion by Dr. Maurits Dekker that prompted this work, an effort that spanned three years and drew on the expertise of 19 authors. Dr. Dekker recognized the need for a comprehensive text to serve as a reference for scientists and engineers in the imaging industry who are responsible for the design and development of imaging hardware and for the manufacture of the papers and films, toners and developers, inks and coatings, and other materials needed to produce hard copy. He also saw the evolution of imaging science curricula as an increasing number of colleges and universities. This reference handbook was thus planned to serve the needs of both the academic and the industrial world.

I am grateful to Dr. Dekker for his inspiration, enthusiasm, and patience in commissioning the effort that resulted in this unprecedented text. I also would like to acknowledge the efforts of the authors who contributed to the successful completion of this formidable task and to the unflagging optimism of my dear wife, Becky, whose winning smile has seen me through the most ambitious undertakings of my career.

Arthur S. Diamond

Contents

<i>Preface to the Second Edition</i>	<i>iii</i>
<i>Preface to the First Edition</i>	<i>v</i>
<i>Contributors</i>	<i>ix</i>
1. Conventional Photographic Materials <i>J. F. Hamilton</i>	1
2. Color-Forming Photographic Materials <i>L. E. Friedrich and J. A. Kapecki</i>	35
3. Diazo Papers, Films, and Chemicals <i>Henry Mustacchi</i>	63
4. A Brief Introduction to Electrophotography <i>B. E. Springett</i>	145
5. Dry Toner Technology <i>Paul C. Julien and Robert J. Gruber</i>	173
6. Carrier Materials for Imaging <i>Lewis O. Jones</i>	209
7. Liquid Toner Materials <i>James R. Larson, George A. Gibson, and Steven P. Schmidt</i>	239
8. Dielectric Papers and Films <i>Lubo Michaylov and Dene H. Taylor</i>	265
9. Photoreceptors: The Chalcogenides <i>S. O. Kasap</i>	329

10. Photoreceptors: Organic Photoconductors <i>Paul M. Borsenberger and David S. Weiss</i>	369
11. Photoreceptors: Recent Imaging Applications for Amorphous Silicon <i>Robert Joslyn</i>	425
12. Thermal Imaging Materials <i>Klaus B. Kasper</i>	437
13. Photothermographic and Thermographic Imaging Materials <i>P. J. Cowdery-Corvan and D. R. Whitcomb</i>	473
14. Ink Jet Ink Technology <i>Walter J. Wnek, Michael A. Andreottola, Paul F. Doll, and Sean M. Kelly</i>	531
15. Papers and Films for Ink Jet Printing <i>Douglas E. Bugner</i>	603
16. Applications of Amorphous Silicon and Related Materials in Electronic Imaging <i>J. Mort</i>	629
<i>Index</i>	663

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1

Conventional Photographic Materials

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1.1 INTRODUCTION

1.1.1 Advantages

It is an interesting exercise to imagine that conventional silver halide photographic film had only recently been invented, after a century or so in which the only imaging systems known to the world were electrostatic and electronic imaging such as charge-coupled devices. What would the creative advertising agencies of today tout as its superior improvements over previously existing technologies?

Surely they would welcome the liberation from external power sources, the small size and light weight of a piece of film, its flexibility, allowing it to be wrapped on a compact spool, and the fact that it can sit for months, even years, on a shelf and be ready for use instantaneously. They would point out that the sensitive material of this very inexpensive product is itself converted to the recorded image by a relatively simple chemical treatment requiring, in its basic form, no complex auxiliary equipment. They would marvel that it can be made sensitive to select spectral ranges from the ultraviolet well into the infrared and to high energy particles or radiation, and over the remarkable extent to which it can be made to yield a true (or, if desired, false) color rendition of an original, or a black-and-white image with archival stability. They would extoll the superior image quality of this new product, emphasizing its extremely high information packing density, its sharpness, its uniformity, its low level background noise, and its freedom from defects.

They would hail its ability to integrate (albeit not with constant efficiencies) over exposure times from hours to the picosecond range, and they would emphasize that over

* Retired.

the most commonly used range of times it has virtually no temperature dependence or sensitivity, at least within the range of normal ambients.

In addition, they would emphasize the versatile ability of photographic manufacturers to tailor this material for special uses, producing negative or positive images, instant or thermal processing, etc. And no doubt this represents only a scratching of the surface of the virtues that could be attributed to this remarkable new accomplishment of modern chemical ingenuity. Even discounting the obvious excesses of this tongue-in-cheek scenario, it would have to be admitted that the conventional silver halide imaging process has set the standards to be aimed at by designers of rival technologies and that it still remains superior in a number of respects.

1.1.2 Uses

Alternative processes have certain attributes, however, that make them better adapted for some applications, in which they are replacing silver halide materials. Even in these fields, however, which we now think of as the exclusive domain of electrostatic or electronic imaging (e.g., document copying, news and amateur cinematography), there was often a silver halide special-purpose material that at one time served the need. The current major classes of conventional silver halide based products manufactured can be found in any of a number of financial reports on the industry, but the total listing of special-purpose materials, either current or superseded, is astoundingly large.

1.2 FILM COMPOSITION

Photographic films, papers, and other media consist of one or more sensitive layers along with certain ancillary layers (filters, chemical barriers, etc.) coated on a suitable flexible or (occasionally) rigid support. Typical color films contain at least six sensitive layers (high and low sensitivity of each of the three color sensitivities) and several other nonsensitive ones.

The principal component of the sensitive layers is individual crystals (often called *grains*, in the photographic literature) of silver bromide, silver chloride, or mixed crystals of the two, frequently containing also up to several percent silver iodide in solid solution. Gelatin is normally used as a binder. Linear crystal dimensions vary greatly among special-purpose materials, covering the range from about 0.03 μm to several micrometers. A single sensitive layer normally has a thickness averaging a number of monolayers of grains.

Depending on the type of material, the sensitive layers will also contain other components as well. Chemical sensitizers are almost always applied to the grains, as are sensitizing dyes in all materials having spectral sensitivity to longer-than-blue wavelengths (see later sections). The most common color negative materials also contain color couplers, organic precursors of the dyes that form the color image. Spreading or wetting agents, chemical hardeners for the gelatin, fungicides, and other active chemical components are also sometimes incorporated, and, with the great variety of special-purpose materials offered, the combinations are extensive.

1.3 SILVER HALIDE STRUCTURE

1.3.1 Crystal Structure

Silver bromide and silver chloride are the simple monovalent ionic salts of the two components. They both exhibit sixfold symmetry and have the sodium chloride crystal structure

under ambient conditions with lattice constants of 0.5547 nm for AgCl and 0.5775 nm for AgBr (Wyckoff, 1964). These values are slightly lower than twice the sum of the standard ionic radii, indicating some inadequacy of the hard-sphere ionic model. This feature is one of several manifestations of the presence of some covalent component of bonding in these materials, based on ionicity rankings (Phillips, 1970).

Silver chloride and silver bromide form coherent mixed crystals in all proportions (Chateau, 1959), by simple substitution on the halide sublattice. The iodide ion is reported (Chateau et al., 1958) to be soluble in silver bromide to a maximum concentration of about 30 mol% and in silver chloride to only a few mol%. The limited solubility reflects the fact that pure silver iodide has fourfold symmetry and crystallizes in either the sphalerite or the wurtzite crystal structure (Wyckoff, 1964), but not the sodium chloride form. The standard ionic radius of the iodide ion is 19% greater than that of chloride and 11% greater than that of bromide.

1.3.2 Electronic Characterization

These crystals are classified as electronic insulators. The filled valence bands and the empty conduction bands are separated by forbidden gaps of 3.25 eV in the chloride and 2.68 eV in the bromide. From simple Fermi statistics, the expected free carrier concentrations in intrinsic materials at room temperatures are 10^{-28} and 10^{-23} cm^{-3} , respectively.

1.3.3 Electronic Structure of the Elements

The electronic structures of the four principal atoms and ions along with those of several related species are given in Table 1.1. The halogen ions Cl^- , Br^- , and I^- form by acquiring a single electron to fill the 3p, 4p, and 5p shells, respectively, which are fivefold occupied in the atomic state.

The silver atom consists of a rare gas Kr core, a filled 4d electron shell, and a single 5s electron. The positive ion forms by loss of the 5s electron.

The alkali atom Rb has the same Kr core and 5s electron but is missing the 4d shell. This difference, as subsequent discussions will show, is responsible for many of the unique properties of the silver halides, particularly in contrast with those of the superficially similar alkali halides.

The closely related noble metal, Au, differs from silver mainly in the order of the rare gas core. Gold is in many ways similar to silver and has become an important ingredient in the photographic process. As indicated in Table 1.1, the first ionization potential of gold

Table 1.1 Electronic Structure of Selected Elements

Element	Z	Electronic structure (atom)	Ionization potentials (eV)		Electron affinity (eV)
			First	Second	
Cl	17	$[\text{Ne}]3s^2 3p^5$			3.63
Br	35	$[\text{A}]3d^{10} 4s^2 4p^5$			3.38
I	53	$[\text{Kr}]4d^{10} 5s^2 5p^5$			3.08
Ag	47	$[\text{Kr}]4d^{10} 5s^1$	7.57	21.48	
Rb	37	$[\text{Kr}]5s^1$	4.18	27.5	
Au	79	$[\text{Xe}]4f^{14} 5d^{10} 6s^1$	9.22	20.5	

is larger than that of silver, and this feature is largely responsible for its photographic consequence.

1.3.4 Emulsion Precipitation

For commercial photographic purposes, the silver halide crystals, being very sparingly soluble in water, are formed by precipitation from aqueous solutions of more soluble salts of these elements (Duffin, 1966; Wey, 1985). Typically, two solutions of reactants such as KBr and AgNO_3 are introduced with vigorous mixing in separate streams to a reaction vessel containing some of the halide solution and dilute gelatin or another peptizing agent. The finished suspension of crystals in the gelatin solution is generally referred to as an *emulsion*, a terminology clearly not consistent with general chemical use.

In modern equipment the electrochemical potentials of the reagent ions are monitored continuously at all stages of the precipitation, and these data are fed to automated flow equipment that controls the concentrations of the two reacting ions in the solution over the growing crystals.

Extensive exploration of the variables involved in precipitation has produced a wealth of technological data that allows rigid control of such features as size, size distribution, crystal habit, halide compositional structure, and defect content of the grain population. For example, silver bromide crystals grown with only slight excess bromide ion concentration have stable [200] faces and thus are cubic, whereas a higher bromide ion excess results in stable [111] faces and octahedral crystal shape. Still greater halide excess forms complex ions such as AgBr_3^{2-} in solution. These ions lead to the formation of growth twins in the precipitate and more complex crystal shapes. One such form is that of a triangular or hexagonal tabular platelet, which results when the crystal contains two or more parallel twins. Precipitates containing almost exclusively grains of this form can be made, and these are now used in some commercial materials. When the thickness-to-breadth ratio is made quite small, such grains have a large specific surface and therefore certain practical advantages (Berg, 1983).

Many of the basic physical properties of the silver halides have been determined from experiments using macroscopic melt-grown crystals or from vacuum-deposited thin films (Berry et al., 1963).

1.3.5 Chemical Sensitization

Virtually all commercial emulsions are subjected to chemical sensitization treatments between precipitation and coating to improve their sensitivity to light (Duffin, 1966; Harbison and Spencer, 1977).

The most commonly used procedure involves the addition of compounds containing labile sulfur in combination with gold salts and usually certain other modifying chemicals, followed by digestion at elevated temperature. This practice results in the formation of adsorbed molecules of Ag_2S , AgAuS , and/or Au_2S . Following the chemical conversion, there is evidence (Roth and Simpson, 1980; Corbin et al., 1980) for a second essential stage of the process, thought to involve surface migration and reorganization of the sulfide molecules into aggregates. Some features of this process have been interpreted (Keevert and Gokhale, 1987) to be consistent with the formation of dimers as the critical step.

Even in the relatively small amounts normally used, the conversion of labile sulfur to insoluble sulfide can be followed quantitatively by extraction (Sturmer and Blackburn, 1979) using the radioactive species ^{35}S . The dependence of sensitivity (log reciprocal

exposure for some fixed photographic response) on the amount of converted sulfide is typified by the results given in Fig. 1.1. The sensitivity first increases with added sulfide but eventually reaches a plateau and usually declines if the sulfur is further increased. When expressed as a surface coverage, the sulfur content at the plateau position is reported to vary little among preparations, and an optimum coverage of 2×10^4 sulfide molecules per square micrometer of silver halide surface has been reported (Sturmer and Blackburn, 1979). In a typical high-speed film, this value translates to the order of a few milligrams of sodium thiosulfate per mole of silver halide. The gold salt (e.g., KAuCl_4) is typically present in a similar weight ratio.

Neither the position of the subsequent decreasing portion of the curve (see Fig. 1.1) nor the extent of the decline is as reproducible among preparations. Nevertheless, it is encountered with enough regularity that it can definitely be attributed to an excess of sensitizer and not to some other spurious cause.

The treatment also invariably causes an increase in fog—a fraction of the crystallites that develop without exposure. The fogged fraction increases with increasing sensitizer content.

Historically, the sensitizing effect of the labile sulfur compounds was discovered some years before the important effect of adding gold salts was revealed. During that period, therefore, many materials were made and many mechanistic studies undertaken using only *sulfur sensitization*. Scientific studies frequently still involve such preparations, to separate the complex effects of the two components in what is commonly called *sulfur-plus-gold sensitization*. However, even without absolute knowledge of the practices of all manufacturers, it is reasonably safe to conjecture that all high-speed camera films today

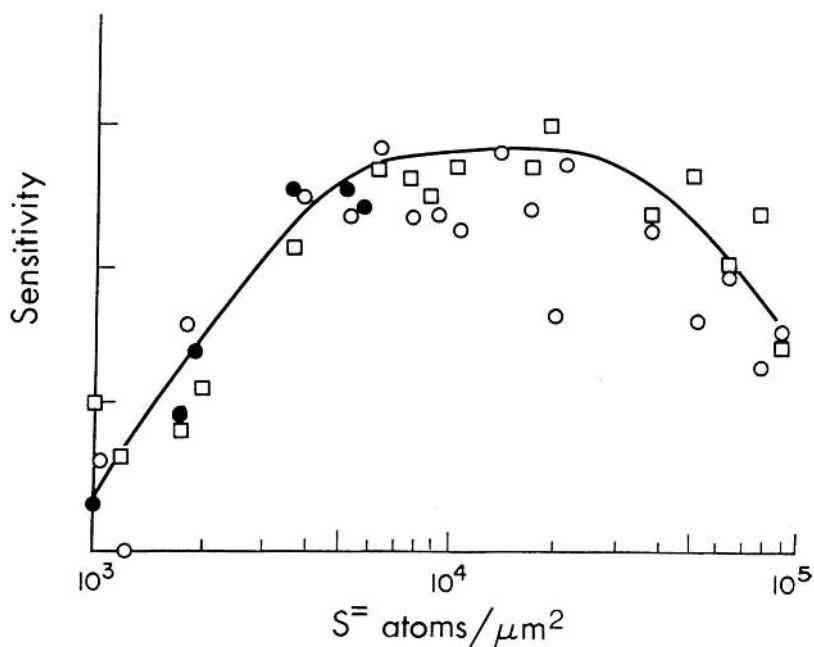


Figure 1.1 The dependence of photographic sensitivity on the surface concentration of sulfide converted in chemical sensitization.

are sensitized with sulfur and gold treatments. This generalization cannot be made for other materials for other applications.

1.4 THE LATENT IMAGE AND DEVELOPMENT

1.4.1 The Development Reaction

After a photographic material has been exposed to a sufficiently strong pattern of light or ionizing radiation, it is said to bear a *latent image*. This latent image is capable of being transformed by a *developer* into a visible image corresponding to the light pattern. The essential active ingredient of a photographic developer is a moderately strong chemical reducing agent. The reducing agent transfers electrons to grains that have received some minimum exposure, causing them to begin to be reduced to metallic silver, but not to those that have received less than the minimum requirement. It is now broadly agreed that the latent image consists of centers at which the absorption of radiation has caused the formation of small clusters of mixed Ag/Au metal atoms—the latent image centers. When gold has been used in the sensitization, the latent image centers are composed at least partly of gold atoms. These centers in turn control the development reaction so that there is *discrimination* between exposed and unexposed grains.

1.4.2 Fog and Discrimination

The energy level pattern of the silver halide and silver phases, shown in Fig. 1.2, leads directly to an electronic description of discrimination in development. Injection of electrons into the silver halide conduction band would lead to indiscriminate reduction even of unexposed grains and thus what is known as fog. A developing agent must therefore be chosen whose chemical potential places its frontier electrons well below the silver halide conduction band in energy. The rate of the thermally activated injection will then be given by the product of a preexponential factor including a proportionality to the number of potential surface injection sites and a Boltzmann term involving the energy discrepancy. The developer must be chosen so that the fog rate is tolerable.

In energy, the silver Fermi level lies far enough below the silver halide conduction band that nonfogging developers can be found whose chemical potential allows thermodynamically favored electron transfer to bulk silver. Thus silver acts as an electrode (Pontius et al., 1972; Pontius and Willis, 1973), accepting electrons from developer molecules and transferring them to defect silver ions within the exposed crystal, thus producing more silver, in an autocatalytic reaction. For every electron transferred to the developing grain, a halide ion passes into solution thus maintaining charge balance and assuring the continued supply of defect silver ions.

1.4.3 Size Dependence of Latent Image Centers

There is extensive evidence for a size requirement for a latent image center capable of initiating development. In fact, this evidence leads to the conclusion that there is a smallest range of sizes that is unable to initiate development, a range of larger sizes for which this occurs very slowly (i.e., with activation), and finally a size limit beyond which the reaction proceeds very rapidly. These observations are rationalized (Trautweiler 1968; Jaenicke, 1972) by a proposed regime of size-dependent energy levels for silver clusters, allowing for the lowest unfilled level of the smallest clusters to lie well above the bulk silver Fermi

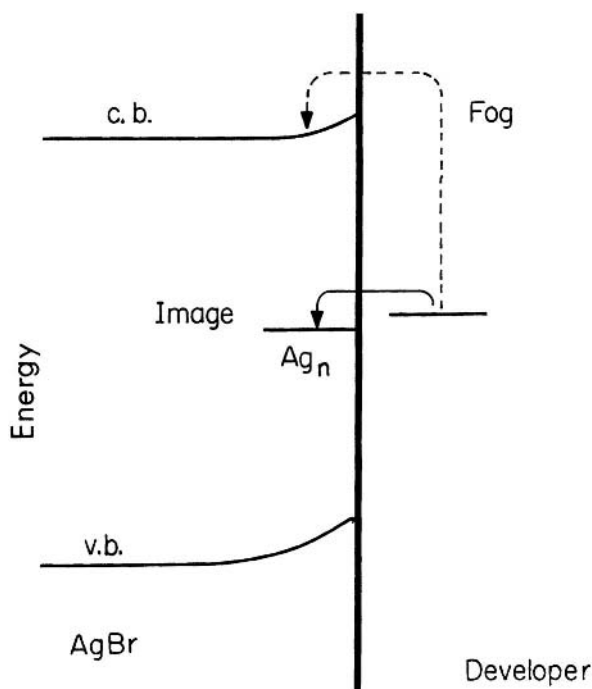


Figure 1.2 The energetics of electron transfer in photographic development. Transfer to silver is thermodynamically favored, but that to the conduction band (c.b.) of an unexposed crystal, to produce fog, requires considerable thermal activation; v.b. = valence band.

level and also above the level of the developer electrons, those of the intermediate size class to lie marginally above the developer level, and finally a size limit beyond which all clusters can favorably accept electrons from the developer. In the intermediate range, the initiation of both image and fog development is thermally activated and, even though the activation barrier is much lower for the image, discrimination is nonetheless problematic, owing to the much higher density of sites in the preexponential of the fog reaction.

Basic molecular orbital concepts (Hamilton and Baetzold, 1981; Tani, 1983) predict that there is an odd—even oscillation of the lowest unfilled level with size in simple geometric forms of clusters of atoms such as silver with a single s-electron, and experimental studies have confirmed this principle for vapor phase copper and silver clusters (Powers et al., 1983). If this is true also for photographic clusters, all odd-sized clusters should easily accept an electron and grow to the next larger size; all limiting reactions should occur at the even sizes (Hailstone and Hamilton, 1987). It is possible that geometric constraints and/or electronic interaction with the host silver halide would modify or even totally eliminate this pattern, and neither experimental nor theoretical analyses have been able to resolve the uncertainty.

However, a number of photographic (Hailstone and Hamilton, 1985, 1987; Hailstone et al., 1987; Hada et al., 1980; Hada and Kawasaki, 1985) and model studies (Hamilton and Logel, 1974; Fayet et al., 1985) agree on some general aspects of the size dependence of developability. The smallest size class of clusters consists of the metal dimer, which appears not to be able to exert discrimination. This feature can be rationalized with no

difficulty in terms of the expected energy level of the lowest unfilled level of the dimer. The excitation energy of the silver dimer in vacuum—that is, the energy to raise an electron from the highest occupied to the lowest unfilled level—is 2.85 eV (Brown and Ginter, 1978), larger than the AgBr forbidden gap. The lowest unfilled level must lie near the bottom of the conduction band. Thus the activation energy for electron transfer is not greatly smaller and the Boltzmann probability of transfer is not greatly larger than that of the fogging reaction. The differences in the density-of-sites factor has the effect of making fog more likely and eliminating any possibility of discrimination by the dimer.

When gold is used in the sensitization and therefore becomes incorporated in the latent image center, the next size class, the three-atom cluster (or perhaps three and four atoms, if the oscillating energy level pattern does apply) is developable with only a very small thermal activation, so that under most practical development conditions grains containing these centers are all developable. All larger centers are developed with no detectable activation delay.

Without gold in the sensitization, the latent image centers are exclusively silver and the characteristics are different. Clusters of three (or three and four) atoms have higher activation barriers to electron transfer and have only a very marginal chance of initiating discriminating development before fog becomes excessive. The next size class, four atoms (or five and six), have lower but still significant activation barriers and develop, though slowly. Only by the next size class, five atoms (or seven and eight), does the activation delay become undetectable.

The effect of gold on decreasing the developable size of the latent image is the result of the greater electron affinity of gold-containing clusters. Replacement of one or more silver atoms in a marginally developable cluster by gold causes the lowest unfilled level to be nearer to the developer level and thus more accessible to the electrons of the developer molecules.

To summarize, for practical development conditions the minimum size of the developable latent image is three atoms in emulsions sensitized with sulfur plus gold. In materials without gold, the development probability of sizes between perhaps seven and four atoms increases with development time, all contributing significantly to discrimination.

1.5 THE DEVELOPED IMAGE

1.5.1 Composition and Structure

Once initiated, the development of a given center is autocatalytic and proceeds with an increasing rate unless it becomes inhibited by exhaustion of either the silver halide or the reducing agent or unless some other species interferes with the reaction.

In most black-and-white materials, the developed silver is the light-absorbing material of the final image. On a microscopic scale, the silver is a tangled mass of silver filaments, for reasons that have never been adequately explained. In color materials, on the other hand, the image consists of dyes formed by reaction of the oxidized developer species with precursor molecules called couplers, which are either incorporated into the coating or dissolved into the developer solution. The technology employs couplers of varying molecular structure such that the three necessary image dyes are selectively formed from a common oxidized developer species. The developed silver is removed from the color image by dissolution along with the undeveloped silver halide.

1.5.2 Sensitometry

For a developed silver image, the optical density in any region is reasonably well given by the Nutting equation (Nutting, 1913):

$$D = 0.434n\bar{a} \quad (1.1)$$

where n is the number of developed grains per unit area, $\bar{a}$ is the mean projected area per grain, and 0.434 is $\log_{10} e$. This equation holds rigidly for the so-called random-opaque-dot model (Picinbono, 1955). In real materials the value of $\bar{a}$ must actually be the optical cross section of a developed grain, including the effect of light scattering in the coating (Farnell and Solman, 1963). The optical cross section of a tangle of silver filaments is not easily accessible except by Eq. (1.1), but it is obviously different from the measurable area of the undeveloped grain from which it is derived. When the undeveloped grain area is used in Eq. (1.1), as is often done, the expression is only approximately valid.

Photographic response is customarily depicted by plotting the developed optical density versus the logarithm of the incident energy of the exposing radiation. Such a plot produces a *characteristic curve* having the general form shown schematically in Fig. 1.3. Typically there is a background $D_{\min}$ value or *fog*, followed by a gradually rising *toe*, frequently an approximately linear portion, and finally a *shoulder* at the $D_{\max}$ value. The slope of the linear portion is the *gamma* γ or *contrast* of the material, and the log E difference between the toe and shoulder regions gives the exposure latitude. The reciprocal of the log exposure required, usually to produce some fixed low density, gives a measure

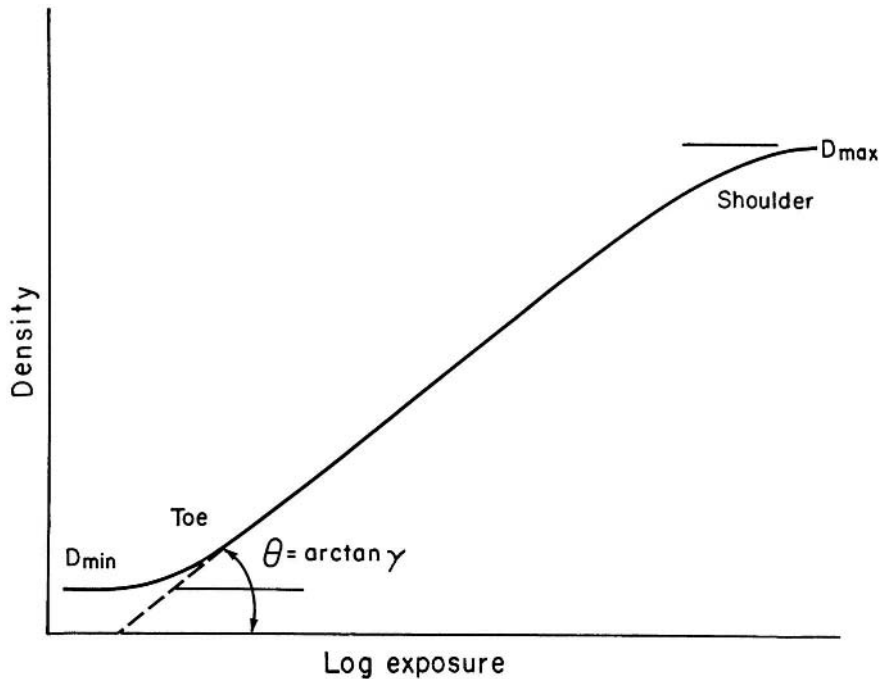


Figure 1.3 Sketch of a typical characteristic curve (D versus $\log E$) for a photographic material.

of the *sensitivity* S or speed of the materials. A variety of conventions have been proposed for measuring sensitivity, and that applied commercially is specified in detail by the International Standardization Organization (ISO).

1.5.3 Reciprocity Law Failure

In general, photographic sensitivity is not independent of the exposure time/light intensity combination. This dependence is termed reciprocity failure. The most common form is a loss of sensitivity for very weak images that require long exposure times, an inefficiency called low-intensity reciprocity failure (LIRF) (Webb, 1950). Most common photographic materials show quite significant failure for exposure times greater than perhaps 0.1 to 1 second, and for applications such as astronomy, which require much longer exposure, very specialized techniques have been developed to minimize the inefficiency (Babcock et al., 1974). Some types of material also exhibit high-intensity reciprocity failure (HIRF), a loss of sensitivity for very short exposure times. The common practice of using gold salts in the chemical sensitization has all but eliminated this defect in modern commercial camera films (Hailstone and Hamilton, 1985).

1.5.4 Quantum Sensitivity

Under certain limited conditions it is possible to measure the quantities necessary to convert a conventional characteristic curve of density versus log incident energy into an absolute one whose variables are the fraction of grains made developable and the number of absorbed photons per grain. This allows for specification of the *quantum sensitivity* of the material, that is, the number of absorbed photons to make some particular fraction of the grains developable. Such measurements have been made on a number of materials by now (see Hamilton, 1988, Refs. 1–11), and the results indicate that the best conventional chemical sensitization methods are able to approach but not exceed a quantum sensitivity value of about 8 absorbed photons per grain at the 50% developable level. To be sure, some commercial and experimental materials fall far short of this position, but the clustering of results at about this value is strongly indicative of some kind of limit there. The limit is not strongly dependent on grain size up to a linear dimension of 1 or 2 μm , but above that value a deterioration of quantum sensitivity appears to be normally observed (Farnell, 1969; Tani, 1985).

1.5.5 Grain Size and Sensitivity

Below this limit, however, where the quantum sensitivity is nearly independent of grain size, the size directly affects conventional sensitivity, owing to the larger collecting power of larger grains. The range of ISO speeds available among commercial camera films and other materials is in fact achieved largely by changes in grain size. In spectral regions where the light is absorbed by the silver halide, it is approximately true that

$$S \propto l^3 \quad (1.2)$$

where l is a mean grain linear dimension; but when the absorption is by dyes at the grain surface,

$$S \propto l^2 \quad (1.3)$$

It is obvious that a narrow spread of crystal sizes in general produces high contrast and short latitude, whereas a broad size distribution gives extended latitude and lower contrast.

In spite of the reservations expressed earlier, there is a general correlation between the undeveloped grain size l^2 and the optical cross section $\bar{a}$ of the developed grains in Eq. (1.1). Thus it also follows that for a given mass or volume of silver halide per unit area ($nl^3 = \text{Ag}$) the maximum density, or in fact the density corresponding to any given fraction of grains developed, is

$$D = 0.434 \frac{\text{Ag}}{l^3} \bar{a} \quad (1.4)$$

or

$$D/\text{Ag} \approx \text{const} \left(\frac{1}{l} \right) \quad (1.5)$$

The density per unit mass of silver, termed the covering power, is greater for small grain size and decreases in roughly inverse proportion to grain size. To achieve a given D_{max} , therefore, more silver coverage is required for larger grain size.

1.5.6 Graininess

It is also true that as the crystal size and therefore the film speed increases, so does the familiar *graininess* pattern of the image. This property is only indirectly related to the size of the crystals, however, for even the largest of those used are far below the resolution limit of the eye or any other readout system, under normal conditions. The subjective perception of graininess has been shown to correlate with the measured *granularity* G (Selwyn, 1935, 1942), which is defined as the root-mean-square fluctuation of optical density in a nominally uniform image area, when measured with an aperture of specified area. The density fluctuation results principally from the variance of the number of image elements within the aperture area. With random statistics, the variance is given by $n^{1/2}$. Thus in an ideal black-and-white material, granularity is expected to increase with the $1/2$ power of the image density. Among materials of different crystal size, the foregoing relationships may be combined to predict that speed and granularity are related by

$$G \propto S^{1/3} \quad (1.6)$$

in the intrinsic absorption region and by

$$G \propto S^{1/2} \quad (1.7)$$

in the region of dye absorption.

For color development, other considerations make the situation more complex. Nevertheless, it is still true that the perception of graininess results from the condition that within the image areas (pixels) resolved by the visual system the number of contributing

image centers is small enough that the variance of that number among nominally identical pixels is perceptible.

1.6 ABSORPTION OF IMAGING LIGHT

1.6.1 Electronic Band Structure

The conduction bands of the silver halides in question are simple isotropic bands with minima at the center of the Brillouin zone. However, the valence bands of both AgCl and AgBr are significantly influenced by the strong admixture of the silver 4d atomic levels with either the chlorine 3p or bromine 4p levels in that energy range. Owing to the inversion symmetry of the crystal, these levels do not mix at the Brillouin zone center, but at the zone boundaries they hybridize and spread to produce an inverted valence band (Kunz, 1982) as shown in Fig. 1.4.

The minimum energy transition corresponding to the long wavelength limit of light absorption is an indirect or nonvertical transition from the zone boundary of the valence band to the center of the zone of the conduction band. To conserve momentum, one or more phonons is either absorbed or emitted in the transition.

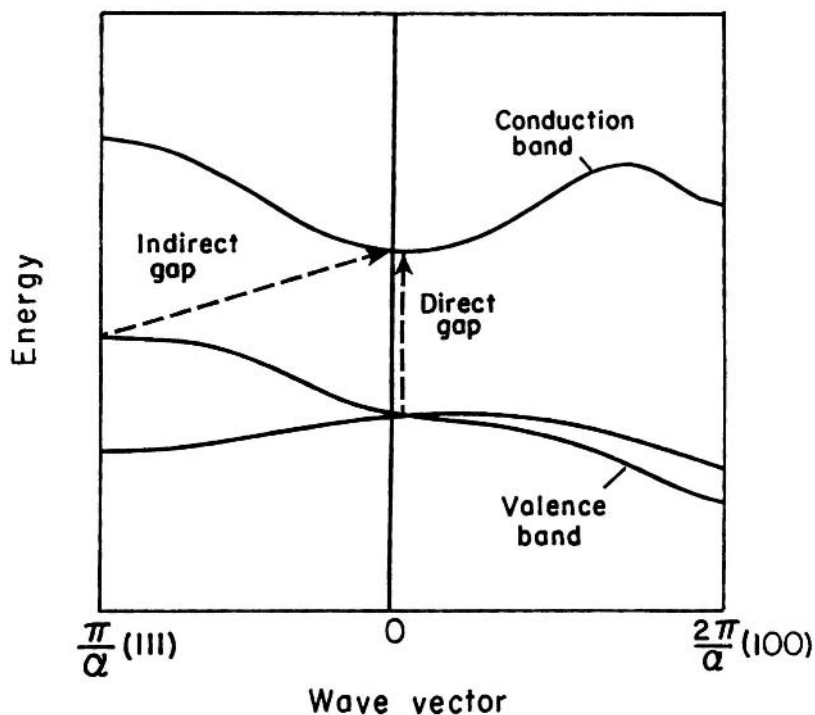


Figure 1.4 Sketch of the forms of the uppermost valence band level and the lowest conduction band level of silver bromide in reciprocal space. The valence band is inverted, having its highest energy point at the Brillouin zone boundary. Thus the indirect gap is smaller in energy than the direct gap.

At room temperature the indirect absorption edges extend through the near-ultraviolet spectral region for AgCl and well into the blue for AgBr (Moser and Urbach, 1956), but with absorption coefficients orders of magnitude lower than for the higher energy direct or vertical transitions, as shown in Fig. 1.5.

Studies of the quantum yield of free carriers indicate that absorption of a photon produces an exciton, which is autoionized to give a free electron-hole pair with near unit efficiency.

1.6.2 Spectral Sensitization with Dyes

In all except the ultraviolet and blue spectral region, the photographic process depends on absorption of the incident light by organic sensitizing dyes adsorbed to the surfaces of the grains. This process has been known and studied in the silver halides (West, 1974; West and Gilman, 1977) for more than a hundred years.

Relative Quantum Efficiency

A procedure to measure the relative efficiencies of photons in the spectral region of dye absorption and those absorbed by the silver halide itself has become standard. The expo-

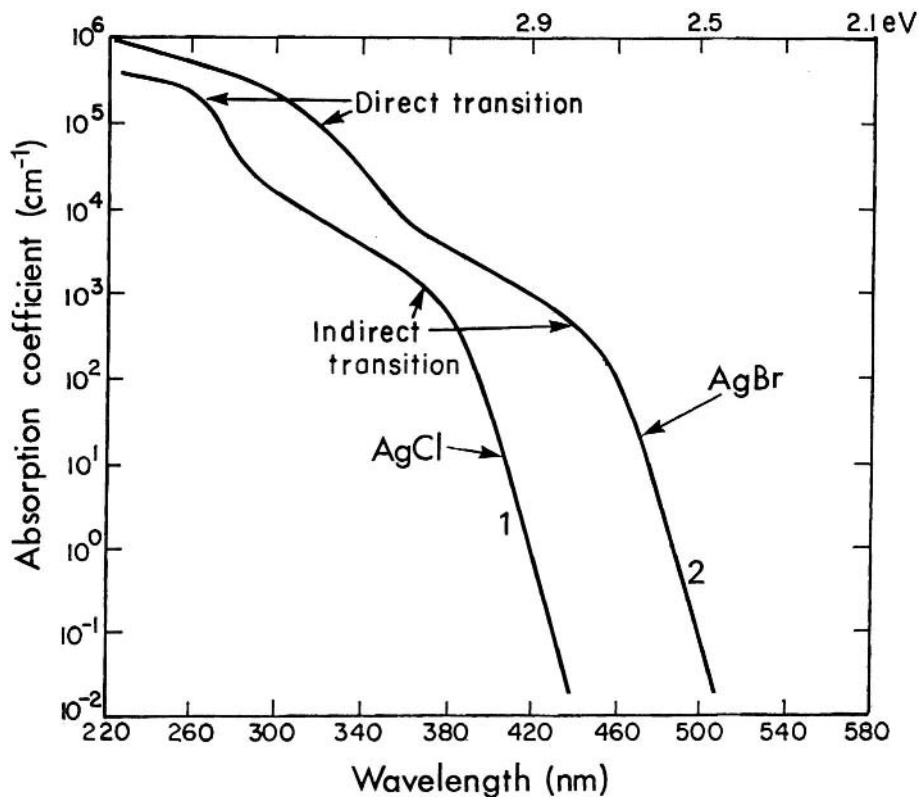


Figure 1.5 Absorption coefficients of silver chloride and silver bromide. The exponential form of the edges is apparent below the indirect transition energy.

sure (in energy density) to produce some fixed developed density is measured for monochromatic light of 400 nm wavelength (E_{400}) and also for light at the wavelength λ of the dye absorption maximum (E_λ). The absorption of the film at the two wavelengths (A_{400} , A_λ) is also measured. When the exposure values are converted to quanta, the ratio of the required number of photons at the two wavelengths is given by

$$\phi_r = \frac{400E_{400}A_{400}}{\lambda E_\lambda A_\lambda} \quad (1.8)$$

The quantity ϕ_r is termed the *relative quantum efficiency* (RQE) and has the significance that when $\phi_r = 1$, a photon absorbed by the dye is as effective in producing latent image as one absorbed by the silver halide. Dyes with ϕ_r between 0.8 and 1 are not uncommon.

Electron Transfer

By far the majority of practical sensitizing dyes are of the cyanine or merocyanine classes, consisting of a conjugated carbon chain linking cyclic end groups. In the ground state of such a molecule, the bonding highest occupied (HO) orbital is filled, and absorption of light promotes an electron to the lowest vacant (LV) antibonding orbital, usually in a $\pi \rightarrow \pi^*$ transition. The energy levels involved depend on molecular structure, and most of the relationships are now well understood.

A feature of major practical importance is the spectral location of the maximum of the dye absorption band, which is a measure of the energy difference between the HO and LV energy levels. The spectral characteristics, however, give no direct information on the absolute positions of either of the two levels involved. Such information is obtained either by theoretical calculations or experimentally, by photoemission measurements, or, more commonly, by electrochemical studies of dyes in solution.

A great many tests have been made in search of a correlation between sensitizing efficiency (i.e., RQE) and oxidation and/or reduction potentials. The result is that almost all effective sensitizing dyes for silver bromide have reduction potentials more negative than about -1.1 V relative to a silver–silver chloride electrode. This correlation is taken to indicate that the lowest unfilled electronic level (LV) of this group of dyes lies above the bottom of the silver bromide conduction band. The mechanism of the effective spectral sensitization process is therefore concluded to be the direct transfer of an electron from the excited state of an adsorbed sensitizing dye molecule into the silver halide conduction band, where it becomes indistinguishable from one formed by intrinsic absorption.

1.7 ELECTRONIC TRANSPORT

1.7.1 Electrons

Classic time-of-flight measurements have been employed with single crystal materials to measure electron drift mobility μ_D , for comparison with values of Hall mobility μ_H obtained from the photo-Hall effect (Brown, 1976; Evrard, 1984).

As related to the normal applications of the photographic process, it suffices to say that in high-quality single-crystal materials the room temperature electron drift mobility values agree with those for Hall mobility and are given along with effective mass values determined from cyclotron resonance in Table 1.2. The mobilities increase with decreasing temperature as expected from simple phonon-scattering theory.

Table 1.2 Transport Properties of Electronic Carriers in the Silver Halides

	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Polaron effective mass
Electrons		
AgCl	50	0.32
AgBr	60	0.288
Holes		
AgCl	10^{-2}	^a
AgBr	1	1.71, 0.79 ^b

^a Unmeasured owing to self-trapping.^b Double valued because of band anisotropy.

1.7.2 Holes

Silver Chloride

The low temperature transport properties of holes in the silver halides are markedly different from those of electrons. The situation is more clearly understood for the hole in AgCl, which at liquid helium temperature is self-trapped (Höhne and Stasiw, 1968; Toyozawa, 1961).

Electron spin resonance (ESR) studies (Höhne and Stasiw, 1968) have revealed that the carrier is localized on a silver ion and that the nearest-neighbor chloride ions are displaced in the tetragonal Jahn–Teller mode, as illustrated in Fig. 1.6.

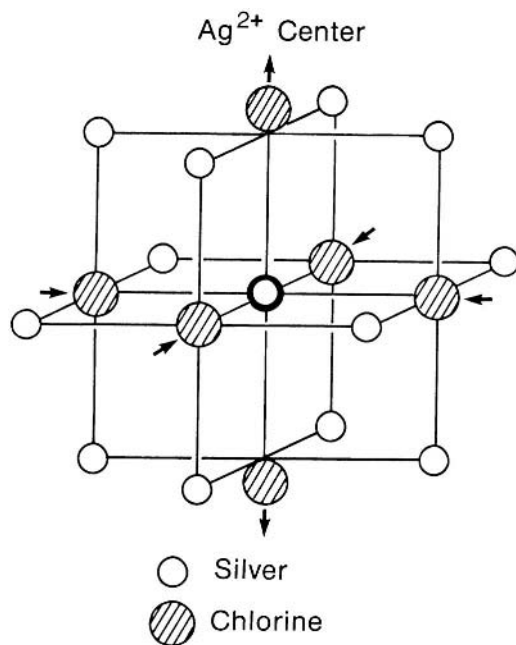


Figure 1.6 The Jahn–Teller distortion of the six chloride ions around a self-trapped hole (Ag²⁺) in silver chloride.

A broad optical absorption centered at 1.2 eV has been attributed to the optical excitation of the AgCl self-trapped hole center (Ulrich, 1970). The thermal ionization energy has been estimated (Laredo et al., 1983) as 0.12 eV, indicating that at room temperature the self-trapped state is transient only. Nevertheless, it is important enough to limit severely the drift mobility of the hole in silver chloride. Direct electrical measurements have not been successful, but indirect measurements of diffusion effects (Müller et al., 1970) give a room temperature mobility value of about $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, thus nearly four powers of 10 lower than that of the electron.

Silver Bromide

Studies show that in silver bromide the hole is not self-trapped at liquid helium temperature (Hodby, 1969). Nevertheless, the room temperature drift and Hall mobilities of the hole in this material are about $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, about 50 times lower than that of the electron, and exhibit a relatively steep negative temperature dependence, as shown in Fig. 1.7. Interpretations generally (Toyozaawa and Sumi, 1974) attribute these mobility characteristics also to the self-trapped state, which is regarded as metastable in the bromide salt but stable in the chloride. A weak photoinduced transient absorption centered at 0.88 eV has

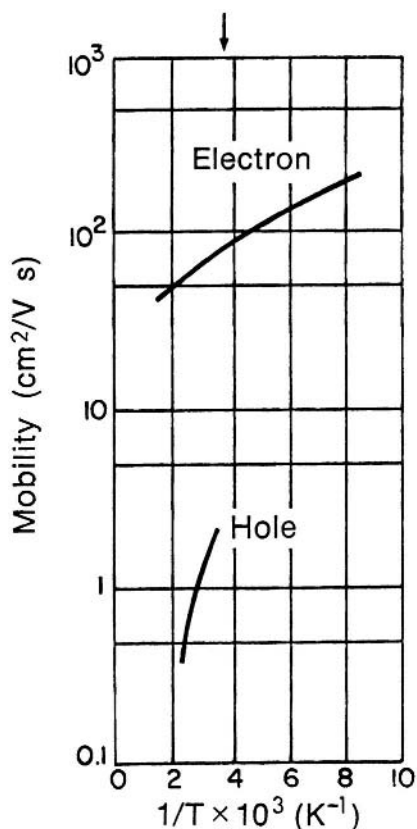


Figure 1.7 Comparison of electron and hole mobilities in silver bromide in the temperature range near room temperature.

been observed (Ulrich, 1970) at 20 K in AgBr and attributed to the metastable self-trapped hole, by analogy to the stable 1.2 eV absorption in AgCl.

1.8 CHARGED POINT DEFECTS

1.8.1 The Dielectric Constant

Electrostatically charged defect sites and ionic charge carriers play crucial roles in the photographic process, and the presence of these species is strongly influenced by the dielectric properties of the silver halide materials. Table 1.3 lists the room temperature values of the static ϵ_0 and high frequency ϵ_∞ dielectric constants of silver chloride and bromide (Lowndes, 1966; Lowndes and Martin, 1969) along with those of select alkali halides. It is clear that the values for the silver salts are considerably higher than those of the related alkali salts. Since electrostatic energies are related to the inverse square of the dielectric constant, and the charged-defect concentration depends on the formation energy in a Boltzmann-type factor, it follows that defects are present in far higher concentration in the silver halides than in many other ionic crystals.

The high ionic component (i.e., $\epsilon_0 - \epsilon_\infty$) of the silver halide dielectric constant is attributable to the particular electronic structure of the silver ion. Resonant coupling between the d- and s-electronic levels of the silver ion results in a prominent quadrupolar deformation mode (Bilz and Weber, 1984). Because the silver ion is not rigidly restrained to a spherical shape, the lattice of the silver halide crystals is unusually “soft” and particularly compliant to certain stress modes. Among those are the ionic displacements induced by electrostatic forces. Thus the high dielectric constants.

The quadrupolar deformability also strongly influences the static elastic constants and the lattice dynamics of the silver halides and the ionic transport properties as well.

1.8.2 Static Defects

The classic stationary charged defect is the surface kink site on the [200] face (Seitz, 1951), as illustrated in Fig. 1.8. The formal charge of such a site is $\pm e/2$ depending upon its occupancy by a cation or an anion (Amelinckx, 1979). A dislocation jog is the volume analogue of the surface kink, and the electrostatic formalism is precisely the same, although the energetics are modified because of the very different considerations of lattice strain.

Strictly analogous sites cannot be envisaged for the photographically important [111] surface of the silver halides. However, a [111] surface bounded by a perfect ionic plane has an effective charge of either plus or minus $e/2$ for each ion in that plane. Only for a boundary layer of exactly half the number of ions in a normal plane is charge neutral-

Table 1.3 Static (ϵ_0) and High-Frequency (ϵ_∞) Dielectric Constants of the Silver Halides and Selected Alkali Halides at Room Temperature

Constant	Halides				
	AgCl	AgBr	RbCl	RbBr	KBr
ϵ_0	11.15	12.5	4.92	4.86	4.90
ϵ_∞	3.92	4.62	2.18	2.34	2.36

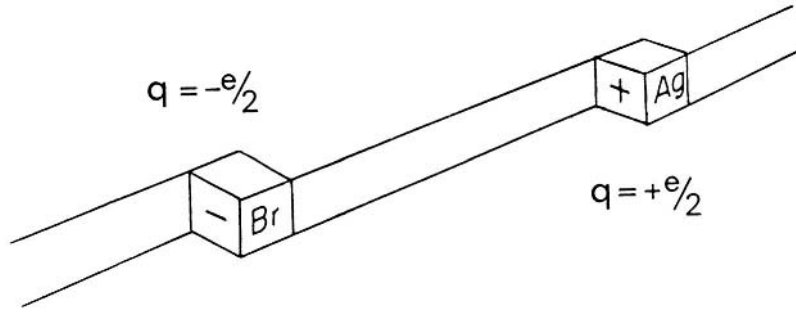


Figure 1.8 Negative and positive kink site structures on the [200] face of a cubic ionic crystal.

ity achieved. Rearrangement of half of the ions in a plane in register with the threefold symmetry of the underlying lattice is not straightforward, and some type of rather severe reconstruction is necessary (Hamilton and Brady, 1970). At best some statistical discontinuities are to be expected. Such sites will have formal partial electronic charges, as do the [200] kink sites, and can therefore be referred to as *kinklike* sites.

The Coulomb energy of these partially charged structural defects is particularly low in the silver halides owing to the high dielectric constants. They are therefore present in relatively high dynamic concentrations, and arguments can be and have been made that they play a major role in the photochemical processes of practical significance in these materials. They interact with mobile charge carriers, both electronic and ionic, and because of their nonintegral electrostatic charge impart unique properties to the centers so formed.

1.8.3 Intrinsic Frenkel Disorder

The dominant mobile ionic defects in the silver halides (Friauf, 1984) are of the Frenkel type on the cation sublattice (i.e., interstitial silver ions Ag_i^+ and silver ion vacancies V_{Ag}^-). These are illustrated in Fig. 1.9. Owing to the larger ionic radii, defects on the halide sublattice are many powers of 10 lower in concentration. The thermodynamic equilibrium is expressed by

$$n_F^2 = n_i n_v = 2N^2 \exp\left(-\frac{\Delta G_F}{kT}\right) \quad (1.9)$$

where n_i , n_v , and N are the volume concentrations of interstitials, vacancies, and lattice sites, and ΔG_F is the Gibbs free energy of formation of a Frenkel pair. The equilibrium intrinsic value of n_i and n_v is designated as n_F . Extensive studies of the thermodynamic quantities have been made by measurements of the temperature dependence of conductivity and radiotracer diffusion.

The conductivity σ_i is given by the expression

$$\sigma_i = (n_i \mu_i + n_v \mu_v) e \quad (1.10)$$

where μ_i and μ_v are the mobilities of the interstitials and vacancies.

Currently accepted values (Friauf, 1984) for the formation enthalpies and entropies in AgCl and AgBr are given in Table 1.4 along with the room temperature concentrations

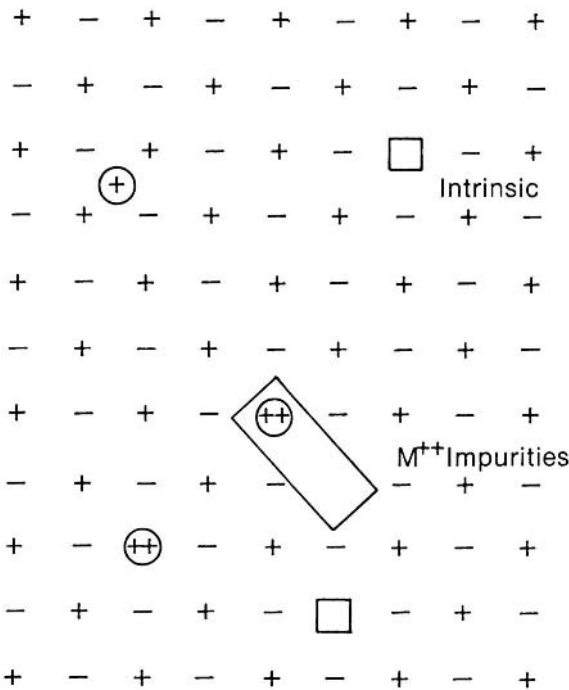


Figure 1.9 Schematic diagram of intrinsic and impurity-induced Frenkel disorder in a silver halide crystal. The diagram shows a [200] plane, but the interstitial silver ion is in fact displaced by $\frac{1}{4}$ [200] out of the plane.

of defects in each. Comparison with numbers given in Section 1.3.2 emphasizes that the concentration of ionic carriers is some 15 powers of 10 greater than that of electronic carriers in AgBr and 18 powers of 10 greater in AgCl.

1.8.4 Surface-Induced Defects

In addition to the classical Frenkel mechanism for pairwise formation of interstitials and vacancies, each of these point defects can be produced individually at a crystal surface of an extended internal defect (Hoyen, 1984). Kinklike sites on the surface or jogs on

Table 1.4 Thermodynamic Constants for Frenkel Disorder Formation in Silver Halides

Constant	Halides	
	AgCl	AgBr
Formation enthalpy, h_F (eV)	1.49 ± 0.021	1.163 ± 0.023
Formation entropy, S/k (e.u.)	11.13 ± 0.20	7.28 ± 0.58
Mol fraction defects at room temperature	4.92×10^{-11}	4.71×10^{-9}
Defect concentration, n_F at room temperature (cm^{-3})	1.15×10^{12}	9.80×10^{13}

Source: R. J. Friauf (1984).

dislocations are usually envisioned as the sources and sinks for silver ions in these extrinsic processes. From a simple thermodynamic cycle it follows that

$$\Delta G_F = \Delta G_i + \Delta G_v \quad (1.11)$$

where the three terms represent the Gibbs free energies for formation of a Frenkel pair, for formation of a silver ion interstitial at some defect site, and for formation of a silver ion vacancy at the complementary site. In general, ΔG_i and ΔG_v are unequal, and the more readily formed defect is produced in excess. This leaves the surface (or dislocation) with a nonzero charge and a diffuse space charge region of the opposite sign near the surface or around the dislocation.

The spatial distribution of defects within the space charge region may be derived by solution of the Poisson equation with appropriate boundary conditions, and thorough theoretical analyses of this situation have been made.

Because of the relatively large specific surface of the microcrystalline dispersions of photographic materials, the surface generation process has a dominant effect on the ionic defect concentrations, which may differ by two or more powers of 10 from those in the volume of macroscopic samples. Among the techniques used to explore these properties experimentally, the most common is a contactless measurement of conductivity by means of the frequency dependence of dielectric loss, applied directly to photographic coatings (Van Biesen, 1970). These measurements are supported by more conventional conductivity measurements on thin films of the pure or doped silver halide materials, and a very few direct investigations of the surface potential or the profile of the potential distribution near the surface.

Results consistently indicate that on silver bromide microcrystals or thin films, ΔG_i is less than ΔG_v , leaving the surface with a net negative charge, compensated by a corresponding excess concentration of subsurface interstitial silver ions, as much as two or three powers of 10 greater than the intrinsic value. From the concentrations given in Table 1.4, it is easily seen that in a photographic microcrystal of silver bromide with a typical volume of $0.1 \mu\text{m}^3$, there may be of the order 10^3 or more silver interstitials and on average far fewer than one silver ion vacancy.

Schematic diagrams of the defect concentration and electrostatic potential profiles are shown in Fig. 1.10. The most recent determinations (Hudson et al., 1987) of surface potential give a room temperature value for AgBr of about -0.1 V .

1.8.5 Impurity Effects

In impure materials or at reduced temperatures, the volume defect content can be determined by impurities. The most common controlling impurities are polyvalent metal ions, by which are introduced a corresponding concentration of silver vacancies (Fig. 1.9). Thus at low temperatures

$$[\text{M}^{2+}] \approx n_v \gg n_i \quad (1.12)$$

Less frequently, divalent anionic impurities can be present in excess concentrations such that the defect balance is dominated by the corresponding excess silver interstitials.

Divalent cations bind the corresponding silver vacancies in nearest-neighbor lattice sites with energies of 0.2 or 0.3 eV. Thus at room temperature, depending on the impurity level, there may be finite concentrations of both species: the electrically neutral bound impurity–vacancy pairs and the isolated charged impurities. Higher valent cations have

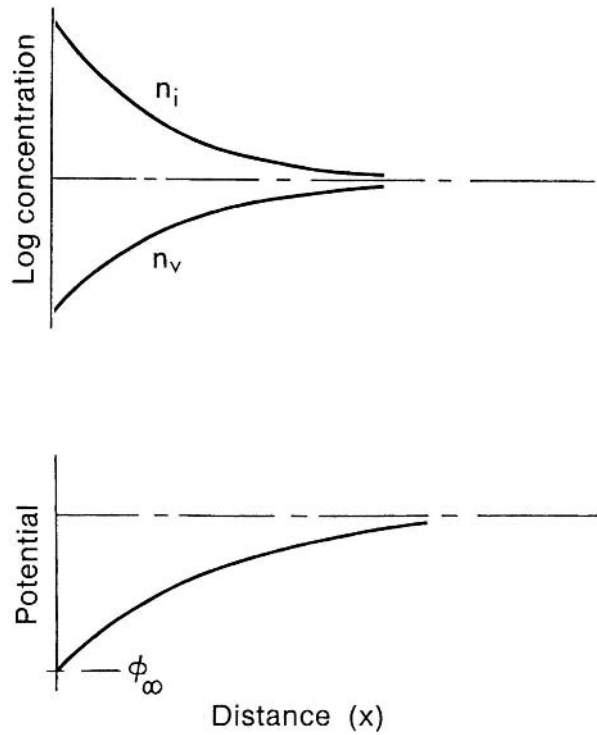


Figure 1.10 Schematic plot of interstitial and vacancy concentrations and electrostatic potential versus distance from a silver halide surface.

correspondingly higher numbers of charge-compensating silver vacancies, and it is generally true that the dissociation energy increases for removal of successive vacancies. The corresponding association considerations apply for the polyvalent anions and the compensating silver interstitials.

1.8.6 Transport

The mobility μ of an ionic carrier is quite simply derived as

$$\mu = \frac{el^2\nu_0}{6kT} \exp\left(-\frac{\Delta G_\mu}{kT}\right) \quad (1.13)$$

where l is the distance of an individual jump, ν_0 is the vibrational frequency of the defect, ΔG_μ is the Gibbs free energy of the jump, and the other symbols have their usual significance. The enthalpy and entropy contributions to ΔG_μ are also obtained from computer fitting of conductivity data. Values for both carriers determined in this way (Friauf, 1984) are given in Table 1.5, along with the corresponding room temperature mobilities, as obtained from Eq. (13). The room temperature mobility of the interstitial silver ion is many times higher than that of the vacancy in both materials. For this carrier the dominant mechanism for motion is the collinear interstitialcy jump. In this process a silver interstitial

Table 1.5 Thermodynamic Constants for Frenkel Defect Motion in Silver Halides

Constant	Halides	
	AgCl	AgBr
Vacancy/jump		
enthalpy (eV)	0.306 ± 0.008	0.325 ± 0.011
entropy (e.u.)	-0.65 ± 0.12	1.01 ± 0.28
Room temperature mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	6.1×10^{-7}	1.7×10^{-6}
Collinear interstitialcy jump		
enthalpy (eV)	0.018 ± 0.008	0.042 ± 0.011
entropy (e.u.)	-3.83 ± 0.12	-3.34 ± 0.28
Room temperature mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	3.3×10^{-3}	7.7×10^{-4}

Source: R. J. Friauf (1984).

moves by $\frac{1}{4}\langle 111 \rangle$ into a lattice position, the lattice silver ion being similarly displaced by $\frac{1}{4}\langle 111 \rangle$ into the adjacent interstitial position.

Both the silver ions involved in the interstitialcy jump (i.e., the initial interstitial and the lattice ion that is displaced) encounter identical energetic barriers as they pass through the center of the triad of halide ions between the interstitial and lattice sites. There is a sizable spatial overlap, and the low jump enthalpy is possible only because of the quadrupolar deformability of the silver ion, as discussed above.

The enthalpies for the collinear interstitialcy jumps, 0.02 eV in silver chloride and 0.04 eV in silver bromide, are unusually low, making these among the most highly conducting ionic solids known.

1.8.7 Shallow Electron States

Charged point defects provide electrostatic potential wells at which electronic carriers of the opposite charge are bound. The binding at such a center is reasonably approximated by simple effective mass theory (Stoneham, 1975). If q is the charge of the defect, m^* the effective mass of the carrier, and ϵ_0 the static dielectric constant of the medium, the total binding energy W is given by

$$W = -\frac{q^2 e^2 m^*}{2\hbar^2 \epsilon_0^2} \quad (1.14)$$

The carrier is bound in an orbit of radius r given by

$$r = \frac{\epsilon_0 \hbar^2}{q e m^*} \quad (1.15)$$

Calculated values of binding energy and orbital radius for electrons and holes at Coulomb centers in AgCl and AgBr are given in Table 1.6. The most significant feature to be seen is that, owing to the high dielectric constants, the binding energies are very small, comparable to room temperature thermal energy, and the orbital radii several lattice constants.

Table 1.6 Coulombic Levels in the Silver Halides from Effective Mass Theory

	Binding energy W (meV)	Orbital radius r (nm)
AgCl		
electron	39	1.53
hole ^a		
AgBr		
electron	23	2.39
hole	140	0.41

^a Input data not available.

Because of the difference in effective mass, the binding energies of shallow hole states are expected to be larger and the radii smaller. Calculated effective mass values for AgBr give a binding energy of 140 meV and an orbital radius of 4.1 Å. However, the effective mass model may be inapplicable in this range of radii. Because of the dominant self-trapping, input data for the hole in AgCl are not available.

These shallow electron states have been observed and identified at low temperature in both materials, as exposure-induced changes in absorption, luminescence, or conductivity in the infrared spectral region (Brandt and Brown, 1969; Sakuragi and Kanzaki, 1977). Experimental values of binding energies are about 24 meV in AgBr and 36 to 40 meV in AgCl, in remarkably good agreement with the predictions of effective mass theory.

Coulombic trapping centers in the silver halides are expected to have simple Langevin (1903) cross sections σ_c , with values given by the expression

$$\sigma_c = \frac{4\pi q\mu_m}{V_t\epsilon_0} \quad (1.16)$$

in which q is the charge of the trapping center, μ_m is the microscopic mobility of the carrier, V_t is its thermal velocity, and ϵ_0 is the static dielectric constant. Substitution of appropriate values for these quantities gives cross sections as indicated in Table 1.7 for electrons and holes in two halides.

Thus the shallow electron levels in both AgCl and AgBr appear to be simply explained. Any closed-shell, positively charged center provides a shallow potential well that will bind an electron in a diffuse orbit with a radius of several lattice spacings and a binding energy of some 20 to 40 meV. In spite of the weak binding, however, they have capture cross sections many times larger than lattice dimensions.

Table 1.7 Calculated Langevin Cross Sections σ_c for Charged Trapping Centers in the Silver Halides (nm)

	AgCl	AgBr
Electron	6.4×10^2	5.9×10^2
Hole		2×10^1

1.9 DEEP ELECTRON LEVELS

Certain localized centers, when incorporated within or on the surface of silver halide crystals, introduce specific electronic energy levels within the forbidden gap owing to the chemical energy levels of the particular centers. These levels can act as deep trapping levels for electrons and holes. Many chemical impurity effects have been studied in single-crystal samples (Eachus and Spoonhower, 1987). However, only a few types of foreign center play important roles in the photographic process, and others will not be treated here.

1.9.1 Two-Step Capture

Carriers are usually trapped at deep levels (i.e., with binding energy greater than a few times the phonon energy) by a two-step mechanism, as illustrated in Fig. 1.11 (Gibb et al., 1977). A direct one-step capture is unlikely because the moving carrier does not remain in the vicinity of a deep trapping center long enough for any of the various mechanisms for losing the required energy to occur with any significant probability. A shallow level at the same center, accessible by the emission of no more than a few phonons, is required if the carrier is to be localized long enough for this to occur. In charged centers, the Coulombic binding provides the initial shallow level. Under these conditions, the overall cross section of the deep center is given by

$$\sigma = \sigma_c \eta \quad (1.17)$$

where

$$\eta = \frac{\nu}{\nu + \nu_i} \quad (1.18)$$

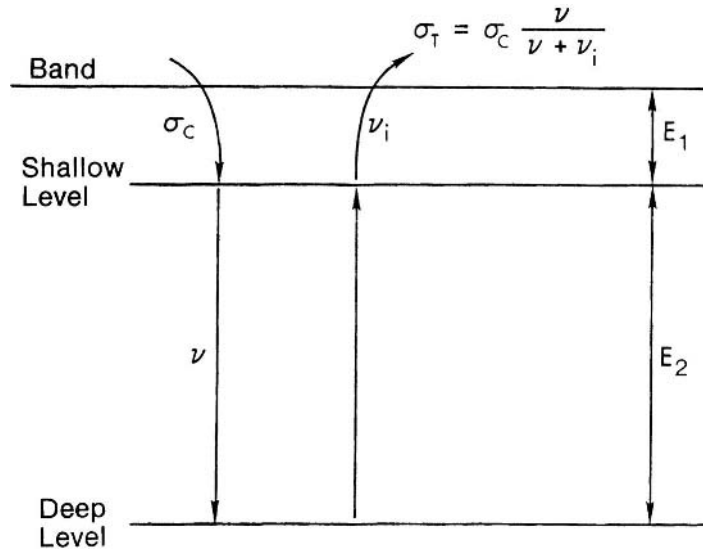


Figure 1.11 Schematic diagram of the transitions in the two-step trapping of a carrier at a deep level in silver halide. The overall cross section is reduced from the shallow level value σ_c by the factor $\eta = \nu/(\nu + \nu_i)$, the deexcitation efficiency, owing to the possibility of reionization to the band.

σ_c is the cross section for the shallow level (Section 1.8.7), v is the rate of deexcitation from the shallow level to the deep, and v_i is the ionization rate of the carrier from the shallow level to the band.

For the cross section to be large, not only must there be a shallow level but also η must approach unity. This can happen only if there is an efficient mechanism for the carrier in the shallow level to lose its excess energy in the deexcitation to the deep level. The deexcitation comes about by coupling to the host lattice, which relaxes locally and absorbs the energy as emitted phonons. The “soft” crystal lattice of the silver halides (Section 1.8.1) serves well in this regard.

The required lattice distortion is far smaller, the smaller the energy loss in a transition. Thus the deexcitation rate is increased significantly if there are one or more intermediate allowed levels between the shallow and deep ones shown in Fig. 1.11. This principle becomes important for the photographic process.

1.9.2 Halide Impurities

The impurity halide ions are one notable case of an impurity with practical importance. Owing to the differences in the electron affinities of the halogen atoms (Table 1.1), the higher atomic number halide ions, when substitutionally inserted in a silver halide of lower atomic number, introduce a filled level just above the valence band of the crystal. Thus I^- in AgBr and both I^- and Br^- in AgCl act as shallow hole traps. Evidence is that the binding energy of holes at these centers is in the range from 40 to 50 meV, thus similar to that expected from Coulombic defects. They do not constitute deep levels, and probably do not require the two-step trapping mechanism. Since the halide impurities simply replace the host halide ion with the same charge, they have no long-range attraction for holes and are expected to have capture cross sections of the order of lattice dimensions. Their location at kinklike defects, however, would confer the charge of the defect and increase the cross section. There is reason to expect that at the high iodide content used in many commercial materials there would be hopping of holes between impurity centers or even impurity banding.

1.9.3 Atomic Silver

A silver atom in or on the surface of a silver halide crystal has a singly occupied 5s electronic level near the middle of the silver halide forbidden gap. It is capable, therefore, of acting as a deep trap for either an electron or a hole. A neutral atom would be expected to have only a geometric cross section for either carrier, but Ag located at either a positive or a negative kinklike defect would have the larger Langevin cross section for the oppositely charged carrier and a much reduced cross section for the like-charged one. Once again, the charge also provides the shallow level for the two-step trapping process. Calculations show (Hamilton and Baetzold, 1981) that location at a charged site affects also the energy of the 5s level.

1.9.4 Silver/Gold Clusters

As the preceding discussions of photographic development have intimated, similar considerations apply for larger silver clusters as well. In the silver dimer, Ag_2 , the atomic 5s levels of the two atoms combine to give a filled bonding molecular orbital and an empty antibonding one. An electron from the conduction band could in principle be captured

into the antibonding orbital or a hole from the valence band to the bonding one. Vapor phase studies (Brown and Ginter, 1978) and model calculations (Hamilton and Baetzold, 1981) indicate that the energy difference between these two levels, the excitation energy of the dimer, is comparable with or perhaps even greater than the silver halide band gaps, so that it can be imagined that one or the other of these levels, but not both, would lie within the band gap of the host crystal. The calculations, in fact, indicate that this is the case and that the energy manifold is shifted by the electrostatic charge of the defect site at which the dimer resides so as to make it a favorable trap for an electron at a positive site or for a hole at a neutral or negative site but to be incapable of trapping the opposite carrier. Note that this is an energetic argument, over and above the difference in cross section, which affects the propensity in the same sense.

The silver trimer, Ag_3 , again is expected to have a singly occupied orbital near midgap, in addition to the filled bonding and empty antibonding orbitals. Larger clusters have an increasing number of intermediate filled and unfilled levels and should be able to interact in similar manner with electrons and holes. The Fermi energy of bulk silver lies some 1 to 1.2 eV below the conduction band edge. The same effects of charge on cross section are expected to apply. The increasing multiplicity of levels causes the deexcitation step to be more facile in larger clusters.

When the clusters contain one or more atoms of gold, the 6s electron has a larger ionization energy than does the 5s electron of silver (Table 1.1), and this has the effect of depressing the manifold of energy levels, both filled and unfilled. This is in keeping with interpretations of the effect of gold in the sensitization on the photochemical and development processes.

1.9.5 Silver/Gold Sulfide Centers

It has been indicated earlier that aggregates of silver/gold sulfide molecules play a principal role in achieving current sensitivity levels of photographic films. Bulk silver or gold sulfide is a semiconducting solid whose band gap is evidently some 1 to 1.5 eV, for it absorbs throughout the visible spectrum and luminesces in the red and near-infrared regions. The electronic structure of small clusters is unknown, but some indications from luminescence are that they have similar but somewhat smaller energy gaps.

Several different types of measurement (Hamilton et al., 1988; Sturmer et al., 1974; Gilman et al., 1987; Kellogg and Hodes, 1987) place the lowest vacant electronic level of these sensitizer centers some 0.2 to 0.3 eV below the silver bromide conduction band edge and therefore the filled level near midgap. Assuming that the charge affects the cross section for interaction with electronic carriers, as suggested for silver clusters, those aggregates located at positive kinklike defects should provide effective but reversible traps for electrons. This expectation is confirmed by measurements of photoconductivity (Kellogg, 1974).

1.9.6 Sulfide/Metal Centers

When a silver atom forms at charged sensitizer centers, the manifold of allowed energy levels includes the shallow Coulomb level, the 0.2 to 0.3 eV level arising from the sensitizing aggregate, and the deep level associated with the silver atom. A current proposal (Hamilton et al., 1988; Hamilton, 1988) for the mechanism of sensitization (Fig. 1.12) is that the presence of the sulfide level facilitates the deexcitation step of the electron capture at the silver atom, thus increasing the overall cross section at this center. This step in the

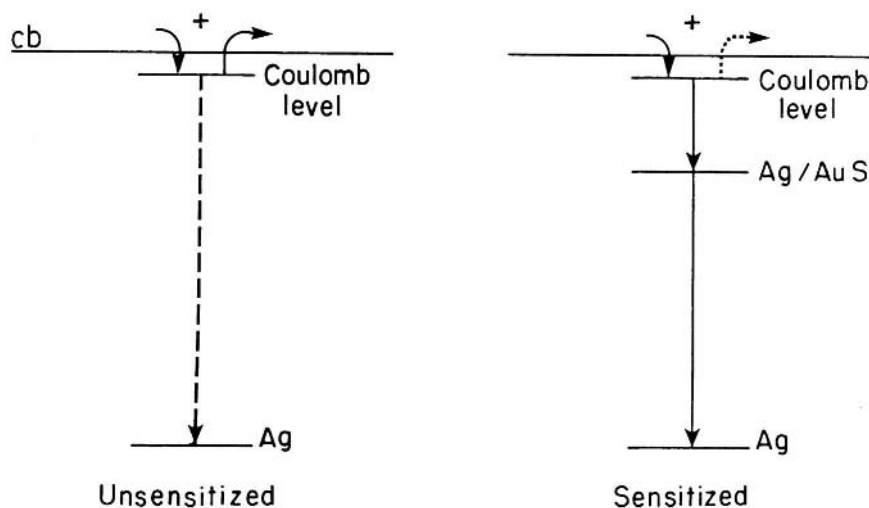


Figure 1.12 A proposed mechanism for the chemical sensitization effect. The intermediate level of the sensitizer material on the right-hand side improves the efficiency of deexcitation to the deep level, compared with the unsensitized case on the left.

process has been shown (Hamilton, 1983a, 1984) to be the limiting inefficiency in unsensitized emulsions. The deexcitation at larger silver clusters is promoted by the multiplicity of silver levels and therefore depends less on the presence of the sulfide level.

1.10 PHOTODECOMPOSITION

1.10.1 Silver

A key feature of the silver halides, which leads directly to their photochemical decomposition as opposed to the simple reversion of other photoconductors to the original state, is the combination of the photoconductive properties and the ionic defect structure. An electron in a localized state, even a shallow trapping level, has a likely possibility of capturing and combining with a mobile interstitial silver ion or a gold ion from the sensitizer. This extra ion, since it is not subject to the normal Madelung potential experienced by a lattice silver ion, has its vacant level well below the conduction band and normally also below the level in which the electron is trapped. In a successful combination, the electron loses the excess energy to the lattice and is deexcited into the metal valence s-level, forming what may be loosely termed a metal atom. Such a process was first clearly stated by Gurney and Mott (1938) and has come to be known (Mitchell, 1957) as the *Gurney–Mott principle*.

When the site at which the electron is trapped is adjacent to a positive kink or jog, the partial residual charge aids in the addition of the metal ion. Since the initial site has a partial positive charge, trapping of the electron does not render it electrically neutral but rather leaves it, for long-range effects, with a partial negative charge. Thus there is an electrostatic attraction for the mobile ion. Under this driving force, it can be shown (Berg, 1940; Hamilton and Brady, 1962) that the mean time for the ionic step corresponds roughly to the dielectric relaxation time of the crystal. For microcrystalline samples with

their high concentration of surface-generated interstitial silver ions, this time can be determined by dielectric loss measurements and is found to be of the order 10^{-7} s, depending on crystal size. In this case the ion just at the defect site is also not a normal lattice ion, and the electron must presumably be considered to be shared between it and the added metal ion. It may be that this is the manner in which the gold of the sensitization material becomes part of the metallic center formed.

After electron trapping at any defect-associated silver atom or cluster, the net charge again becomes negative by a partial charge, and the electrostatic driving force for capture of another silver ion is restored. The addition of this silver ion modifies the energy level scheme accordingly, once more reversing the odd-even character of the center.

Thus the repetition of the electronic and ionic steps in a strictly alternating sequence makes possible the continued growth of silver centers at partially charged defects, eventually producing clusters large enough to act as latent image centers. The importance of the unique effective fractionally charged character of kink-type and jog-type structural defects at every stage during this sequence is apparent.

1.10.2 Halogen

A complementary process applies to the formation of halogen. If a silver ion vacancy combines with a trapped hole center, the net effect is the loss of a lattice silver ion and conversion of the corresponding halide ion to a halogen atom. In emulsion grains, where the vacancy concentration is suppressed by the surface effect, the ionic process involved at a trapped hole center has been shown to be the ejection of an adjacent lattice silver ion into an interstitial position and its motion away from the center (Platikanova and Malinowski, 1978).

1.10.3 Reversibility of Atomic Species

Both the silver and the halogen atomic species are thermally reversible in the silver halides, decomposing by the reverse of the ionic steps by which they are formed and ionization of the then weakly bound electronic carriers into their respective electronic bands. This instability is a very significant feature distinguishing the silver halides from other ionic crystals such as alkali halides, in which trapped electron and hole centers of atomic dimensions are thermally stable at room temperature. It is this property, generally attributed to the high dielectric constants of these materials, that permits the extremely efficient concentration of the effect of the spatially dispersed absorption events into a localized photochemical change at one or a few centers per grain.

1.10.4 Nucleation and Growth

When the instability of the single silver atomic center is included, silver formation becomes a classic nucleation-and-growth process (Burton and Berg, 1946). It may be represented (Hamilton, 1984) by the diagram of Fig. 1.13, which emphasizes the reversibility of the initial interactions, the separate nucleation and growth stages, the regularity of the alternating electronic and ionic stages, and the reversal of charge, which provides an electrostatic driving force for each step. The nucleation-and-growth feature of the process is particularly effective in controlling photographic response.

Specifically, if photons arrive at any one crystallite slowly enough, each electron will be consumed individually by growth on the first nucleus formed. The simultaneous

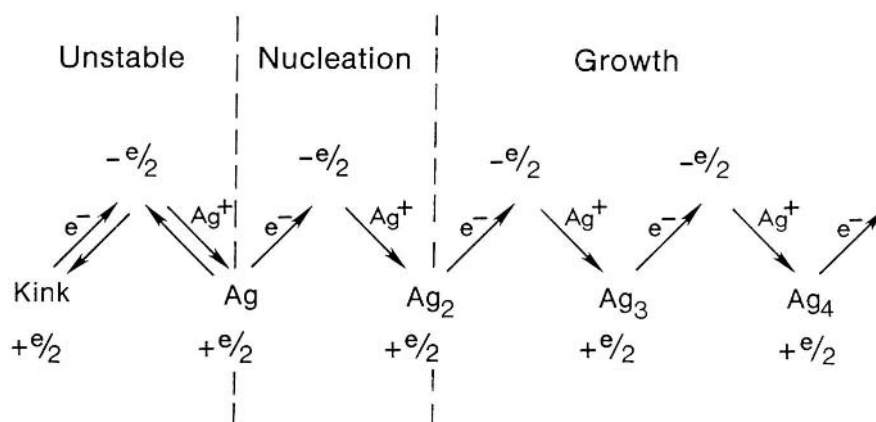


Figure 1.13 The steps in the growth of a silver cluster in silver halide, showing the nucleation-and-growth process, the alternating electronic and ionic steps, and the reversal of sign of the partial charges.

presence of two electrons, the condition necessary for a second nucleation event, never again occurs, and all silver is concentrated into a single cluster. Thus fully efficient concentration requires nothing more than the nucleation-and-growth process resulting from the instability of the single silver atom.

1.11 EFFICIENCY CONSIDERATIONS

The sequence depicted in Fig. 1.13 is a process that could lead to a cluster consisting of one silver or gold atom for each absorbed photon. The numerical analyses of quantum sensitivity and the minimum latent image size cited earlier, however, indicate otherwise. The most efficient photographic emulsions appear to require about 8 absorbed photons to produce a three-atom developable center. Clearly, the process is only about one-third to one-half as efficient as is theoretically possible.

1.11.1 Recombination

The principal residual inefficiency, and also the inefficiency addressed by chemical sensitization, has been shown (Hailstone et al., 1988) to be electron-hole recombination, which proceeds in competition with the reactions of Fig. 1.13.

In these materials direct band-to-band recombination is of negligible importance, being momentum-forbidden as a consequence of the indirect gap. Recombination of any consequence therefore occurs exclusively at lattice singularities, where first one carrier becomes localized, forming what may be termed a recombination center, and then the opposite carrier is also captured. The sequence forms some type of localized exciton, which then is deexcited by loss of its excess energy.

The lower diffusion velocity of the hole has the result that the principal recombination process is the capture of a free electron at a localized-hole center. The defect centers expected to provide recombination sites are the transient self-trapped hole centers, the isoelectronic iodide impurities (and bromide in silver chloride), negative kinklike physical defects, and iodide ions at such defects. Holes localized in the self-trapped states and at

isolated halide impurities have a full positive charge and the corresponding Langevin cross sections for subsequent electron capture, whereas holes at either bromide or iodide kinks would have only a partial positive charge. Their cross section for electron capture might be expected to be smaller, but only by perhaps a factor of 2 or so, as would those of partially charged silver centers. However, because the initial charge of species associated with these defect sites is negative, their cross section for the prior hole capture would be far greater than those of isoelectronic traps, and they might well dominate the recombination process.

The opposite process, the capture of a free hole at a trapped-electron center, is also charge favored but in practice less likely because the hole is so much more localized than the electron.

At cryogenic temperatures, a significant mechanism for deexcitation of the exciton so formed is luminescent emission. As the temperature is raised, however, the luminescence is totally quenched well below room temperature, owing to the dominance of a much more rapid thermally activated nonradiative decay.

1.11.2 The Symmetry Principle

If this type of interaction is the principal recombination channel, there is a basis for quantitatively rationalizing the observed approximately half-efficient formation of silver (Hamilton, 1982, 1983b). When two competing processes have equal 50% efficiency, it follows that they have equal rates. In the present case the two rate-determining steps are shown in Fig. 1.14. Both consist of the capture of an electron from the conduction band by a deep center with a positive charge. The initial cross section of each center is the Langevin value as determined by charge, and the deexcitation of both has near unit efficiency, at least in chemically sensitized emulsions (Hamilton, 1990). This provides a logical explanation for the near-equivalent quantum sensitivity limit of the best emulsions, even those

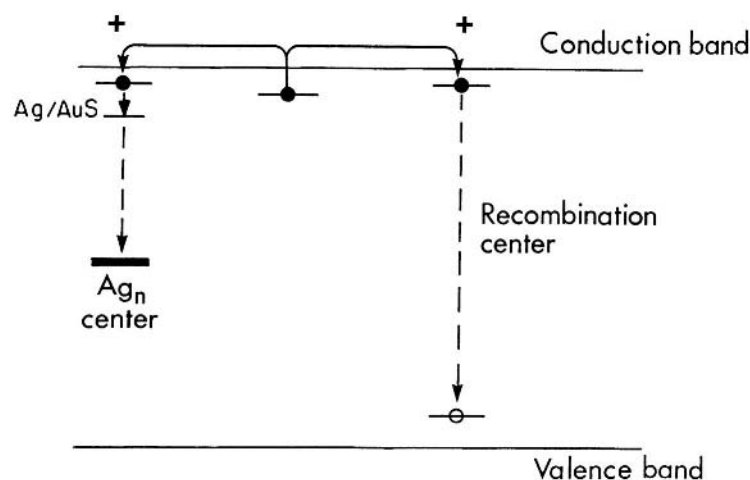


Figure 1.14 The symmetry of the competing steps that determine photographic sensitivity. The electron, in the course of being repeatedly trapped and released, encounters one or the other of the indicated positively charged centers.

from different sources. Their efficiencies fall short of the ultimate limits, but they lie at a secondary statistical limit set by the inherent symmetry of the competing processes.

1.11.3 Dye Holes

All of the discussions above have been cast in terms of recombination at localized hole centers in the silver halide crystal. Yet, as has been emphasized earlier, much of photography depends on electrons injected from sensitizing dyes with ground state energy levels well above the valence band of the crystal. Thus recombination must often occur by capture of a free electron at a dye-localized hole. The argument can be made that this does not significantly alter the points previously stated. If the dye molecule is originally electrostatically neutral or, by virtue of a preferred adsorption site, charged by $\pm e/2$, it will become a positively charged center after injection of the electron, and the same arguments about cross section for electron capture apply. The recombination then is completed when the captured electron is deexcited to the ground state level of the dye.

The similarity of photographic sensitivity in the intrinsic and dye-induced spectral region (i.e., RQE values near unity; see Section 1.6.2), argues strongly that the recombination probabilities are much the same regardless of whether the hole is localized at a crystal defect or a dye molecule. The quantitative aspects of the sensitivity argument presented above depend on the retention of holes in a state subject to recombination by electron capture with a cross section comparable to that of silver centers for a time long compared with the silver-forming steps.

1.12 SUMMARY

Several unique physical properties of the photographically important silver halides (i.e., silver bromide and silver chloride) are intimately involved in the workings of conventional photography. To a surprising degree, these properties can be ascribed to the presence of the 4d outer electron shell of the silver ion. This feature of the electronic structure distinguishes the halide salts of the Group 1B elements of the periodic table from those of the otherwise similar alkali metals.

Alkali halides and silver halides are both electronic insulators with relatively wide forbidden gaps separating the valence and conduction bands. In both types of material the conduction bands are derived from the first vacant s-level of the cation. In the alkali halides, the valence band is also simply related to the appropriate filled halogen p-level. In the silver halides, however, this halogen level is strongly hybridized with the nearly energetically coincident silver d-levels. Thus the valence band is broadened at the Brillouin zone boundary, giving the two silver salts much narrower indirect forbidden gaps of 2.68 eV in the bromide and 3.25 eV in the chloride. Although the population of thermal carriers is still negligible, this shifts the indirect absorption edge of the silver salts strikingly toward the visible part of the spectrum.

This aspect of the electronic structure also introduces a coupling between the d- and s-levels of the silver ion, making it much more easily deformable in a quadrupolar or football-shaped mode. This in turn has profound effects on many ionic and crystalline properties. The dielectric constants are high, as are the elastic compliances of the lattices; the formation energy of charged point defects is low, as is the binding energy of shallow electron states; and the enthalpy for motion of a charged interstitial cation is lower than in any other conventional ionic crystal.

All these features play a role in the photographic process. The sensitive salts are photodecomposed as photoconduction electrons, and mobile interstitial silver ions alternately collect at charged-defect sites to produce clusters of silver atoms. The unoccupied or singly occupied energy levels of the silver clusters provide deep traps for capture of electrons from the conduction band, provided it is possible to dispose of the excess energy to be deexcited to the deep level. The soft crystal lattice provides for strong electron–lattice coupling, which plays a strong part in the energy disposal.

Before the silver atoms begin to accumulate, however, only shallow electronic levels are available, and the earliest stages of the process are totally reversible. This produces in effect a conventional nucleation-and-growth process, which is capable of very efficient concentration of the silver into one or a few clusters.

The current sensitivity position of the best available photographic materials is close to but significantly below the theoretical limit. This position can be understood in terms of a statistically determined limit set by the symmetry of the forward, silver-producing step, on the one hand, and the competing recombination reaction, on the other.

The details of the positioning of the unfilled electronic levels of silver clusters of various size within the silver halide forbidden gap provide a rational explanation for discrimination in photographic development and for the size dependence of activation delays.

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2

Color-Forming Photographic Materials

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2.1 INTRODUCTION

2.1.1 The Three-Color System

This chapter reviews the major dye-forming materials that are used in color negative films and papers. For perspective, a brief overview is given of conventional photographic phenomena. More comprehensive reviews of color photographic systems are available (1–3) and can be examined for documentation of concepts that are not referenced in this chapter.

The photographic system is used to capture the spatial and spectral distributions of light so that they can be stored, transmitted, and viewed at a future time. The spatial information is captured through the use of lenses, which focus light from points in the scene to points in the film plane. The spectral information is a continuous distribution of visible wavelengths from the scene, which is the difference between the illuminant spectrum and light that is adsorbed or diffracted by the object within a scene.

Fortunately, a high-quality photographic system does not have to capture the continuous distribution of visible wavelengths from a scene because human eyes are not analog receptors of continuous visible radiation. Retinas have cones with three receptors that absorb light in the violet-blue (ca. 400–500 nm), blue-green (ca. 450–610 nm), and green-red (500–700 nm) regions (4). The three optic signals provide human brains with data that are perceived as color (5)

Because human brains convert analog information in colored light into signals in three optic channels, a high-quality photographic system can be constructed by conversion of continuous wavelengths of light into images in three records of different color. This knowledge led to the invention of the integrated tripack for conventional films and papers, in which the three-color recording and reproducing records are stacked on top of one

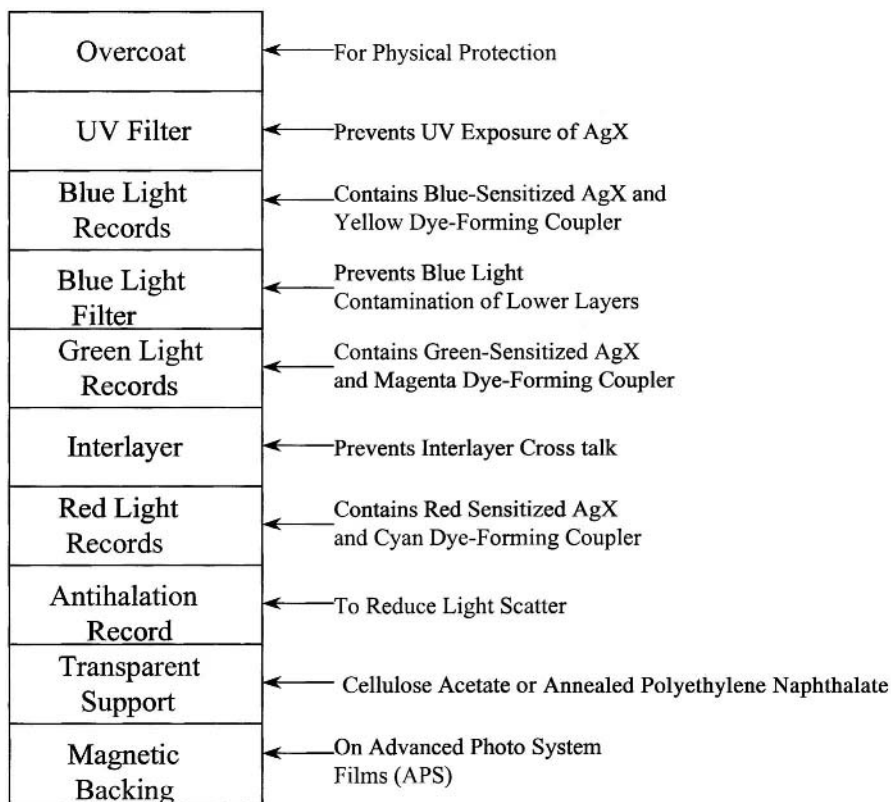
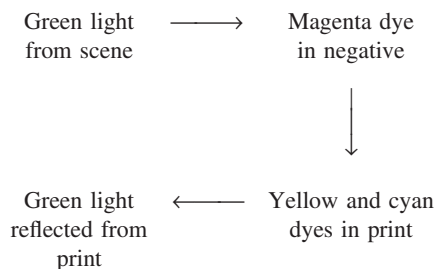


Figure 2.1 Structure of a typical color negative film.

another (see Fig. 2.1) (6). In such systems, the three subtractive primary dyes are generated in processing (cyan, magenta, and yellow, each of which modulates one of the additive primaries, red, green, and blue). Before processing, each color record of the tripack stores information from the scene in the form of a “latent” silver image that is capable of catalyzing the formation of the visible dyes, which are the major subject of this chapter. Reddish light of 600–700 nm gives a cyan dye, greenish light of 500–600 nm gives a magenta dye, and bluish light of 400–500 nm gives a yellow dye. This negative film image is used as a mask between a printer illuminant and a photographic paper that has similar negative-working dye chemistry. The end result is a positive colored image that reflects from the photographic color print paper.



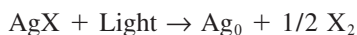
This two-stage negative-negative system has enjoyed widespread use even though it is complex, because color films can be constructed with very wide latitudes in sensitivity to different light intensities. Therefore color negative films can be used in a wide range of situations, from low to high light intensities, and from still images to snapshots of kinetic images with fast shutter speeds. When low light levels expose the negative, the exposure times of the printer are lessened to deliver moderate light exposures to the paper prints. When high light levels generate large amounts of dyes in the negatives, greater printer exposures times are used, also to deliver moderate light exposures to the print materials.

So-called reversal or single-stage systems such as Ektachrome film faithfully map specific exposures from a scene to specific light transmission through the slide medium, yielding a positive image. If such single-stage films are under- or overexposed, these materials yield correspondingly dark or light projected images.

Before describing the classes of color-forming materials used in color negative films, it is useful to review the major sequential chain of events that converts scene light to recorded dye in the negative. Knowledge of these events is basic to appreciation of photographic chemistry and underscores the importance of the couplers or dye-forming materials, which form the detail of this chapter.

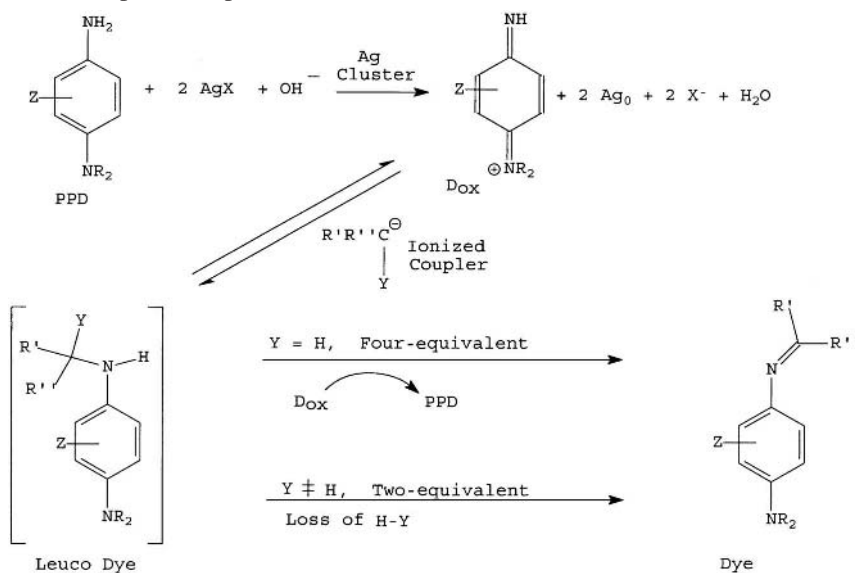
2.1.2 The Photographic Chain of Information

Most simply, wherever light from the scene illuminates a silver halide crystal, that light generates a silver atom cluster called the latent image. The overall elementary chemistry of this process is



The result is a photochemical reaction to effect a disproportionation: Ag^+ goes to Ag_0 and X^- goes to X_0 (as bromine gas in the case of $\text{X} = \text{Br}$). Silver atom clusters of only several atoms may be thermally unstable or subject to oxidation by ambient oxidants. Therefore a minimum threshold of light must impinge on the film to store scene information.

The next two stages of the imaging chain occur when the film is processed during the development step.



In the first stage, only those silver halide crystals with a stable silver atom cluster are reduced by the color developer, a substituted paraphenylenediamine (PPD), because the silver atoms are a miniature metallic electrode on which the oxidation–reduction preferentially takes place. As the redox reaction proceeds, further elemental silver is formed, and the reaction becomes autocatalytic. The purpose of this reaction is to transform the original miniscule latent image into an amplified signal of oxidized developer (D_{ox}). In the second stage, the highly electrophilic D_{ox} cation reacts with a dye-forming material or “coupler,” to form first an unstable leuco “colorless” dye and then the stable image dye.

As the scheme shows, there are two types of couplers, depending on whether Y is hydrogen or an electronegative leaving group. Examples of leaving groups are halides, or fragments with a nitrogen, oxygen, or sulfur atom attachment. When Y is hydrogen, a cross-oxidation of the leuco dye with a second molecule of D_{ox} occurs to generate the image dye. When Y is a good leaving group, a simple elimination of H-Y takes place to convert the leuco dye into the image dye. The terms “four-equivalent” and “two-equivalent” in the scheme refer to the change in oxidation state as the two classes of couplers are transformed to dyes. These are the same as the number of silver ions that are stoichiometrically reduced to silver metal when one mole of dye is formed.

Following the development or dye-forming step, the silver metal formed in the process is reconverted to a silver salt by an oxidant or “bleach,” so called because it removes the black silver metal. Then, usually in another process step, the silver salt is solubilized and removed by a silver complexing agent known as a “fix,” leaving only the stable or fixed dye image.

2.1.3 The Integrated Tripack

In a typical color negative film, the uppermost layers contain silver halide sensitized to blue light and a yellow dye-forming coupler. The middle layers contain green-sensitized silver halide and a magenta dye-forming coupler, and the bottom image-forming layers contain red-sensitized silver halide with a cyan dye-forming coupler. The blue-sensitized layer is typically overcoated with a layer to remove ultraviolet light. A blue-light filter is placed between the blue and green records because the silver halide in the lower layers retains its native sensitivity to blue light. The couplers themselves are often dissolved in high boiling organic media called coupler solvents. When the mixture is dispersed in the aqueous gelatin matrix, the dissolving property of the coupler solvent confers chemical reactivity to the couplers. Figure 2.1 (shown previously) gives a schematic of a typical color negative film.

The materials in film are related to their function. The main materials are the so-called “emulsions” of silver halides, their adsorbed sensitizing dyes, and the couplers. Necessary infrastructure includes the polymeric gelatin phase in which the silver halide and coupler are suspended and the flexible support (usually cellulose acetate, though polyethylene 2,6-naphthalene dicarboxylate is used for the Advanced Photo System films). Additional classes of materials include coating aids (that give coatings without bubbles, streaks, or other defects), scavengers of D_{ox} (that are placed between imaging layers to prevent cross talk among sublayers), and antihalation dyes (that prevent internally reflected light within the film from exposing silver halide grains). Also, the film contains abrasion resistant materials.

2.2 IMAGE COUPLERS

2.2.1 Characteristics of Image Couplers

Image couplers are the premier organic materials in color films. The function of these couplers is to convert faithfully the fleeting color information carried by D_{ox} into the

permanent storage in dyes. Couplers, therefore, are ionizable and potentially nucleophilic materials that have the all-important ability to form a colored azomethine-containing product. The azomethine group is the link between the developer and coupler halves.

The coupling reaction links an electron-rich moiety with an electron-poor moiety. The link hybridizes the highest occupied molecular orbital (HOMO) of the oxidized developer with the lowest unoccupied molecular orbital (LUMO) of the ionized coupler, which generates a product with a relatively low-energy transition in the visible region (a dye). The different hues of the visible dyes are determined in part by the LUMO levels of the coupler moieties and the conformations of the dyes.

This description suggests that molecular orbital calculations might be useful in the search for couplers with desired dye hues. However, computations of λ -max have not always been accurate, in part because of the nature of the π - π^* transition (7). The transition involves charge transfer from the paraphenylenediamine HOMO part of the dye to the coupler LUMO part. Such a transition has a large transition dipole moment and a variable solvent effect. Computations of solvent effects, still in their infancy, account for only the bulk dielectric effect of the medium.

Couplers have three primary chemical properties of interest (along with other important factors such as manufacturing cost, coupler and dye stability, and environmental benignancy). The primary properties are

The pK_a or acidity of the coupler

The k_c or nucleophilicity of the coupler at the processing pH, e.g., pH 10 for many color negative and paper processes

The visible absorption band of the resulting dye

pK_a is important because most neutral couplers are relatively unreactive to D_{ox} . To be reactive, couplers need to be nucleophilic, and this is achieved by ionization. For ionization, their pK_a s in dispersion are optimally near, or less than, the pH of the developer processing solution.

For water-insoluble couplers, there are several methods for determining the pK_a s. One is to measure the pK_a in micelle media, such as aqueous Triton X-100. These pK_a s are approximations to all-aqueous pK_a s. Another is to measure the $pH_{1/2}$ (or pH for half ionization) in liquid dispersion media, such as a 1:2 ratio of coupler:tri-tolylphosphate coupler solvent with gelatin and a surfactant. Such values are approximations to in-film half-ionization points and are typically several units higher in value than pK_a s measured in aqueous micelle media. Also, when extraneous absorptions and light diffraction can be tolerated, spectral measurement of in-film $pH_{1/2}$ s are sometimes possible.

Partial (or complete) coupler ionization at a processing pH of 10 is not sufficient for reactivity. The resulting anion needs to have reactivity toward D_{ox} (8). This feature is tracked by the rate constant, k_c^- , of the fully ionized coupler anion. For some series of couplers, there is a relationship between the pK_a s of the couplers and their $\log k_c^-$ s. As might be expected, as the pK_a increases, the coupler anion becomes more reactive, and k_c^- increases (9). Therefore there is often an optimum pK_a near the processing pH (e.g., 10). If substituent changes were to increase the pK_a much above 10, the coupler would not be ionized sufficiently for reaction. If the pK_a were much lower than the processing pH, the coupler anion would have a reduced nucleophilicity.

The last major requirement is a useful visible absorption band for the dye. It is easily appreciated that the hue of the dye in the film must appropriately control light transmission. Hue encompasses not only the λ -max of the absorption but also the shape of the absorption band. For some dyes, the absorption band will be too broad in shape, and the challenge

is to narrow or “sharpen up” the band. Theoretical considerations are of marginal use in this research effort, because band broadness relates to the number of dye conformations that are present, dye aggregate formation, and flexibility of the dye in its ground and excited states. Besides hue, there is also covering power, which is defined as the amount of density delivered by a unit amount of dye per unit area in the film. Covering power has many subtleties, but a major factor is the extinction coefficient, or oscillator strength, of the absorption.

2.2.2 A Quantitative Description of the Imaging Chain

A simple model that connects observed density (D) in film negatives to mechanistic quantities is

$$D = Ag \left(\frac{1}{2} \right) \left(\frac{1}{S} \right) (F_{\text{Dye}})(C_p) \quad (2.1)$$

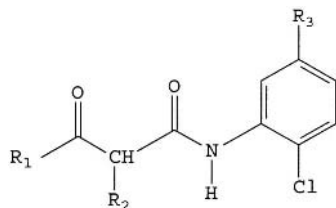
Here, Ag is the mole per meter squared of the silver that is formed, which can be independently determined in a process that excludes the silver bleaching step. As described previously, D_{ox} is stoichiometrically one-half the amount of silver and is the reason for the fraction $(1/2)$. If all the D_{ox} were converted to dye, the amount of dye would be $Ag/2S$, where S is the stoichiometry of D_{ox} that is theoretically needed to produce one mole of dye. The product of 2 times S is the equivalency of the coupler, which is the moles of silver that stoichiometrically accompany the formation of one mole of dye. The quantity F_{Dye} is the fractional amount of theoretically possible dye that could be formed from the D_{ox} . Not all D_{ox} goes to dye, because of side reactions, such as the reaction of D_{ox} with sulfite in the developer. Lastly, C_p is the covering power of dye that relates the density of a dye deposit to its amount. The units of C_p are square meters per mole.

The equation is both qualitatively and quantitatively useful because it illustrates the chain of quantities that give dye density: silver and D_{ox} , stoichiometric dye, efficiency of dye formation, and covering power. Different imaging chemistries usually do not have a large impact on the silver and D_{ox} terms. Different coupler chemistries impact the density mainly through the stoichiometry factor S , through the influence of pK_a and coupler reactivity on the term F_{Dye} , and through the molar extinction coefficient of the dye in C_p .

2.2.3 Yellow Image Couplers

Conventional Yellow Image Couplers

One generic structure dominates the yellow couplers that are in use, that of the beta-ketocarboxamides,

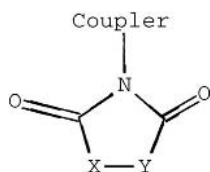


where R_2 is a coupling-off group (COG) that is eliminated after reaction with D_{ox} . Of the three coupler classes, the yellow dye formers are the only ones that are acyclic. The resulting dyes are not totally planar, which contributes to their short absorption of blue light and leads to a lower extinction coefficient.

Typically, R_1 is either t-butyl or aromatic. The quaternary carbon of the t-butyl group is desired for light stability of the dye (10), and these couplers are therefore widely used in color paper materials. Even though these dyes have greater light stability (11), the couplers are not generally as reactive as when R_1 is aromatic (12). A way to improve the reactivity of the couplers with a t-butyl group is to “tie” two of the methyl groups into a cyclopropane ring (13). This preserves the quaternary carbon that is good for light stability, and it reduces the steric hindrance.

A variety of COGs have been used at position R_2 . The need is to provide a substituent that is electronegative enough to be a good leaving group, so that the intermediate leuco dye readily forms the yellow dye. However, if the electron withdrawal is too great, then the coupler anion is less nucleophilic toward oxidized developer.

One good compromise for R_2 is the N-1, 5-membered heterocyclic 2,5-diones.



Various combinations of X and Y include the oxazolidine diones ($X = O$, $Y = C$) (14), triazolidine diones ($X = Y = N$) (15), and imidazolidine diones ($X = N$, $Y = C$) (16).

The role of R_3 is usually as a ballast group to hold the coupler in its coated layer, although ballasting can also be put into an R_1 aryl group. Various substituents can be used for R_3 including carbamoyl, ester, and sulfamoyl.

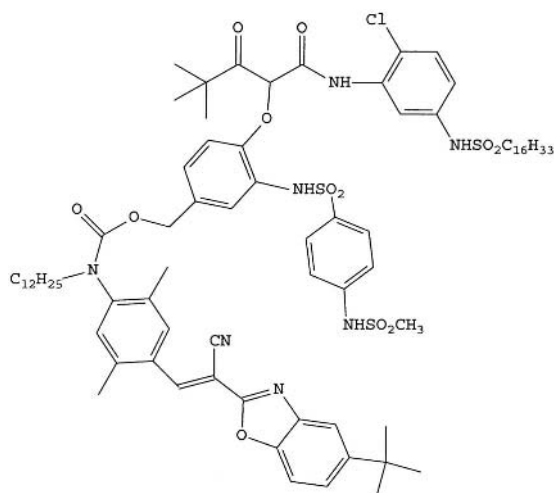
The most often used group in the ortho anilino position is a chloro group as shown in the general structure. One property is that the chloro group increases the extinction coefficient of the dye by almost 40% (17).

The Challenge of High Extinction Coefficients for Yellow Dyes

An interesting challenge in yellow coupler chemistry is to improve the low extinction coefficients of the acyclic beta-keto amides. As mentioned earlier, the nonplanarity of yellow dyes results in a reduced extinction coefficient (typically 15,000 to 21,000 L/mol-cm) relative to cyan and magenta dyes ($>30,000$). This means that more silver halide and coupler dispersions need to be coated in yellow layers than in other layers, in order to match their densities with neutral scene exposures.

Two approaches are evolving to achieve higher dye extinctions. The more modest approach is to investigate novel R_1 groups. When R_1 is t-butyl, the extinctions are between 15,000 and 17,000, whereas when R_1 is aryl, the extinctions are between 19,000 and 22,000. Indoliny substituents for R_1 have been found to give extinctions of between 24,000 and 25,000, and these higher extinctions probably relate in part to the dihedral angle between the beta carbonyl and coupling site carbon (18).

A second, ingenious approach utilizes a preformed but shifted yellow dye as the COG (19,20).

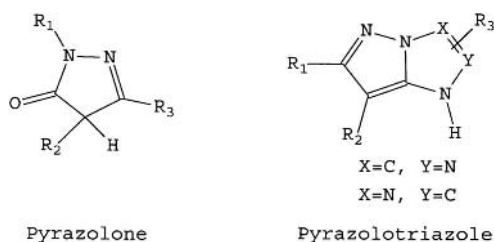


A conventional yellow coupler releases a COG that forms a quinone methide (see discussion of quinone methides in Section 2.4.6). Sequentially, the quinone methide releases a carbamic acid that decarboxylates to give a second yellow dye. In its carbamate form, the second yellow dye hue is shifted hypsochromically mostly out of the visible region. Coupling produces two molecules of dye. The conventional yellow dye has an extinction of ca. 15,000. The dye that is released has an extinction of ca. 50,000. The sum is 65,000, which is truly a breakthrough. With use of these materials, the coupler and silver halide laydowns in the film can be drastically reduced.

2.2.4 Magenta Image Couplers

Two Major Classes of Magenta Image Couplers

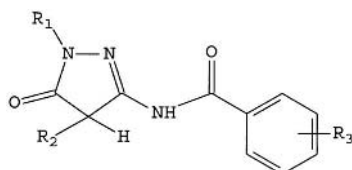
There are two major classes of magenta image couplers, the pyrazolones and the pyrazolotriazoles.



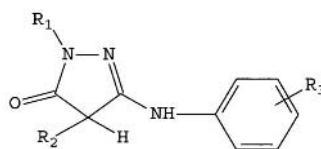
These classes are structurally quite different as well as being different photographically. The pyrazolones have been known since the 1930s (21), while the pyrazolotriazoles were identified in the 1970s (22). As a class, the pyrazolones were more difficult to convert into successful two-equivalent couplers and existed for years as only four-equivalent couplers, whereas the 7-chloropyrazolotriazoles ($R_2 = \text{Cl}$) were readily available once routes to these heterocycles became available.

Pyrazolone Magenta Image Couplers

There are two subclasses of pyrazolones, which are the C-4 arylcarbamoyl and anilino materials, respectively, and are shown below.



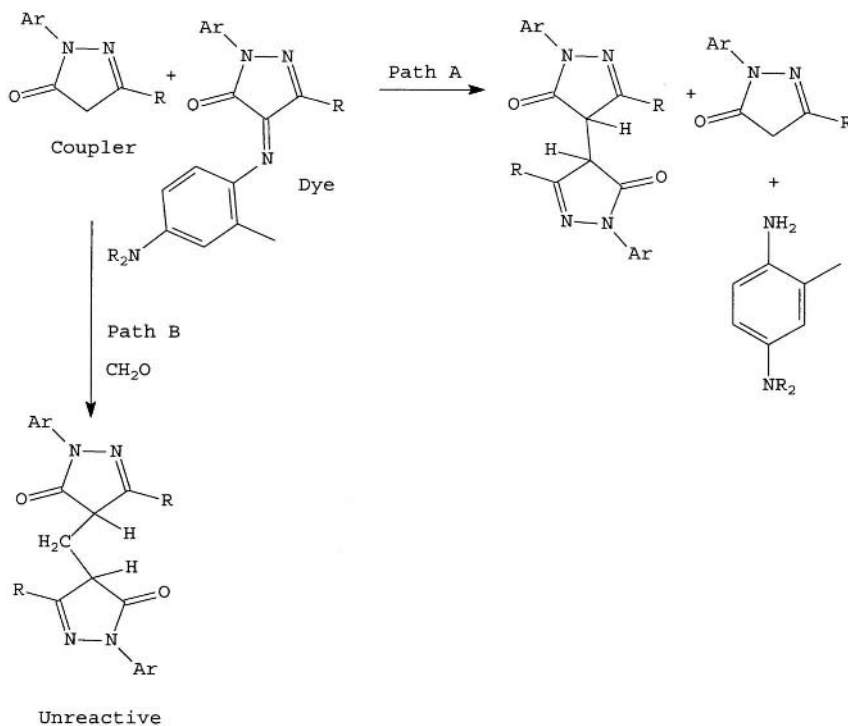
Arylcarbamoylpyrazolone



Anilinopyrazolone

By far the most prevalent R_1 group is the 2,4,6-trichlorophenyl group. Higher chlorinated phenyls (23) have also been used, but the use of highly chlorinated materials can pose environmental concerns.

Three common R_2 groups have been used. The four-equivalent couplers with $R_2 = H$ are active materials toward oxidized developer, but a reaction between the coupler and its dye can lead to dye loss during storage of the negative. This phenomenon was studied in solution by Vittum and Duennebier (24) with the finding of some amazing chemistry. The end products formed from the dye are the starting coupler and paraphenylenediamine (Path A). This is formally a four-electron reduction that splits the azomethine double bond. The source of the electrons (and protons) are four unreacted pyrazolone couplers that oxidize and combine to form two moles of a bis-pyrazolone. An implied intermediate in the reaction is the leuco dye.



These findings explain why fade occurs mainly in the lower density “toe” regions of low green exposure where excess coupler is present as the reductant. If excess coupler is destroyed by postprocess treatment of the film with a reagent like formaldehyde (which makes a bis-methylene pyrazolone by an aldol-elimination-addition process, Path B), then the fade process is eliminated.

Another way to avoid the dye loss is to use two-equivalent pyrazolones with a COG. Much research has been done to produce two-equivalent materials with a leaving group at C-5. There are four potential classes of useful leaving groups: halides, oxy-, nitrogen-, and sulfur-linked materials. All have their limitations, but the one that has been most successful is the arylthio class of coupling-off groups (25). In order for the released thiols not to interfere with silver development, the COG is typically ballasted so that the arylthiol stays in the oil droplet until it is oxidized to its final disulfide product by oxidized developer. Because of the consumption of an extra mole of oxidized developer to form the disulfide, pyrazolones with arylthio COGs do not effectively function as true two-equivalent couplers.

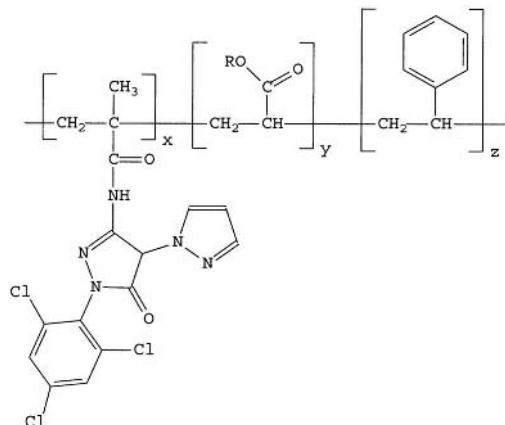
Another class of COG on pyrazolone image couplers is the pyrazolo group (26). Among the various nitrogen heterocycles, the pyrazolo COG provides the right amount of electron withdrawal to be a good leaving group, while not lowering the nucleophilicity of the coupler anion toward oxidized developer.

The choice of R_3 depends on the subclass of pyrazolone. With the C-4 arylcarbamoyl materials, an o-chloro is seldom used in the aryl group (27). A standard ballast is typically substituted in the meta position. With the C-4 anilino materials, an o-chloro is usually used to get the proper hue along with meta ballasting (28).

While the C-4 arylcarbamoyl materials are active couplers, the anilino materials are even more reactive with oxidized developer, because the more electron donating anilino raises both the pK_a and the coupling rate constant (29). If the pK_a (or $pH_{1/2}$) of the coupler were much above 10, there might not be an advantage to this scenario because there would be less of a more nucleophilic coupler anion with the possibility of no net benefit. But the anilino pK_a s are near 10, so these couplers enjoy high ionization at pH 10 along with high nucleophilicity.

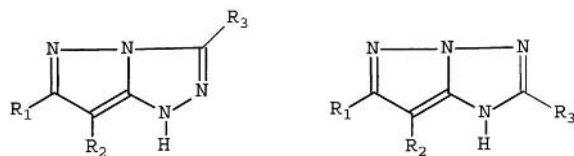
Another property of the anilino pyrazolones is their greater resistance to formaldehyde. Formaldehyde is a ubiquitous pollutant that can destroy pyrazolones in film by forming an unreactive methylene-bis-coupler at the coupling site (the same reaction that can be used post-process to destroy excess coupler; see Path B in the above scheme). Perhaps the lower pK_a s of the carbamoyl pyrazolones produce greater concentrations of coupler anion that react with formaldehyde.

A major exception to the use of monomeric coupling materials is the polymeric magenta couplers, which are intrinsically ballasted by attaching a pyrazolone nucleus to a copolymer of propene, butylacrylate, and styrene (30). These novel couplers are also used in tandem with a pyrazolo COG for efficient use of oxidized developer. To achieve the correct hue of the dye, a carbamoyl link is used between the pyrazolone ring at C-4 and the polymer.



Pyrazolotriazole Image Couplers

Pyrazolotriazoles also have two important subclasses shown below.



There are two big appeals that these couplers enjoy. First, their magenta dyes have less unwanted blue absorptions (ideal magenta dyes should absorb in the green region only). Unwanted absorption of the dyes can be compensated by the use of colored masking couplers (see below). Such technology cannot be used in color paper where white backgrounds are needed, so pyrazolotriazole couplers are very valuable for imaging the green information in prints.

Second, these couplers are almost always used as efficient two-equivalent materials with a simple chloro COG at R₂, which also addresses the high pH_{1/2}s that are usually well above 10 in liquid dispersions. Using a chloro COG lowers the pH_{1/2} closer to 10, and this gives more activity to the coupling reaction.

Another way to improve ionization of these high pH_{1/2} pyrazolotriazoles is to include, usually in the ballast, a carboxylic acid, phenol, sulfonamide, or other group that is capable of ionizing below or near pH 10. This ionization is believed to raise the dielectric constant of the organic phase, perhaps by pulling water into the dispersion droplet. This effect serves to lower the pH_{1/2} of pyrazolotriazole couplers.

The nature of the R₁ substituent at C-6 depends on the use. In products that do not have to endure the stress of dye light stability, such as color negative films, a simple methyl group is usually used, providing reactive couplers. However, since the pyrazolotriazole dyes, particularly those represented by the first structure above, are less light stable than pyrazolone dyes, their use in output products such as color print paper requires a sterically large group in the C-6 position (31).

The reason a group like t-butyl enhances the light stability of a pyrazolotriazole dye is complex. Pyrazolotriazole dyes typically aggregate in the oil droplet dispersions, and it is these aggregates that are particularly photosensitive toward bleaching (32). The t-butyl group is thought to disrupt partially the aggregation of the dyes.

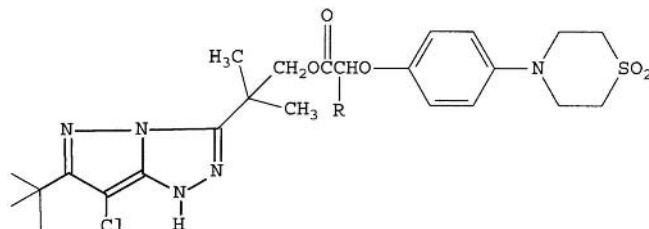
Use of the t-butyl group does not come without a price, however. Its steric bulk dramatically lowers the coupling rate, so that such materials cannot be used with high-competition sulfite-containing developer formulations that are typically used in color negative processing. Fortunately, developers for color papers need not be formulated as high in competition, so these t-butyl substituted materials can be used there for enhanced dye light stability.

For R₃, an electrically neutral alkyl-like group provides the proper hue of the dye for most photographic uses (33). A large variety of linking groups further down the R₃ substituent chain and different ballast groups have been used. In the last decade, 2-arylp-razolotriazoles have been found to have higher dye extinction and narrower bandwidth dyes (34).

Pursuit of Further Dye Light Stability for Pyrazolotriazoles

An area of active research has been to enhance the steric effect at C-3, just as has been done at C-6 with the t-butyl group. For example, the coupler below has a 6-t-butyl group,

a 3-quaternary carbon atom, and on the end of the ballast chain, a group said to impart further light stabilization (35). Often, light stabilizers are coated as separate molecules in a codispersion with the coupler.

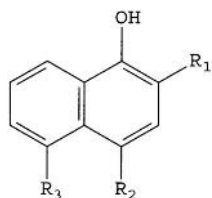


2.2.5 Cyan Image Couplers

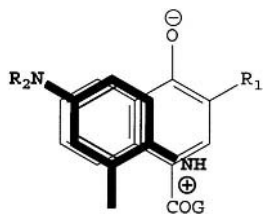
Naphtholic Cyan Couplers

There are two major classes that have found widespread use in films and papers. Again, each of these comes in two subgroups.

The first type are the naphthols, many of which have ideal in-film $\text{pH}_{1/2\text{S}}$ that are near the developer pH of 10.



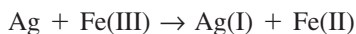
This feature makes them more highly ionized than the second type of couplers (phenols, see below), and the naphthols generally enjoy high reactivities with D_{ox} . We speculate that this reactivity may be due to secondary orbital overlap of the D_{ox} cation and naphtholate anion pi orbitals, which may lower the energy of the transition state for coupling.

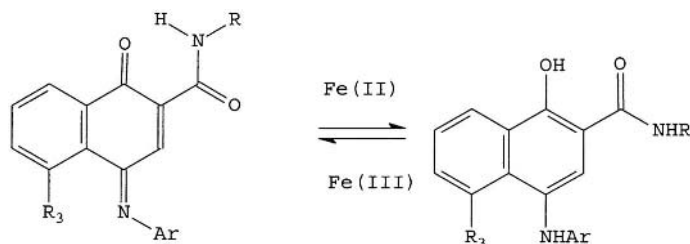


By far the most used substituent at R_1 is the carbonamido group. This group creates the opportunity for H-bonding both in the coupler and in the dye. The former affects the pK_a of the coupler and the latter the hue of the dye.

Both two- and four-equivalent (36) naphthol couplers are known. The most useful COGs on two-equivalent couplers are linked through oxygen and include aryloxy and alkyloxy with auxiliary functional groups in the alkyl chain (37).

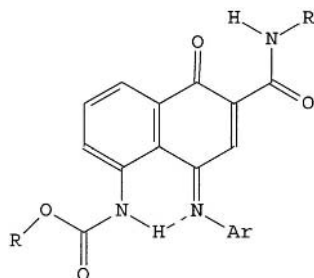
A fundamental problem with naphthol dyes is a potential to reform the leuco dye in the bleach step, commonly an iron complex formulation.





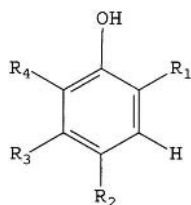
During the bleaching process, the ratio of Fe(II) to Fe(III) increases in the film, particularly in regions of high silver (high exposure). The increased ratio of Fe(II) to Fe(III) locally lowers the redox potential in the film and allows the possibility of cyan dye reduction. The naphthol dyes are kinetically prone to this reduction, and once formed they are sluggish to reoxidize back to the dye as diffusion reestablishes the bulk ratio of Fe(II) to Fe(III).

One solution is to use a carbamate group ($-\text{NHCO}_2\text{R}$) at R_3 (38). The carbamate group provides stabilization of the dye by internal hydrogen bonding.



Phenolic Cyan Couplers

A second solution to the problem of leuco dye formation relies on the phenolic class (39) of cyan couplers that come in two major subgroups.



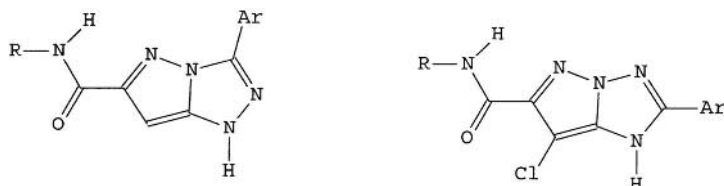
For film uses, the first subgroup usually has R_4 as H with carbamoyl-like groups at R_1 [or ureidoaryl groups with electron withdrawing substituents (40)] and R_3 (41). Both two- and four-equivalent materials are available. Their dyes have good dark stability (42) but have less robust light stability.

In paper, where light stability is more critical, the predominant phenolic coupler comes from the second subgroup, with R_4 as chloro and R_3 as alkyl (and R_1 still carbamoyl) (43). This subclass has greater light stability and a more hypsochromic hue that is better for color rendition in prints. Chloro COGs are common at R_2 .

Novel Cyan Couplers

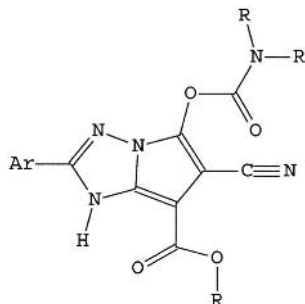
There has been a rush of activity in recent years to invent new heterocyclic cyan couplers that use traditional magenta-like couplers or totally new heterocyclic systems with electron

withdrawing groups and extended conjugation. Such substituents lower the LUMO energy of the dye, which produces the batho shift into the cyan. Two examples include conventional-looking pyrazolotriazole couplers. The hue shift is accomplished by the use of further aryl conjugation and a carbamoyl substituent (44).



The dyes from these materials are reported to have molar extinction coefficients over 60,000 (45).

Another class includes the pyrrolotriazoles that typically have a cyano group and further conjugative substituents to move the hue into the cyan (46). The system shown below has a carbamate coupling-off group and is also reported to have a high extinction coefficient for the dye (47).



It is challenging to introduce a new class of coupler into photographic products. Not only must the new material be reactive with D_{ox} under development conditions and produce a dye with a correct hue, but more than a dozen other attributes must not be compromised. These include the raw stock keeping of the coupler, the dark and light stabilities of the dye, the granularity and acutance of the image, and a host of other practical aspects. Furthermore, these complex materials must fit within the cost structure of a competitively marketed product.

2.3 MASKING COUPLERS

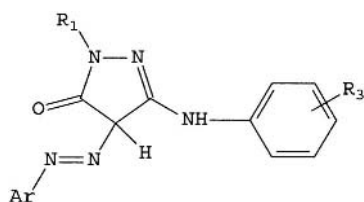
2.3.1 How Masking Couplers Correct for Unwanted Dye Absorptions

Masking couplers are members of a class called image-modifying couplers. Such couplers are not used primarily to form the color image but rather to modify it, improving attributes like color, grain, or sharpness. They usually are two-equivalent couplers that have a chemically blocked photographically useful group (PUG) in the coupling position. After D_{ox} reacts with the image-modifying coupler, the PUG is eliminated from the leuco dye. In the case of masking couplers, the chemistry modifies the effective hue of the dye image in film to compensate for unwanted absorptions of the image dyes. For example, magenta dyes have a major π - π^* absorption in the green (500–600 nm) but also have a tail or

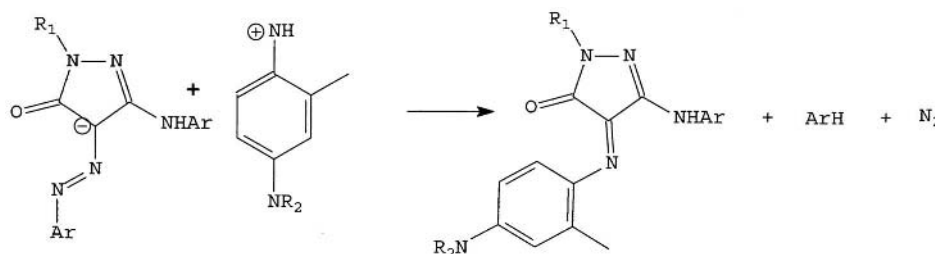
minor absorption in the blue (400–500 nm). Similarly, cyan dyes tail into or absorb in the green and/or blue regions. This is a fundamental problem. (Masking couplers can also be used to generate interlayer interimage effects (IIEs), which are discussed in the next section.)

Unwanted absorptions in the negative absorb light of a different color than that which generated the image dye, leading to desaturated or muddy colors. For example, suppose a picture is taken of midsummer grass that has a pure green color. Light from the scene exposes the green record, such that during development a magenta dye is formed in the negative. This magenta dye has an absorption that tails into the blue (or yellow) region and it may also have absorption of lower extinction in the blue region. Even though the light from the scene was pure green, the record in the negative acts as though both green and blue light came from the scene. When a print is made from this negative, the grass will appear bluish-green, not green.

Because the film-print system has two stages, adding masking couplers in the sublayers that contain the image couplers bearing unwanted dye absorptions can achieve a very clever masking of these unwanted absorptions (48). Carefully follow the logic. Masking couplers are designed to possess the unwanted color before development. Typically azo chromophores (which can tautomerize to hydrazo forms) are used as coupling-off groups (or PUGs) on a parent coupler.



During development, when D_{ox} reacts with the masking coupler (in competition with image couplers), the azo group is coupled off, and the starting color is destroyed. Ideally, the amount of color destruction is exactly matched by the amount of unwanted color formation caused by formation of the image dye in the coating.



In the example of a green scene exposure given above, the film would be built with both a magenta image coupler and a yellow-colored masking coupler in the same sublayers that are sensitive to green light. Before exposure from the scene, the film has a uniform yellow tint caused by the masking coupler. Green light from the scene produces on development the magenta dye with its unwanted yellow color, as well as a corresponding loss of yellow color from reaction of the masking coupler with D_{ox} . The net result is that the yellow masking coupler and its chemistry with D_{ox} has masked (removed from view) the unwanted yellow *image* of the green grass, replacing it with a uniform yellow color in

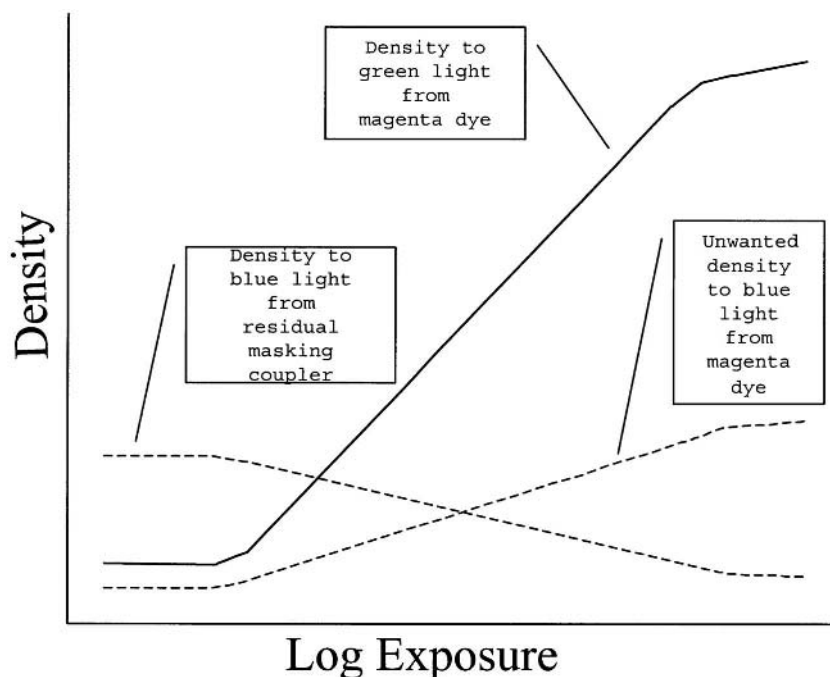


Figure 2.2 Use of yellow-colored coupler to mask the unwanted blue density from a magenta image dye.

both green and nongreen areas of the scene. Figure 2.2 shows how this masking is accomplished.

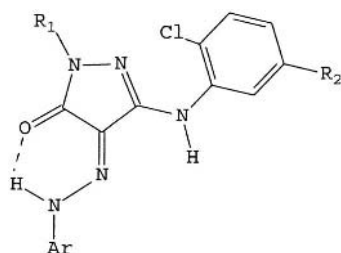
Though the uniform yellow cast in the resulting negative will filter blue light from the printing lamp, this can be compensated by a longer blue exposure during printing.

The final consideration is the choice of parent coupler that bears the colored masking chromophore as a coupling-off group. There is an obvious choice. If the goal is to mask unwanted absorptions that are originating in the green record, then a magenta coupler is ideal, as further magenta dye is then made as the masking color is destroyed. An obvious need is for the loss of masking color to be matched to the gain of unwanted color from the image dye. This is controlled in part by the choice of the reactivity of the coupler to which the masking dye is attached. The relative rates of D_{ox} coupling with image and masking couplers must be properly matched.

This masking technique is extensively used in color negative films but is inappropriate for directly viewed materials like slides and prints where the color of the mask would be visible. Cyan dyes also have unwanted absorptions in both the green and the blue, so there are both magenta-colored cyan masking couplers and yellow-colored cyan masking couplers. There are also magenta-colored yellow masking couplers (49) in the literature, although there is limited need for them because yellow dyes do not tail badly into the green region.

2.3.2 Yellow-Colored Magenta Couplers

The most common of the masking couplers that is used in the magenta record is based on the anilino pyrazolone magenta couplers (50). They are drawn below in their hydrazone form where there is hydrogen bonding to the C-5 carbonyl group:

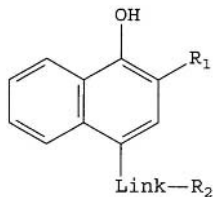


The types of substituents that are used at R_1 and R_2 are typical of the magenta image couplers described earlier. Trichlorophenyl is most common at R_1 along with lesser use of the pentachlorophenyl group. At R_2 , the carbonamido group and its variants are common. Often, simple electron donating substituents are used in the Ar group, such as ethers.

The detailed mechanism for coupling of these materials with oxidized developer is uncertain. Certainly, the first step is ionization of the hydrazone proton to form an anion. Collapse of D_{ox} at the C-4 carbon is likely to form an azo leuco intermediate. At this point, one pathway could be elimination of the azo group to form the magenta image dye. D_{ox} would likely further oxidize the released azo group, which is an imide, into an aryl diazonium radical or cation, both of which would give colorless products.

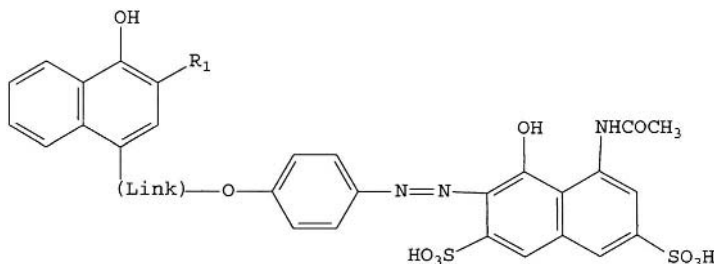
2.3.3 Masking Couplers in the Cyan Layers

Masking couplers in the cyan layers are largely based on the naphthol cyan image couplers.



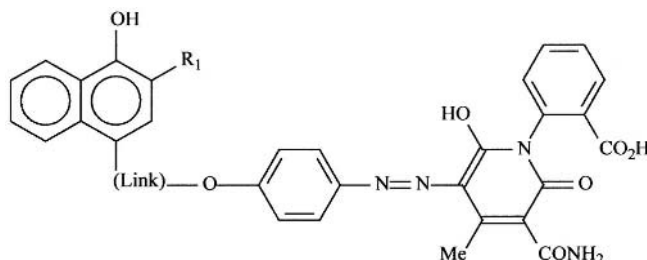
The usual carbamoyl group is used as R_1 , and the link is often an ether coupling-off group. Various R_2 groups are used, depending on the color of the mask that is desired. All of them are formally azo chromophores.

The following structure represents the most common type of magenta-colored cyan masking coupler (51).



The structure is drawn in its azo form, but it could be a hydrazo tautomer. Coupling of the naphthol anion with D_{ox} releases the link, and the ionizable sulfonic acid groups solubilize the magenta azo chromophore so that it washes out of the film. In this way, red light from the scene removes magenta color.

A yellow-colored naphthol masking coupler (52) that can be used in the cyan layer to account for unwanted blue absorptions in the cyan dye is shown below.



This material can also be drawn in its hydrazo tautomeric form, and it has solubilizing groups that can also cause the released chromophore to wash out of the film.

The use of masking couplers has its drawbacks, and image dyes without unwanted absorptions would be preferred. There are speed penalties to pay, because the preformed dye absorbs light that could expose silver halide. The resulting higher minimum densities in the negative also mean that a lesser exposure range is available before encountering density maximum limitations. Last, when a masking coupler (e.g., yellow colored) is used for IIE (mentioned at the beginning of this section, and see below under “How Masking Couplers Deliver IIE”), extra yellow image coupler is needed. The higher use of yellow image couplers costs more and may give greater graininess in the image.

2.4 DEVELOPMENT INHIBITOR RELEASING COUPLERS (DIRs)

2.4.1 Interlayer Interimage Effects

What Are DIRs?

DIRs are both development-modifying (formation of D_{ox} and silver) and image-modifying (formation of color) materials. The mechanistic use of these couplers in film is to retard silver development and D_{ox} formation.

It is fair to say that DIRs do not simply fix problems from image coupler chemistry; they deliver more pleasing photographic images over and above what even ideal image couplers can deliver. Two uses will be described, and they are both as creative as the use of masking couplers for unwanted absorptions.

The first use is for enhanced interlayer interimage effects (IIEs), which was mentioned in passing in the masking coupler subsection. IIE refers to chemistry that produces greener greens (grass), bluer blues (sky), and redder reds (Santa Claus) than are true in the scene. This has been found to be desirable by customers. IIEs convert “muddy” colors of many real scenes (e.g., bluish-greens) into purer colors (greens).

How does this happen? DIRs are couplers with a silver development inhibitor in the COG position. When chemically blocked in this manner, the inhibitor is inert. When the DIR couples with D_{ox} (in competition with the image and masking couplers), a dye from the parent coupler is formed along with a free inhibitor molecule. A development inhibitor is a molecule that can diffuse to a silver halide grain and can react with surface silver ions of high free energy to form insoluble silver-inhibitor salts on the surface. These high-free energy silver ions are likely those that replenish interstitial silver ions that are reduced at the minielectrode of the latent image. Therefore lowering the free energy

of surface silver ions by reaction with inhibitors serves to reduce the overall development rate.

Inhibitors can be designed with appropriate diffusion coefficients so that they diffuse during development to adjacent color records and inhibit development chemistry there. This means that red light from the scene generates unblocked inhibitors that slow development not only in the red sublayers but also in the green sublayers (and to a lesser extent, in the blue sublayers that are farther away). Green light leads to inhibition in the green sublayers as well as in both the blue and red sublayers (which straddle the green sublayers), and so on for blue light.

With inhibitors diffusing within and among all sublayers, the rates of these processes (inhibitor generation, diffusion, and inhibition) need to be balanced. This is necessary so that “neutral” or shades of gray light from the scene produces the equal amounts of densities from the cyan, magenta, and yellow image dyes.

Why is it desirable to do this? Consider a segment from the scene that is green (or red or blue). Only the green chrome is exposed. Inhibitors are not released from the red and blue sublayers. Therefore, there will be more silver halide development occurring in the green layer from green light than when the green layer is exposed by neutral light. More magenta dye is produced, which translates to a higher density of green color in the print. Green grass appears greener (more saturated green) than real. Blue skies appear bluer than real. Reds are redder. This potentially desirable effect is the result of IIEs.

It is now easy to understand why the inhibitors need to be blocked as COGs on couplers so that they are released “imagewise” with development chemistry. If they were not blocked, inhibitors would be present to operate on the development of red, green, or blue images as well as neutral images. If inhibitors were not blocked, neutral images would have the same saturation as red, green, and blue images.

The features needed for good DIR couplers include a rapid “imagewise” release of the inhibitor, which means that free inhibitors are generated by D_{ox} on a time scale that is rapid compared to overall development. This is needed so that the inhibitors have a chance to diffuse to adjacent color records before development is complete. Also needed are high diffusion coefficients for the inhibitors.

How Masking Couplers Deliver IIE

In the prior section on masking couplers, it was mentioned that they also serve to increase IIEs. The use of masking couplers in film would be desirable even if there were no unwanted absorptions from the image dyes. To explain this, focus for example on the blue and green layers, where there are yellow and magenta image couplers and a yellow-colored masking coupler in the green layer. Assume that the magenta image coupler gives a dye with no unwanted yellow color. When a scene contains blue, green, and red light (neutral scene color), the blue light will make a yellow dye, and the green light will initiate development chemistry that partially destroys the yellow mask. The final blue density is the sum that remains from the mask, and that density formed from the yellow image coupler. This blue density combines with the green and red densities in the other layers, and when the film is designed right, the combined colored densities produce a gray patch of some saturation in the print.

When pure blue light of the same amount (as in the neutral exposure above) comes from a different segment of the scene, the same amount of yellow dye will be made, but now the yellow mask in the green sublayers is not removed. Therefore there is more total blue density, which translates to a bluer (more saturated) image in the print. This is why

masking couplers are useful, even if image dyes were to have no unwanted absorptions. In the presence of image couplers with unwanted absorptions, the film needs to be built so that the masking density that is lost is greater than the formation of unwanted image dye density.

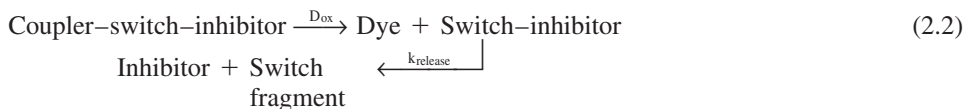
2.4.2 DIRs for Sharpness

A second use of DIR couplers is to increase the sharpness of scene edges. An edge consists of two different scene colors or densities that can be degraded by light scatter during the exposure step or by the horizontal component of D_{ox} diffusion across the edge during its reaction with couplers. However, if inhibitor is generated imagewise, its horizontal component of diffusion at the edge also generates a changing concentration of inhibitor across the edge. Figure 2.3a illustrates these edge profiles for light exposure and released inhibitor. This horizontal concentration profile for inhibitor across a scene edge also occurs when inhibitors diffuse (vertically) into adjacent color records, because diffusion is isotropic. Therefore adjacent to the higher exposure side of the edge (scene), there is a lesser amount of inhibitor than in the bulk of the scene. This gives greater silver halide development at the edge with the formation of greater amounts of D_{ox} and dye. On the nonscene side of the edge, inhibitor that has diffused from the scene side reduces development and density. The overall result is an edge with a greater gradient of density, which appears as a sharper edge. It is as if a child had taken a colored crayon to enhance the density on the scene side of the edge and an eraser to reduce the density on the nonscene side. Figure 2.3b shows the result. The “ears” of the density profile are real.

The same features in a DIR coupler that increase IIE also increase sharpness. DIRs for both IIE and sharpness profit from being more reactive with D_{ox} than image couplers, so that the action of inhibitors on silver halide development can compete with formation of the color image. Inhibitors also enhance IIE and sharpness when they have a long diffusion length. This diffusion path is shortened by high adsorption to silver halide grains, which coincidentally is part of the inhibition mechanism.

2.4.3 Delayed-Release DIRs

A way to prevent temporarily the reversible adsorption of inhibitors to silver halide emulsions so that the inhibitors diffuse farther is to block the inhibitor with an organic linking group, sometimes called a switch. Attached to a coupler, these yield what are called delayed-release DIR couplers. When the k_{release} produces a half-life of the switch–inhibitor combination (that is, seconds to minutes), then the profile of the released inhibitor concentration is broader, and both sharpness and IIE are enhanced.



If the switch releases the inhibitor in a few seconds or less, there are no consequences on IIE and sharpness. Nevertheless, a fast switch may provide a synthetically more accessible coupler. Or the switch may confer more reactivity of the coupler toward D_{ox} than the directly attached inhibitor (DIR) would provide.

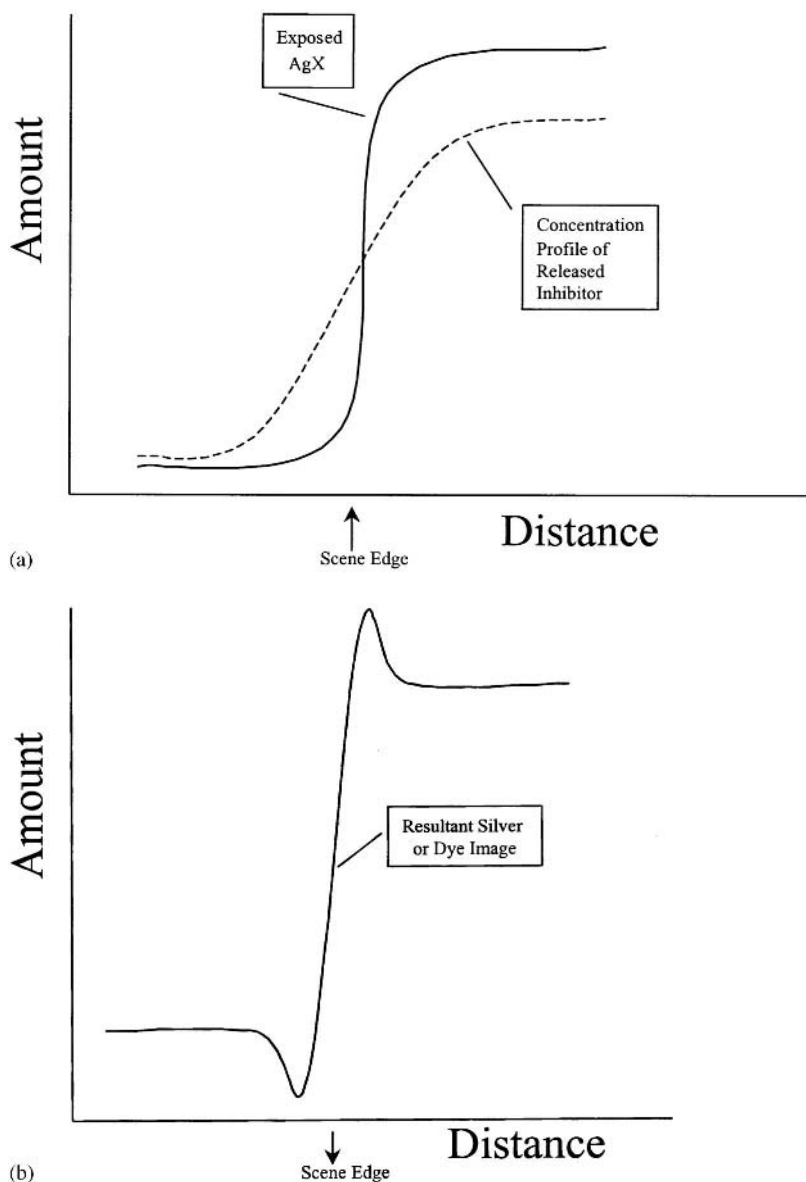


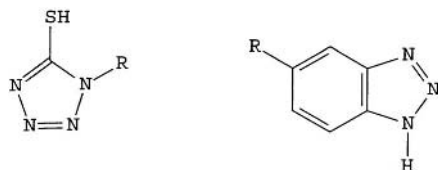
Figure 2.3 (a) The concentration profile of a released inhibitor at a scene edge. (b) The final density profile at a scene edge.

A description of the DIR materials is primarily a description of the switches and inhibitor fragments. All the common coupler parents can be used, although as mentioned, more reactive parents (toward D_{ox}) are needed for DIRs than for image couplers. Furthermore, only ca. 25 to 50 mg/m² of laydown for a DIR coupler is required, compared to tens or scores of milligrams per square foot for an image coupler. This means that changes in the DIR coupler structure can be made to enhance reactivity with D_{ox} or to enhance

release of the COG, even if the structural changes generate dyes with less than optimal hue characteristics.

2.4.4 The Inhibitor Classes

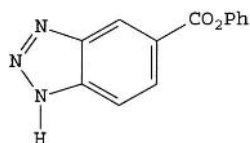
There are two fundamental types of development inhibitors, both of which share the common feature of strong binding constants with silver ions. These two types are the mercaptans and nitrogen heterocycles (where one tautomer contains a NH group). The central class of the mercaptans is the mercaptotetrazoles, whereas the nitrogen heterocycles are most represented by the benzotriazoles.



The mercaptotetrazoles have pK_a s lower than pH 7, so they are fully ionized in pH 10 color developers. The sulfur anions form extremely strong bonds to silver ions, and their solubility products (pK_{sp} s) are typically ca. 15 (53), well above that of silver bromide at 12.3. However, the simple ability to complex the silver ion does not make a development inhibitor. The low molecular weight mercaptotetrazoles (e.g., $R = \text{Me}$) are not inhibitors, nor are higher homologues that contain an ionizable group such as carboxy. Such inhibitors do form complexes with silver ions, but such complexes are soluble in the aqueous gelatin of the film and dissolve the grain. To be an inhibitor, the silver complex needs to be hydrophobic so that it will stay on the grain surface and lower the free energy of surface silver ions. Typically, the most common R group is phenyl, although alkyl groups are also prevalent. Besides the mercaptotetrazoles (54), systems such as substituted mercapto-oxadiazoles (55) and mercaptothiadiazoles (56) also function as inhibitors.

2.4.5 Self-Destruct Inhibitors

Just as mercapto systems need to be hydrophobic to function as inhibitors, so do benzotriazoles. Unsubstituted benzotriazole is a weak inhibitor. A common linking group on the benzotriazole is a carboxylic acid ester (57) such as shown below.



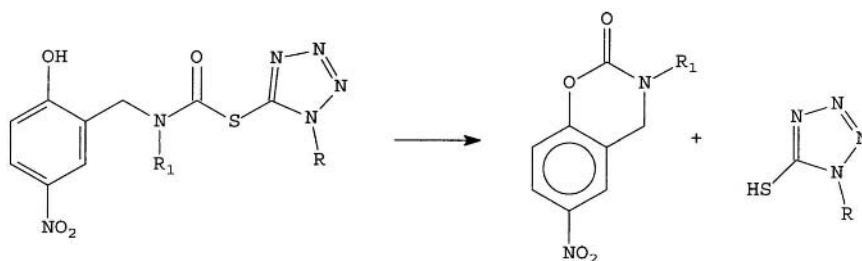
Besides increasing the hydrophobicity, the ester group addresses a potential problem of inhibitor materials referred to as “seasoning” of the developer. Inhibitors that diffuse appropriately in the film also diffuse into the developer bath. Their concentration in the bath can build, and unless there are protective layers built in the top of the film pack, they can enter subsequently processed film and alter development in an uncontrolled fashion. However, the phenyl ester in the benzotriazole shown above can hydrolyze to the carboxylic acid in the developer bath. With a free ionized carboxylic acid group after hydrolysis, the benzotriazole is no longer a moderate inhibitor because it is no longer hydrophobic enough to adsorb and stay on the grain. This feature is called “self-destruct” chemistry

and is also used with the mercaptotetrazoles (58). Typically, the self-destruct link is an activated ester group.

As a class, the benzotriazoles do not adsorb to silver halides as strongly as most of the mercapto systems. They have higher pK_a s, between 6 and 10, and their pK_{sp} s with silver ion are several units lower than mercaptotetrazoles (59). This enables the benzotriazoles to excel at creating longer range IIEs among sublayers without use of a switch. There are a host of other potential heterocyclic inhibitors, but so far the most useful have been variants on the benzotriazoles. Both 1,2,3- (60) and 1,2,4-triazoles (61) show promise.

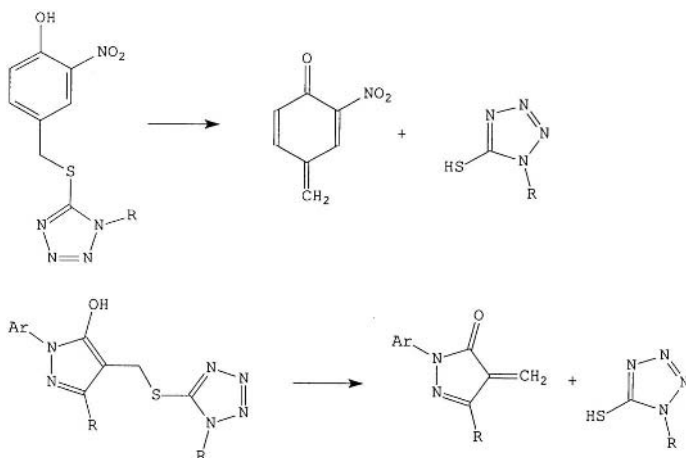
2.4.6 Delayed-Release Switches

For delayed-release DIR couplers, there are three general classes of switches that are commonly used, and they come in different flavors. The first invented were the so-called “carbamate” switches (62) of the general structure below.



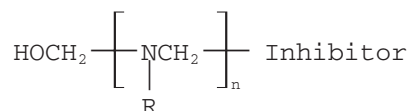
The switch on the left, shown with a blocked mercaptotetrazole inhibitor, is attached to the coupler as a COG through the phenolic OH group. R_1 is typically a small alkyl group. At pH 10 the half-life for release of the mercaptotetrazole inhibitor needs to be seconds for the inhibitor to function properly.

The second major type of switch with many variants is based on vinylogous elimination chemistry. Two examples are



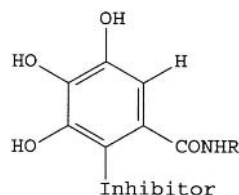
The first of these is called a “quinone methide” switch (63), based on the structure of the fugitive product. This product reacts with a nucleophile to regenerate an innocuous aromatic material. This switch is attached to a coupler through the phenolic group. The second switch based on a pyrazolone nucleus works similarly (64).

A third type of switch, sometimes called a link, is attached to the coupler

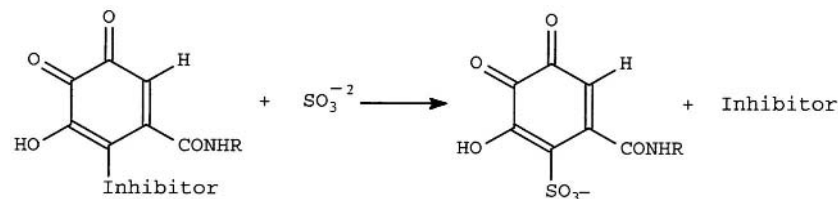


through the oxygen atom (OH group) (65). After release of the COG, formaldehyde is released to give directly the inhibitor ($n = 0$), or to give a second intermediate that can further fragment to release the free inhibitor (n greater than or equal to 1).

A novel idea for a switch is based on redox and addition–elimination chemistry (66) and is exemplified by

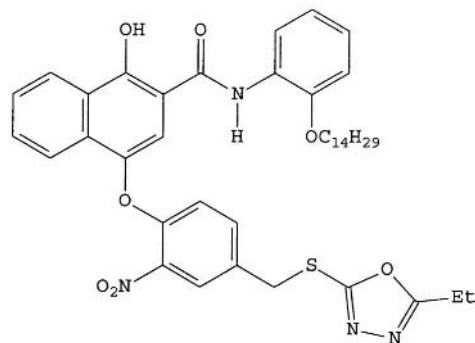


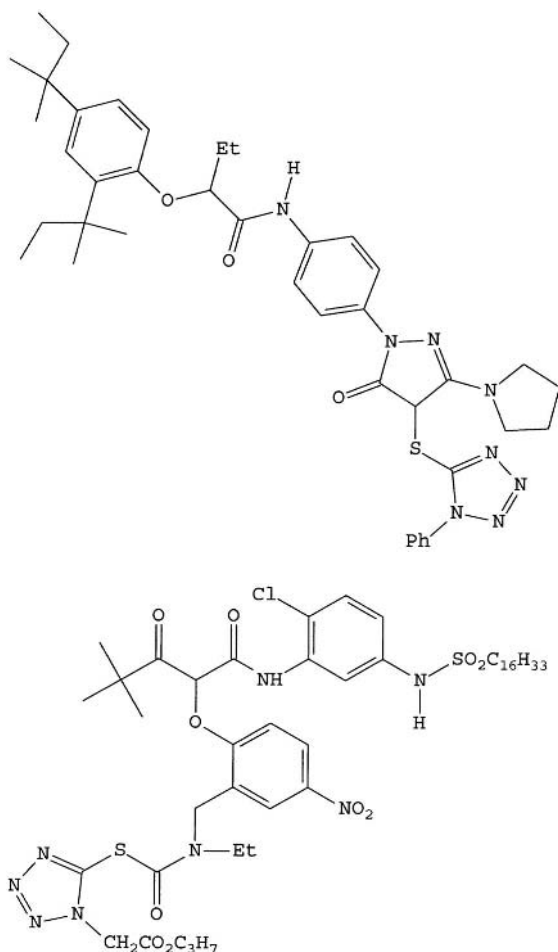
This material is attached to the coupler through the OH group that is para to the inhibitor. This released switch is redox active and can be oxidized by film oxidants (D_{ox}) to an o-quinone. The inhibitor can then be released by nucleophilic addition of sulfite from the developer in a Michael addition–elimination reaction.



2.4.7 Examples of DIR Couplers

The above sections show the pieces of DIRs. Below are some complete examples of DIR couplers (67–69).





DIRs are among the most complex and expensive materials in film. Working from the outside of each structure inward, each contains a ballast ($C_{14}H_{29}$, OAr, or $C_{16}H_{23}$) that holds the coupler in its desired color record. Each contains a coupler so that the COG can be released imagewise with D_{ox} (naphthol, pyrazolone, or pivaloylacetamide). Two contain a switch (quinone-methide or carbamate). Each contains an inhibitor (mercapto-oxadiazole, mercaptotetrazole, or self-destruct mercaptotetrazole). When the function of DIR couplers is understood, so are their structures.

2.4.8 Granularity Advantage from DIR Couplers, Tradeoffs, and DQE

As discussed, image-modifying chemistries (DIRs, colored masking couplers, and other unmentioned materials) can be used to improve sharpness, to correct for unwanted dye absorptions, and to increase color saturation. DIRs and similar materials can also reduce granularity, which is the nonuniformity that is created in a uniform image field by the spatial distribution of silver halide grains and the subsequent dye clouds. The inhibitors from DIRs perform this function by shutting off, or slowing down, D_{ox} production from silver halide grains and thereby forcing more individual grains to contribute to a given density level. The forced use of more information-bearing centers by use of inhibitors contributes to the improved signal-to-noise ratio.

These beneficial effects of image-modifying chemistries do not come without a price. The information recorded during exposure of the silver halide material is fixed. During keeping and processing, this total information can be lost or degraded, but not enhanced or maintained. The roles of image-modifying chemistries are to permit the film designer to trade off this information in various display options to meet the needs of the particular film product.

Photographic scientists have long known of the various trade-offs between, say, sharpness and speed (related to color contrast) or speed and granularity that can be achieved using image-modifying chemistry. More recently, these compromises have been quantified in a metric called Detective Quantum Efficiency (DQE) (70), a measure of the information-carrying capacity of the film, and cast in terms of parameters of interest to the film designer. DQE is a ratio of the measured output signal-to-noise produced by the film (amplification, acutance, and granularity all enter into the output). This permits photographic scientists to assess whether they have optimally used the information recorded by the film and to measure the effectiveness of the chemical trade-offs they have made.

Increasing the information-carrying capacity of the film by designing more efficient silver halide emulsions is one of the major goals of emulsion scientists. This gives the color imaging chemists a greater opportunity to use image-modifying chemistries to create optimally pleasing pictures.

2.5 PUTTING IT ALL TOGETHER

There are over 100 chemicals in a typical modern color negative film. With few exceptions, these chemicals do not act independently but rather in hundreds of two-way and higher-order interactions. A piece of color negative film may be among the most complex man-made chemical devices.

Such complexity creates a challenge for photographic scientists. However, we need to simplify the product, not glory in its complexity. This goal may be achievable, as films can now be digitally scanned and manipulated thereby requiring less chemical intervention.

Even if half the chemistry can be removed, there are many of degrees of freedom left for building a film. There is the freedom to modify the structure of each organic compound in almost an infinite number of ways. There is the freedom to alter the laydown in milligrams per square foot. Each material can be incorporated in different sublayers. Sublayers can be arranged in different orders.

The end use of putting the materials together is to control more than a dozen photographic responses ranging from reciprocity of different exposure times and light levels to the stability of the image dyes. Though digital imaging systems continue to make inroads into traditional photographic applications, silver halide systems with their massive information-carrying capacity continue to set the standard for quality/cost trade-offs. As exemplified by the fusion of chemical and electronic information capture in the Advanced Photo System (APS), the future of imaging may lie with those hybrid systems that make best use of the unique qualities of both technologies.

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3

Diazo Papers, Films, and Chemicals

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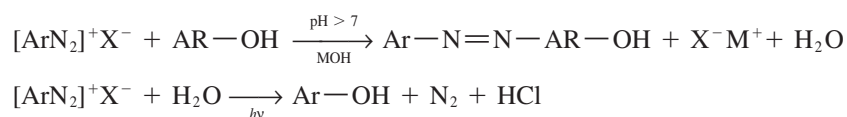
3.1 DIAZOTYPE PROCESS

The diazotype process, because of its simplicity, versatility, and low cost, has remained the most widely used method for the production of copies of engineering and architectural drawings. The manufacture of diazotype materials is still a strong and well-established industry in the majority of the countries in the world. Although no longer growing in the United States and Europe, the use of diazotype papers and films is continuing to expand in other parts of the globe and in particular in developing countries.

The diazotype process owes its existence to the unique characteristics of aromatic diazonium compounds and more specifically to the following properties:

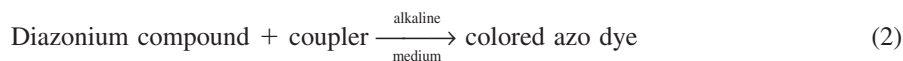
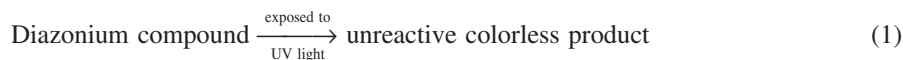
1. In the presence of certain classes of compounds called couplers, and in a range of pH values, diazonium compounds react to form colored azo dyes.
2. Diazonium compounds are sensitive to light, and when subjected to irradiations of light of a specific wavelength (normally in the UV range), they decompose to give colorless substances that can no longer form azo dyes.

These two properties can be translated by the following chemical reactions:



The photolytic decomposition of the diazonium compound is best accomplished in the presence of traces of water, whereas the reaction between the diazonium compound and

the coupler takes place in general in an alkaline environment. Schematically, the diazotype process can then be written as follows:



It can be seen from the reactions above that the diazotype process, in its conventional form, is positive working.

It should be mentioned at this point that the abbreviation of diazonium as well as diazotype to diazo has come into common language and is generally accepted.

Graphically, the production of a positive image by the diazotype process is illustrated in Fig. 3.1. A graphic original composed of a light-transmitting substrate, such as a transparent or translucent paper, on which are lines opaque to light, is placed in close contact on top of a light-sensitive diazotype material, such as a diazotype paper, and exposed to ultraviolet light. The ultraviolet radiations that pass through the nonimage areas will reach the light-sensitive layer containing the diazonium compound and decompose it proportion-

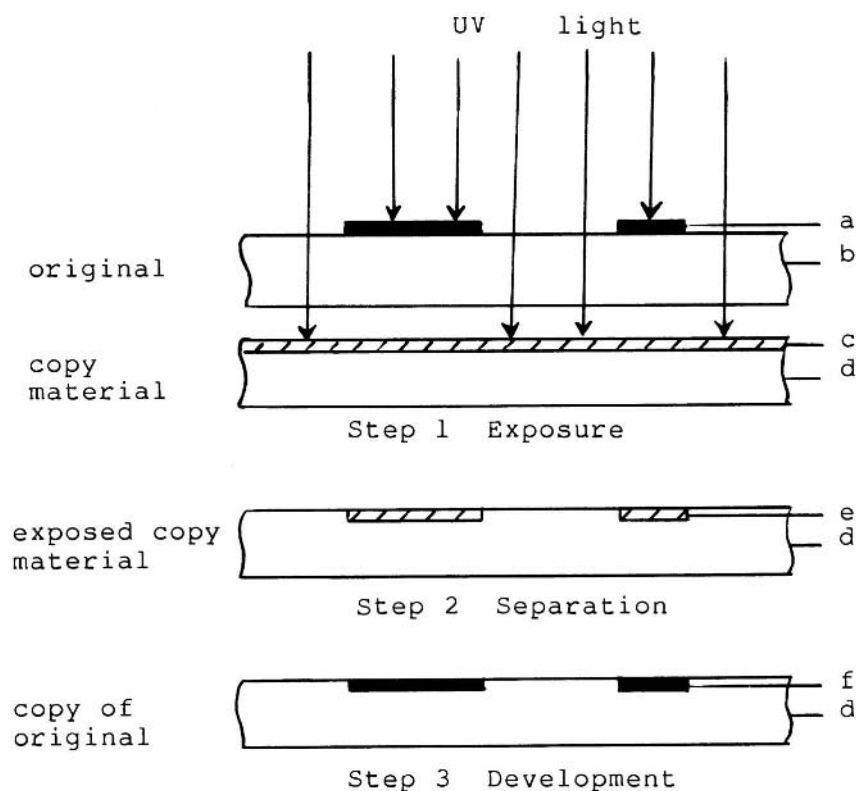


Figure 3.1 Production of a positive image by the diazotype process: a, image area; b, light-transmitting substrate; c, diazotype layer; d, base support; e, latent image area; and f, azo dye image area.

ally to the amount of energy it receives; under the opaque lines, where the light is blocked, the diazonium compound remains undecomposed. The diazotype paper, after exposure, carries a barely visible image formed of the remaining pale yellow diazonium compound on a white background.

To render the image permanently visible, the diazonium compound and the coupling component are allowed to react together to form a highly colored azo dye in the image area. The amount of azo dye formed is proportional to the amount of diazonium compound left undecomposed by the ultraviolet light; it follows that weak actinic opacity originals will give low-density dye images and that high actinic opacity originals will give high-density dye images.

The reaction rate between the diazonium compound and the coupling component is pH dependent. At low pH values, the reaction is either completely inhibited or extremely slow. As the pH value increases, the reaction rate also increases to reach a maximum at pH values above 10 or 11. It can be seen that to prevent the diazonium compound and the coupler from reacting together before exposure, it will be necessary either to separate them physically or to create a strong acidic environment for the diazonium compound and the coupler. Based on these alternatives, two processes emerged.

In one process, the diazonium compound alone, from a solution, is applied to the base support, and only after print exposure is the coupler brought in contact with the diazonium compound; for the foregoing reason, the term one-component is commonly used when referring to this process and its materials.

In another process, the diazonium compound and the coupler, dissolved together in the presence of an acid, are applied to the base support, and after exposure the acid is neutralized with alkali. For this process and its materials, the term two-component is often used.

The choice of the diazonium compound and of the coupling component will determine which process is applicable, which azo dye color will be obtained, and how much energy will be necessary to expose the material. All these elements are discussed later.

The photosensitivity of diazotype materials is limited to a very narrow range of the spectral region, between 350 and 420 nm, which is the region in which most diazonium compounds used in the production of diazotype materials absorb light. Any light source that emits radiations within this spectral range will be suitable for exposing diazotype materials. The most readily available source of light that would decompose the diazo is the sun. Even though solar power is still used practically to expose diazo papers in certain parts of the world, however, the sun is not a controllable source of actinic light and cannot be the base of a commercial system.

Arc lamps and mercury vapor lamps were in the past conventional sources of ultraviolet light and were extensively used in diazo photoprinting equipment. Arc lamps have ceased to be used; but mercury vapor lamps continue to find applications where high-energy outputs are required.

Fluorescent tubes have become very popular as ultraviolet light sources for diazotype printing, since it was found that by doping the tubes (i.e., adding certain metals in the tube) the emission spectrum of the tube can be shifted toward the high wavelengths in the ultraviolet range.

Quantitative studies of the action of light on diazo compounds have shown that the quantum yield of the photolysis of diazos is below unity; the quantum yield is defined as the quotient of the number of molecules activated by light and the number of absorbed

photons. If one molecule of diazo is decomposed by one photon, the quantum yield would be equal to unity. However, part of the energy used to excite the diazo molecule is converted to thermal energy or fluorescence, while the remaining part of the energy produces the photochemical decomposition of the diazo.

In contrast, the quantum yield of silver halide after development is many orders of magnitude higher because of development amplification; it is considered that the energy required to form a diazo image is 700,000 to 1,000,000 times greater than that needed to form a silver halide image.

Because of the nonsensitivity of diazonium compounds to green, yellow, and red portions of the visible spectrum, it is possible to handle diazotype materials in tungsten light for long periods or in low-energy blue light for short periods of time.

3.2 DIAZO PAPERS

The most common diazotype material in the world is what is usually called diazo paper, also called heliographic paper, dyeline paper, and, in the United States, blueprint or whiteprint paper. The term heliographic paper seems best to describe this type of photo-sensitive material because it is derived from the Greek words for “sun” and for “writing”; thus “heliographic” stands for writing with light—a most poetic way of describing diazo paper. In the United States, the term “blueprint” was first used for a type of engineering reproduction paper based on ferrocyanide systems, which gave deep blue negative prints showing white lines on a blue background; the first diazo papers were intended to simulate the negative blueprint paper color and were mistakenly called by the same name.

Different types of diazo paper are available depending on the character, appearance, and properties of the base paper itself. Two main classes of diazo papers dominate the market: the first, with the larger volume and for general purposes, uses an opaque or semiopaque base paper; the second, representing a smaller volume and for specialized applications, uses a more or less translucent or transparent base paper. The opaque diazo papers cost substantially less than the translucent ones.

3.2.1 Base Papers

Opaque Base

To be suitable as a diazo base, the substrate and the coating formulation must be adapted to each other.

The base paper should be receptive to the coating while keeping the coating as close to the surface as possible. Penetration would cause a loss of printing speed due to the filter action of the paper fibers to UV light, and simultaneously a loss of print dye density. The stability of the light-sensitive diazonium compound could also be impaired by a slow reaction with the chemicals contained in the paper and with the cellulosic fibers themselves.

The base paper should be as uniform as possible, and its surface uniformly receptive to the coating solution, to prevent uneven print dye formation.

The base paper should be of a high brightness, to ensure the maximum print contrast. This is achieved frequently with the use of optical brighteners, which are fluorescent dyes. The base paper should be physically strong to withstand processing through the various

operations of the diazo material manufacture as well as to resist rough handling of the finished print: it should therefore have good wet and dry strength, folding endurance, tear resistance, and burst strength. The base paper should produce flat prints and therefore should be as inert as possible to changes in relative humidity of the surrounding atmosphere.

The base paper should be free of chemicals that may affect the diazo compound, the coupler, any of the other additives, or the print dye. Oxidizing agents and reducing agents decompose the diazo and the azo dye; various metal salts react with the diazo and, in particular, ferric salts give undesirable color reactions with many of the blue couplers.

The base paper must not be alkaline, lest premature coupling or diazo decomposition occur.

The base paper should be acidic enough to provide an environment that contributes to the shelf life of the diazo material, without being acid enough to affect the physical stability of the cellulosic fibers or the color of the print dye.

Because of the numerous and critical requirements for a diazo base paper, only a limited number of paper mills in the world have undertaken the task of producing this material, and as a consequence the price of a diazo base reflects its stringent quality requirements.

The choices of pulp and sizes as well as other additives determine the character and properties of the finished base paper. The quality of the available water is of major concern to the base paper mill, and the most important factor is its iron content. While 20 ppm is considered the upper limit of iron content in the paper, there is no limit set at the lower end. Currently standard diazotype materials use a base paper of between 70 and 80 g/m² basis weight, equivalent to between 18½ and 20 lb reams in the U.S. system. Heavier and lighter base papers are also used for special applications. The conversion between the metric system of base paper weight and the U.S. system is given in Fig. 3.2.

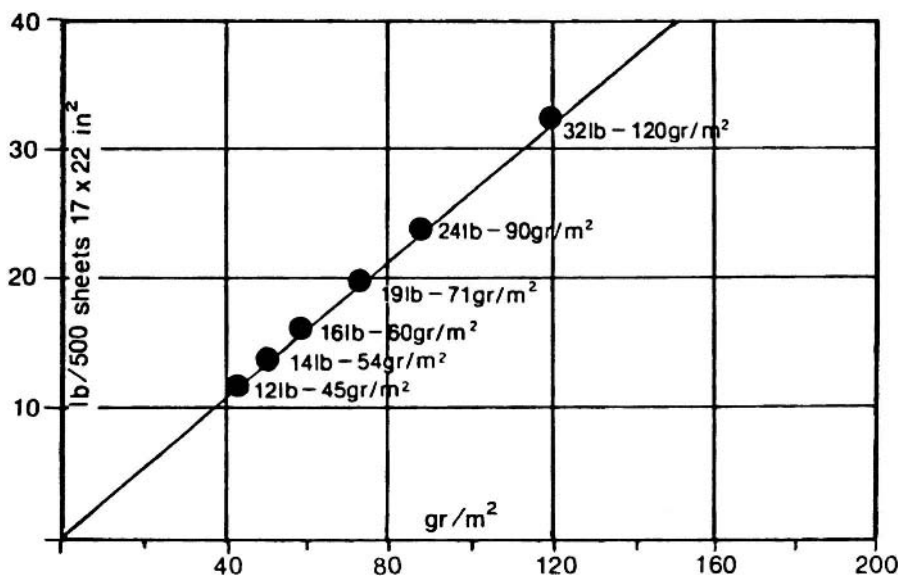


Figure 3.2 Conversion between the metric and U.S. systems of weight of base paper.

A typical specification for a diazo base paper of 20 lb of substance weight is

Basis weight	19–20½ lb/ream
Caliper	0.0036–0.0040 in.
Moisture	3–4%
Smoothness (Sheffield)	90–140
Brightness (TAPPI-T-452m-48)	90 minimum
Opacity	82 minimum
pH (TAPPI-T-435m-52)	4.2–4.5
Porosity (W. L. Gurley)	30–60 seconds
Iron	20 ppm maximum
Fold (Schopper)	100 minimum
Tear (Elmendorf)	60 minimum
Mullen	35 minimum

The majority of diazotype paper prints are made on a white stock base. However, in certain special circumstances, base papers of various colors are used for rapid identification. Tinted in blue, green, pink, yellow, or salmon, these diazo base papers were in the past produced by the paper mills. As demand decreased, tinted bases have become rarer, and diazotype material manufacturers have turned to tinting the white base stock themselves by the addition of water-soluble dyes to their coating solutions. This approach results in the simultaneous tinting and sensitizing of the base paper.

Transparent and Translucent Base

An important group of diazotype materials available in the market has transparent or translucent substrates sensitized with a diazo–coupler combination, giving azo dyes of substantial actinic absorption. These materials have an application in the production of intermediate prints used to make further diazotype material prints. The need to reproduce an original drawing that is the result of many hours of conceptual thought, design, and drafting, whether manual or computer aided, is self-evident; but the risk of damaging this valuable drawing increases rapidly with the number of times it is manipulated. An intermediate diazotype print of the drawing is generally made and used for further copying instead of the original drawing, which is then stored safely. Such a copy is often called the “second original,” “second master,” or “intermediate” because it has all the information of the original and can perform exactly like the initial drawing from which it was reproduced. Further copies of the intermediate can be made either on opaque diazo materials or on other intermediate diazo materials. Before making these copies, it would be possible to modify the intermediate by deletions, additions, or corrections to the drawing, creating in this manner a new drawing without having redrawn the original.

One of the major requirements for a diazotype intermediate material is that the substrate be transparent or translucent to actinic radiations.

Paper in its most common forms does not have a good transparency without further treatment because its fibrous nature causes light to be scattered within it. The degree of translucency of a paper will be related to the proportion of parallel light rays the paper is able to transmit in relation to the total amount of light the paper receives. The more light passes through the paper without being absorbed or scattered, the more distinctly we are able to see objects through the paper.

Paper is a fibrous material composed of a multitude of discrete fibers disposed in a sheet configuration with many voids or interstices between the fibers. The disposed fibers scatter the light; however, if the voids between fibers are reduced or if they have an index of refraction very close to that of the fibers, less light scattering takes place and consequently the paper becomes more translucent. The process of causing the paper to allow more light to be transmitted through it is called transparentizing.

Paper can be transparentized during the course of its manufacture, as in the case of glassine or natural tracing paper. This involves beating the fibers or treating them chemically until they become smaller and more plastic and can be compressed to form a dense sheet, which after supercalendering turns transparent. However, such a sheet, unless plasticized, is brittle and has poor tear resistance or folding endurance. Despite its physical limitations, natural tracing paper has found a practical application as a drafting medium and as a substrate for diazotype intermediates, particularly in Europe.

Another method of rendering paper transparent is to fill the voids between the fibers with a material that has an index of refraction identical or very close to that of the paper fibers. This index of refraction of paper fibers varies with the origin of the cellulose fiber and with other factors such as moisture content. In addition, cellulose fibers are birefringent: they have different values in the axial direction of the fiber and in the transverse direction, and these values vary between a minimum of 1.50 and a maximum of 1.58. It is considered that materials with an index of refraction close to the range of 1.50–1.58 are potentially suitable for transparentizing, with the best ones having an index of refraction around 1.55.

F. V. E. Vaurio (1) gives a list of commercial products that might be useful in controlling the transparency of paper by chemical treatment; the list indicates the index of refraction values in ascending order, giving the commercial product name and the manufacturer when appropriate.

Among the most common materials used for transparentizing paper are mineral oils or waxes, polymeric thermoplastic resins (e.g., polystyrenes, polybutenes, polypropenes), various resin derivatives, and various polymers or copolymers of acrylic monomers and styrene, with or without plasticizers.

Transparentizing materials are applied to the paper either in their original state or in the form of hot melt or organic solvent solution or aqueous emulsion. The application is performed by tub dipping, roller coating, or any other conventional method. The excess material is removed by a doctoring process using solid or air scrapers, squeeze rollers, or a size press. To improve the distribution of the transparentizer within the fibers of the paper and to displace the air in the voids, the paper is sometimes “wet packed,” that is, allowed to stand for a given period of time (from a few hours to a few days) and then passed through a drying oven either to remove the solvent vehicle or condense, cross-link, or polymerize the active ingredients in the transparentizer.

In situ polymerization of transparentized materials is done by heat, photo, or electron beam action immediately after impregnation in a continuing web pass.

The paper base provided for transparentizing is of great importance for achieving the best results, and although a wide variety of papers may be employed, those used in the diazo industry are limited to papers prepared from rags, cotton fibers, and chemical pulp. In the United States, the requirements for high tear and fold strength, as well as permanency, have led to the exclusive use of 100% rag base or mixtures of rag and sulfite

pulp with high rag fiber content. A typical specification for a 100% rag content base paper of 14 lb substance is:

Basis weight	13.3–14.7 lb/ream
Caliper	0.024–0.0026 in
Brightness	78–82
Bursting strength	27–30
Smoothness (Sheffield)	110–140
Fold endurance	
Before aging	
MD	500–800
CD	350–500
After aging	
MD	300–500
CD	225–300
Opacity	
Before aging	72–74
After aging	72–74
Tear strength	
MD	40–45
CD	43–50
Moisture	4.0–6%
Porosity (Geimer test)	3.5 cm ³ , min
pH	4.0–4.5

It should be noted that after transparentizing many of the properties change, and it is expected in general that tear and fold strength will be increased rather than decreased.

Natural tracing paper and transparentized rag paper are the two major types of translucent papers used as drafting media and as diazotype intermediates. Each has some advantages over the other and some disadvantages, which are worth mentioning because the world is passionately divided as to which is preferred.

Natural tracing paper is more transparent to light both by reflection and by transmission; this leads to better look-through and better reprint properties.

Natural tracing paper is also heavier in general (between 80 and 110 g/m²) and therefore is stiffer and handles better. However, because of its relatively short fiber consistency, it is more brittle and cracks easily; in addition, creases form readily upon handling and show prominently in reprints.

Natural tracing paper is more sensitive to atmospheric moisture and absorbs it, causing the paper to curl excessively because of expansion of the fibers and surface distortions.

Natural tracing paper accepts pencil and ink well, and because of its hard surface, the pencil and ink lines can be obliterated readily by physical means (e.g., with an eraser or a razor blade).

Transparentized rag base paper is more opaque to light; to increase translucency, the paper is kept at a low basis weight (between 50 and 70 g/m²).

Transparentized rag base paper has substantially better physical characteristics, because of its long fibers; it shows relatively high fold and tear strength values, is much less sensitive to humidity, and remains more dimensionally stable under a wide range of atmospheric conditions. Pencil and ink lines are also readily accepted, but eradication is more difficult.

Both types of base paper can be coated to overcome some of their limitations and are widely used throughout the world as drafting media and as substrates for diazo intermediates.

3.2.2 Two-Component Diazo Papers

In two-component diazo papers, both the aromatic diazo compound and the coupling component necessary to produce the azo dye image are present in the light-sensitive layer. In addition, to prevent a reaction between the diazo and the coupler prior to exposure and development, acids and/or acidic salts must be present; they create an environment in which the coupling reaction is inhibited.

After exposure, the diazo paper is subjected to an alkaline medium that neutralizes the acids and changes the environment to one in which the coupling reaction proceeds rapidly.

It can be seen that the chemical reactivities of the diazo compound and of the coupling component are of fundamental importance in determining whether the two can coexist in an acidic medium without reacting prematurely with each other. If the reactivities are too high, it will not be possible to stabilize the system against premature coupling, even at low pH values. If the reactivities are too low, it will take too long for the system to produce the azo dye even at high pH values.

Among the very large number of diazos and couplers that could potentially give azo dyes, only a few have been found to have the necessary chemical reactivities to be of practical use in two-component papers. We will review the specific diazos and couplers commercially used in Section 3.3.

The development of a two-component paper is carried out by raising the pH value of the diazo-coupler system until the azo dye formation is complete. This can be achieved by different methods.

Ammonia Development

The method most frequently used for developing two-component diazo papers consists in subjecting the exposed material to ammonia vapor; since the presence of water favors the coupling reaction, the ammonia gas is always mixed with some water vapor when in contact with the paper.

In practice, the development takes place in the developing chamber of a photoprinting machine, where the concentrations of ammonia gas and water vapor are controlled as well as the temperature and the contact time with the paper. During the initial stage in the development, the acids or acid salts are neutralized and subsequently, as the pH value of the paper rises rapidly, the diazo reacts with the coupler to give the azo dye in the image area; at the end of the development, when the paper is saturated with ammonia gas, the pH of the layer may reach a value over 13. Once the paper has been removed from its alkaline environment, the excessive ammonia tends to dissipate from the paper and the pH regresses toward lower values until an equilibrium is reached.

The residual ammonium salts in the layer tend to be from slightly acidic to slightly alkaline according to the type of acid used in the stabilization of the system.

Because the diazo paper remains dry during the entire ammonia development, it is often referred to as “dry developing paper.”

Ammonia fumes, above 25 ppm concentrations, are objectionable to breathe and in large concentrations can be harmful. For these reasons, considerable efforts have been

made to find other ways to develop two-component diazo papers. These efforts, however, have led to only modest commercial successes in two other types of development, which are reviewed below. However, thanks to great improvements in the concept, design, and construction of ammonia developing photoprinting equipment, and because of the high quality of two-component diazotype materials, the ammonia process has become the most practical and most widely used diazo process in the world.

Amine Development

A different way to develop two-component diazo papers consists in the application of an alkaline liquid to the surface of the paper. Theoretically, any solution of an alkaline chemical product, inorganic or organic, would be functional in neutralizing the acids in the diazo layer and in raising the pH value sufficiently to produce the azo coupling reaction. However, it was established at an early stage that aqueous solutions cause the azo dyes of two-component systems to bleed profusely, giving unacceptable blurred images. Focus was then turned to nonaqueous alkaline solutions, and it was found that when an amine solution is applied in a thin layer to the surface of a two-component diazo paper, development is achieved at an acceptable rate and the images are sharp and dense.

The C. Bruning division of Addressograph Multigraph Corporation (2) in the United States first proposed and commercialized a nonaqueous amine developing system. They called it pressure development because the application of the liquid to the paper was under pressure between rollers to reduce the amount of liquid applied to just enough to achieve full development.

Various amines have been proposed, but the ones that are mostly used are monoethanolamine, diethanolamine, and triethanolamine. The developing liquid has to be formulated to meet different requirements such as spreading, wetting, having low volatility, and having an extended shelf life. The following example of an amine developer is taken from U.S. Patent 3,446,620, published in 1969.

Diethanolamine	40%
Diethylene glycol	30%
4-Methoxy-4-methyl-pentanol-2	20%
Water	10%
pH	11.7

The amine development system, which in principle overcomes the drawbacks of the ammonia system, has itself so many limitations that it has not been widely accepted, so only a small proportion of the total amount of diazo paper is currently developed by this method. A comparison between ammonia and amine development shows that the overall quality of the prints is superior with ammonia development. This is because after development, the surface of the amine-developed paper remains alkaline, whereas the surface of the ammonia-developed paper loses its high alkalinity after the ammonia has evaporated. Most of the couplers and the decomposition products of the diazos tend to discolor more rapidly in an alkaline environment than in a neutral one. Moreover, their oxidation products are colored, which means that the background of an amine-developed print will, upon aging, yellow more rapidly than that of a similar ammonia-developed print. Because of the difference in pH value of ammonia- and amine-developed prints, the azo dye colors obtained are slightly different and in general are less bright and less dense with amine development. Although blue azo dyes of acceptable standard are easily obtained with amine development, black and brown azo dyes are much more difficult to achieve and

lead often to unacceptable results. Finally, after development with the amine solution, the liquid applied to the surface diffuses slowly in the substrate. This is possible when the substrate is porous as in the case of paper; with film products, the applied liquid cannot be absorbed satisfactorily by the impervious coating, and the surface consequently remains tacky for a long period of time. Even under the best conditions, amine-developed materials are more delicate to handle.

Thermal Development

Many attempts have been made over the years to create a diazo material whose development would be the result of the application of heat alone.

Most methods of diazo thermal development are based on the fact that upon heating, the pH value of a light-sensitive layer changes progressively to reach levels at which the coupling reaction takes place. The change in pH value is rendered possible by the ability of certain compounds to decompose at high temperatures with the liberation of ammonia or other substances of basic character.

Among the chemicals proposed for pH changes in thermal development are salts of strong bases and weak volatile acids, salts of weak bases and weak volatile acids, and ureas, thioureas, and their derivatives. In conjunction with these alkali-generating substances, it has also been proposed to use heat-decomposable acids and acid salts as stabilizers (3).

Another approach to thermal development has been to use a chemical that is not a coupler at room temperature but when heated to a given temperature decomposes into another chemical, which is a coupler (4).

The thermal developing diazo system is normally applied to the substrate from an aqueous solution containing all the functional chemicals (i.e., diazos, couplers, stabilizing acids, and alkali generators).

At the developing temperature, which is often above 130°C, alkali is generated, causing neutralization of the acidic stabilizers and formation of the azo dye image; simultaneously, the diazonium compounds start decomposing, since most diazonium salts are thermally unstable above a certain temperature. It follows that for such systems, it will be necessary to use a diazo compound of high thermal stability, a coupler of high coupling energy, and an alkali-generating agent that is stable at normal temperatures but decomposes rapidly and completely at the developing temperature.

While workable compositions could be formulated with the above-mentioned chemicals and within the constraints of the system, none have in practice led to commercially suitable materials because of many observed disadvantages, notably very poor shelf life, poor image density and quality, slow printing speed, and background discoloration.

To overcome the stability problems caused mostly by the intimate proximity of the chemicals, various suggestions were made to physically separate the alkali generator from the rest of the chemicals and bring them together by the action of heat. In one type of physical separation requiring a multiple coating technique, a wax layer isolates the diazo layer from the alkali-containing layer. Under heat, the wax melts, allowing the alkali to come in contact with the diazo layer and promote the coupling reaction.

In another type of physical separation, the diazo chemical, the coupler, and/or the alkali are encapsulated in microcapsules whose outer skin protects them from reacting at room temperature. Under the action of heat, however, the capsule skin breaks, to permit the coupling reaction to occur.

In another type of separation, the diazo, the coupler, and the alkali are chosen to be totally water insoluble; they are separately ground with a fusible material, dispersed

in an aqueous matrix, and coated as separate layers. Under heat, the fusible material melts, bringing all the reacting chemicals together. Such a method has the advantage of giving materials with good shelf life but, unfortunately, with poor densities and poor line definition.

A further type of physical separation consists in using the base paper as the barrier between the diazo chemicals and the alkaline developing agent. A solution of ammonia-generating salt is coated on the reverse side of the two-component diazo paper and subsequently overcoated with a gas barrier layer. Application of heat liberates ammonia gas, which cannot go through the gas-impermeable barrier layer and, therefore, must pass through the base paper to cause development of the material.

Thermal development of papers has stirred the imagination of a vast number of researchers, and hundreds of patents were taken on this subject. Although in principle, all the patents are valid in their teaching, in practice, none has led to a material that is entirely suitable commercially, either because of unacceptable shelf life or because of lower quality.

3.2.3 One-Component Diazo Papers

In one-component diazo papers, only the aromatic diazo compound, and various stabilizers, are present in the light-sensitive layer. The coupling component is contained in a separate aqueous developing solution, which is applied to the exposed diazo paper. On contact, the diazo and the coupler react to form the azo dye. Because the diazo paper is wet during the application of the developer, this system is often referred to by one of the terms “semiwet,” “semidry,” or “moist.”

The first one-component diazo paper, which was invented by the van der Grintens (5) in 1932, used a slightly alkaline developer solution to promote the azo dye formation.

Later, W. P. Leuch (6) established that with the use of higher coupling energy diazos, it was possible to obtain adequate development with a neutral or even slightly acidic developer solution.

In both acid- and alkali-type development, upon application of the developer, the azo dye formation must take place very rapidly and must be complete before the thin film of liquid dries up. Also of great importance is the need for the azo dyes formed to be insoluble in the developer, lest they tend to diffuse in the liquid film before it has completely dried, causing blurred images. It is said in such cases that the line “bleeds.” To be satisfactory for this process, the coupling activity of the diazo compounds and the couplers must be very high, and their reaction products must be water fast.

For the acid-type development, the diazo compounds must be of higher coupling energy than for the alkali-type development. There is an optimum pH value at which each diazo-coupler pair performs best; therefore, depending on the system used, the developer pH could vary between 4.5 and 11.5.

With increasing pH values, the shelf life of the developer decreases because oxidation of the coupling component is produced by alkaline conditions.

With decreasing pH values, the rate of reaction between the diazo and the coupler decreases, causing incomplete development. After alkaline development, the surface of the paper remains alkaline; a rapid discoloration of the print background takes place as a result of oxidation of the coupler and the light-decomposed diazo compound. Efforts to improve the background by the use of antioxidants have not been entirely successful; and of the two moist developing systems, only the neutral/acid one is now widely used.

From a practical point of view, a serious limitation of the one-component process is that to obtain different color papers, it is necessary to use different developers, whereas with the two-component process, different color papers are obtained with the same developer.

Under normal conditions, one-component papers require drying after the application of the aqueous liquid developers. To overcome this limitation, it has been suggested (7) that a very small amount of a very concentrated developer be applied; in such an instance, the paper emerges from the developer practically touch dry, without the need of heat to remove the excess water.

Of the four major development methods for diazo papers, thermal is the least used commercially. Each of the other three (ammonia, amine, and moist) has its advantages and drawbacks, and each has its place in industry.

The manufacturers of ammonia-developed papers have reduced the inconvenience and objections associated with the handling of ammonia by offering equipment designed to dispense ammonia only when needed or to use cylinders of compressed anhydrous ammonia requiring infrequent changes. In many cases, ammonia extraction has been eliminated by the use of ammonia-absorbing systems, and residual ammonia smell on the prints has been minimized by print vacuuming inside the machine before delivery.

The manufacturers of amine-developed papers offer convenience and low maintenance with extended shelf life developers.

The manufacturers of moist-developed papers have reduced the inconvenience of their system by offering equipment designed to dispense dry prints and to eliminate in some cases the need to clean the machine at the end of each working day.

Because of the greater versatility of the ammonia system over the moist one, which is translated into a greater choice of available materials and in many cases better quality, ammonia diazo papers are more widely used. This is particularly true in the United States, where more than 95% of all diazo materials are for ammonia development. In Europe and in some other parts of the world, the dominance of the ammonia process is not as great, and moist diazo materials enjoy some degree of popularity.

3.2.4 Intermediate Diazo Papers

Original drawings often need to be reproduced on a diazo paper many times, and to prevent their damage through constant handling, a diazo paper intermediate copy of the original drawing is made to be used exactly in the same way while the original drawing is stored safely away. Such an intermediate copy is also called the second original, submaster, or simply diazo reproduction intermediate.

The requirements of an intermediate diazo paper are many and start with the substrate, which needs to be translucent or transparent to UV light. We have seen in the preceding section on base papers that both natural tracing paper and transparentized rag-based papers, with or without some chemical pulp, meet the requirement of light transmission. These bases are all used in the manufacture of diazo intermediate papers.

The azo dye formed on diazo intermediates must be resistant to the passage of UV light to ensure the satisfactory reproduction of the original drawing. The azo dye must have a high absorption rate (actinic opacity) in the wavelength range emitted by the UV light sources. Yellow azo dye has the highest absorption rate, whereas blue azo dye has the lowest. Orange, brown, and red azo dyes are in between.

Additionally, the azo dye must have a high visual density; in this case, the blue azo dyes have the maximum visual density and the yellow ones the lowest. Therefore, since

both actinic and visual densities of the azo dyes are necessary, a compromise is often required, and intermediate diazo papers have azo dyes varying in shade between sepia and chocolate brown. Occasionally for some special application a black diazo intermediate is produced that has the maximum visual density but not the maximum actinic opacity. The primary function of a diazo intermediate is to act as a second original for the production of diazo copies; a secondary function, not less important, is to allow modifications of the original drawing by additions or deletions. To achieve this, it is necessary to erase or eradicate a part of the azo dye image and replace it by new pencil or ink lines. Since not all drawings require further corrections, it was found necessary to offer two different classes of diazo intermediate papers: those that are nonerasable and those that are easily erasable.

Nonerasable intermediates are available on natural tracing paper and on transparentized paper. On such materials the azo dye tends to penetrate within the fibrous structure of the substrate, and it cannot be removed mechanically (with an eraser or with a razor blade) without destroying part of the substrate. The azo dye can, however, be chemically destroyed (rendered invisible) by the action of chemical eradicators that contain strong reducing agents.

In erasable intermediates, a barrier layer is applied, between the light-sensitive layer and the substrate, to isolate the azo dye image from the base and allow its removal by mechanical means without affecting the substrate.

With natural tracing paper, a resin lacquer, applied from an aqueous or a solvent medium, prevents penetration of the light-sensitive chemicals in the paper. Such intermediates are often called lacquered tracing papers.

With transparentized papers, an impervious aqueous barrier layer is applied prior to the sensitized layer to prevent migration of the azo dye into the substrate.

Diazo lacquered tracing papers are popular in Europe, but not in the United States, whereas the opposite is true with diazo transparentized papers and in particular all-rag erasable transparentized papers.

3.3 CHEMICALS, AQUEOUS SYSTEMS

The preparation of a diazo paper consists primarily in the application to the paper of an aqueous chemical solution that contains the following compounds:

- One or more light-sensitive diazonium salts
- Zero or more coupling components
- Stabilizing agents
- Development accelerators
- Solution flow modifiers
- Auxiliary chemicals

Each of these classes of chemicals will be reviewed in detail.

3.3.1 Diazonium Salts

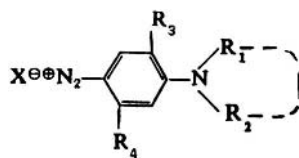
Many thousands of diazo compounds (8) have been synthesized and have at one time or another been mentioned in connection with the diazotype process. To be suitable for use in the preparation of diazo papers, a diazonium compound must meet a number of requirements. It must have adequate light sensitivity; it must be thermally stable enough to be

handled and stored safely; it must be soluble in water to a degree allowing its use. Moreover, its photolytic decomposition products must be colorless and must have a reasonable resistance to oxidation; it must have adequate coupling energy (not too high when used in two-component papers and sufficiently high when used in one-component papers); and it must give with specific couplers azo dyes of desirable shades and brightness and, preferably, of good light and water fastness. In addition, the diazonium compound must be easy to manufacture, ecologically acceptable, and relatively low in cost. With so many requirements, it is no wonder that out of the thousands of diazos listed in the literature, only very few (between one and two dozen) are currently in use for the manufacture of all diazo papers.

The useful water-soluble diazo compounds can be classified according to their structure, their light sensitivity, or their coupling reactivity. However, since we have already distinguished between two-component and one-component diazo papers, it would seem natural to consider the diazo compounds suitable for each type of material, remembering that those with low-to-medium reactivity are used in two-component systems and those with high reactivity are used in one-component systems.

Diazos Used for Two-Component Papers

The commercial diazonium salts used for two-component diazo papers all have the following structure:



where R_1 and R_2 could be chosen from the groups methyl, ethyl, propyl, butyl, isopropyl, benzyl, cyclohexyl, methoxy, ethoxy or be part of a ring, which could be morpholine, pyrrolidine, or piperidine; R_3 and R_4 could be chosen from hydrogen, chlorine, methyl, ethyl, methoxy, ethoxy, isopropoxy, and butoxy. X , an anion, could be chosen from chloride (zinc chloride double salt) bisulfate and sulfoisophthalate. The diazonium ion forms with the anion a stable salt that can be isolated as a crystalline yellow-to-orange solid.

The light sensitivity and the reactivity of the diazonium compound will be greatly affected by the choice of the different radicals attached to the aromatic ring.

For a specific diazonium ion configuration, the flammability and the thermal stability will be greatly affected by the choice of the anion that forms the diazonium salt. For the above-mentioned anions, the flammability decreases and the thermal stability increases when passing from the zinc chloride double salt to the bisulfate and to the sulfoisophthalate. In fact, it has recently been shown that some diazonium zinc chloride salts are too flammable or thermally unstable, and therefore too hazardous to be used in their pure form. The addition of a substantial amount (20–30%) of acid or inorganic salt diluent to these unstable diazonium zinc chloride salts renders them less hazardous and acceptable for practical use.

The following diazo compounds have a low-to-medium light sensitivity and are generally used in standard speed two-component blue, black, red, and sepia diazo papers:

1. 1-Diazo-4-*N-N*-dimethylaminobenzene chloride, zinc chloride; also used as the half-zinc-chloride salt (stabilized by mixing with 30% tartaric or citric acid), or as the 5-sulfoisophthalate salt

2. 1-Diazo-4-*N,N*-diethylaminobenzene chloride, zinc chloride; also used as the half-zinc-chloride salt (stabilized by mixing with 30% tartaric or citric acid), or as the 5-sulfoisophthalate salt
3. 1-Diazo-4-(*N*-methyl, *N*-hydroxyethyl)aminobenzene chloride, half-zinc-chloride; also used as 5-sulfoisophthalate salt
4. 1-Diazo, *N,N*-ethyl, *N*-hydroxyethylaminobenzene chloride, half-zinc-chloride
5. 2-Diazo-1-naphthol-5-sulfonic acid sodium salt

The following diazo compounds have a high light sensitivity and are generally used in fast or superfast two-component blue, black, red, and sepia diazo papers.

6. 1-Diazo-2,5-diethoxy-4-morpholinobenzene chloride, half-zinc-chloride (because of its flammability and relatively poor shelf life, this diazo is currently used only at 70% or lower strength; it is also used as the bisulfate salt at 70% strength or as the 5-sulfoisophthalate salt)
7. 1-Diazo-2,5-dibutoxy-4-morpholinobenzene, bisulfate (80% strength); also available as the half-zinc-chloride salt at 70% strength and as the 5-sulfoisophthalate
8. 1-Diazo-3-methyl-4-pyrrolidinobenzene chloride, zinc chloride
9. 1-Diazo-2,5-dimethoxy-4-morpholinobenzene chloride, half-zinc-chloride

Diazos Used for One-Component Papers

The following diazo compounds have high reactivity and are generally used in one-component diazo papers.

10. 1-Diazo-4-(*N*-ethyl-*N*-benzyl)aminobenzene chloride, half-zinc-chloride
11. 1-Diazo-2,5-dimethoxy-4-*p*-tolylmercaptobenzene chloride, half-zinc-chloride
12. 1-Diazo-2,5-diethoxy-4-*p*-tolylmercaptobenzene chloride, half-zinc-chloride (70% strength)
13. 1-Diazo-2-chloro-5-(*p*-chlorophenoxy)-4-*N,N*-dimethylaminobenzene chloride, half-zinc-chloride (70% strength)
14. 1-Diazo-2-chloro-5-(*p*-chlorophenoxy)-4-*N,N*-diethylaminobenzene chloride, half-zinc-chloride (70% strength)
15. 1-Diazo-3-chloro-4-*N,N*-diethylaminobenzene chloride, half-zinc-chloride
16. 1-Diazo-3-chloro-4-(*N*-methyl-*N*-cyclohexyl)aminobenzene chloride, half-zinc-chloride (70% strength)

It should be pointed out that not all the diazo compounds in one group have equal reactivity: some are considerably more active than others.

In a few cases, it is possible to use a one-component diazo in a two-component system by selecting a low-to-very-low reactivity coupler to form the azo dye, and a two-component diazo in a one-component system by using a strong alkaline developer.

Diazonium salts are relatively complicated chemicals to synthesize, and their cost is somewhat high. In addition, for safety as well as for environmental control reasons, more restrictions are placed on the use and disposal of certain classes of chemicals (e.g., zinc chloride), with the results that a smaller range of diazos are being manufactured today and, whenever possible, the zinc chloride salts are being replaced by bisulfate salts or sulfoisophthalate salts.

3.3.2 Couplers

Couplers are the main color-determining components of diazotype materials and, as in the case of diazonium salts, many thousands (9) have been synthesized and could theoretically be considered to form colored azo dyes.

To be suitable for use in the preparation of diazo papers, a coupler must meet a number of requirements: it must have sufficient reactivity to couple rapidly with the diazo compound to give an intensely colored azo dye, but not too rapidly (for this would cause premature coupling in two-component systems); it should be water soluble to a degree allowing its use, and compatible in solution with the diazo; it should be stable to light and oxidation; it should not absorb ultraviolet radiations in the region where the diazos are light sensitive. The azo dyes formed should be bright, intense with desirable shades, stable to light, and preferably waterfast. In addition, the coupler must be easy to manufacture, ecologically acceptable, and relatively low in cost.

As for the diazos, the existence of so many requirements has limited the choice of couplers currently used to just a few (between two and three dozen).

Couplers belong to the chemical classes of aromatic amines, phenols, phenol ethers, or aliphatic compounds containing active methylene groups. Of these classes, only a few hydroxy and polyhydroxy compounds of the benzene and naphthalene series, in addition to some compounds with active methylene groups, are of practical importance.

Rather than classifying these couplers according to their structure, we list them according to the dye color they generally give with most diazos.

Blue Dyes

The following couplers are used to give blue dyes in two-component diazo papers.

1. 2,3-Dihydroxynaphthalene-6-sulfonic acid sodium salt
2. 2,7-Dihydroxynaphthalene-3,6-disulfonic acid disodium salt
3. 2-Hydroxynaphthalene-3-carboxylic acid-3'-*N*-morpholinopropylamide
4. 2-Hydroxynaphthalene-3-carboxylic acid ethanolamide
5. 2-Hydroxynaphthalene-3-carboxylic acid diethanolamide
6. 2,3-Dihydroxynaphthalene
7. 1-Hydroxynaphthalene-4-sulfonic acid sodium salt
8. 2-Hydroxynaphthalene-3-carboxylic acid-*N*-diethylenetriamine, hydrochloride salt
9. 2-Hydroxynaphthalene-3,6-disulfonic acid sodium salt

Not all the couplers above have the same coupling energy or give the same shade of blue, and some are considerably more popular than others in practical applications.

Yellow-to-Brown Dyes

The following couplers are used to give yellow-to-brown dyes in two-component diazo papers.

10. Resorcinol
11. Diresorcinol sulfide
12. Resorcinol monohydroxyethyl ether
13. 4-Chlororesorcinol
14. 2,4,3'-Trihydroxydiphenyl
15. 2,4-Dihydroxybenzylamine, methane sulfonic acid salt, 60% strength

16. β -Resorcylic acid ethanolamide
17. 2,5-Dimethyl-4-morpholinomethylphenol hydrochloride
18. Catechol monohydroxyethyl ether
19. 3-Hydroxyphenyl urea
20. Cyanoacet-morpholide
21. 1,10-Dicyanoacet-triethylenetetramine hydrochloride
22. Cyanoacetamide
23. Acetoacetanilide
24. Acetoacet-*o*-toluidide
25. Acetoacet-*o*-anisidide
26. Acetoacet-benzylamide
27. 1,4-Bis(acetoacet-ethylenediamine)
28. α -Resorcylic acid

Not all the couplers above have the same coupling energy, and they can give a range of colors varying between pale yellow and dark maroon; only a few are used in large amounts, whereas most of the others are used as minor constituents of a more complex coupler system in diazo papers.

Red Dyes

The following couplers are used to give red dyes in two-component diazo papers.

29. α -Resorcylic ethanolamide
30. 4-Bromo- α resorcylic acid
31. 4-Bromo- α resorcylic acid amide
32. 4-Bromo- α resorcylic acid methylamide
33. 1-Phenyl-3-methyl-pyrazolone

Couplers Used in Developers of One-Component Diazotype Papers

It has been shown that the coupling energy of couplers suitable for the one-component diazo system must be extremely high, particularly in the case of the acid or neutral development. A single coupler meets all the requirements for this application and is therefore universally used; the azo dye colors obtained with it vary from dark magenta to greenish-black; quasi-black colors have also been achieved. This coupler is

34. Phloroglucinol

For one-component alkaline development, in addition to phloroglucinol, various couplers of high coupling energy, chosen among the couplers listed for two-component papers, are used; for instance, resorcinol is used for brown, 2,3-dihydroxynaphthalene for blue, and 1-phenyl-3-methyl-pyrazolone for red.

3.3.3 Auxiliary Additives

In addition to diazos, couplers, and acid stabilizers, diazotype preparations require special chemicals to facilitate the coating application and to optimize the different properties of the finished diazo paper.

To improve the quality of the azo dye image given by a particular diazo sensitizing solution, the diazo paper is often precoated before the application of the sensitizer, and the precoat itself is a preparation that requires a number of special chemicals. These chemi-

cals, which play a fundamental role in achieving the best results, are an integral part of the diazo paper technology.

Acid Stabilizers

Necessary to stabilize the solution against deterioration and to extend the shelf life of the diazo paper, acid stabilizers in the sensitizing solution serve to lower the pH to a level at which coupling is inhibited. Most frequently used are the following organic and inorganic acids: citric, tartaric, oxalic, boric, sulfuric, phosphoric, 5-sulfosalicylic, methanesulfonic, and *p*-toluenesulfonic; acetic and formic acids are used to stabilize the sensitizing solution only, since they are volatile and would be eliminated during the drying process.

An excess of stabilizing acid would tend to slow down the developing speed of the paper, whereas an insufficient amount would shorten the shelf life. Strong inorganic acids have a better stabilizing effect but can be used only in very small amounts; weaker organic acids allow a better compromise to be reached between shelf life and development rate.

Each particular acid stabilizer has also an effect on the shade of the azo dye and on the stability of the azo dye to atmospheric pH changes. Boric acid, which is a good stabilizer in one-component systems, must be used with caution in two-component systems, because it can substantially reduce the coupling activity of certain blue couplers.

Zinc Chloride

Zinc chloride has a special place in two-component sensitizing systems, because of its multiple advantageous effects. It has a stabilizing effect on the diazonium salts, and it also extends considerably the shelf life of the diazo paper; in addition, it often promotes faster coupling, increases the azo dye brightness, and minimizes the printing speed loss of the paper on aging. For these reasons, zinc chloride is included in practically all ammonia developing papers. Zinc chloride is not usually used in one-component sensitizing systems because it shows no specific benefit. It affects developer receptivity, and sometimes it even decreases the stability of the one-component diazo.

Stabilizing Salts

Some salts have a positive effect on improving the stability of the diazo paper, while other salts increase the resistance of the diazonium compound to thermal decomposition. One particular salt might be beneficial to one specific diazo and not to others, and this is what makes formulating diazo sensitizers so difficult. Among the salts most frequently used are aluminum sulfate, sodium sulfosalicylate, zinc sulfate, zinc *p*-toluene sulfonate, and the sodium salts of naphthalene mono-, di-, and trisulfonic acids. Some of these salts have also a solubilizing effect, which manifests itself in an improved compatibility of the diazo in the sensitizer.

Thiourea

It was discovered in the early days of diazo technology (10) that the incorporation of derivatives of thiocarbonic acid prevent rapid deterioration of the print background due to the action of air and light on the decomposition products of the diazo. Thiourea proved to be the simplest and most efficient of this class of compounds, and it has become a common ingredient of diazo layers. As a mild reducing agent effective in acidic conditions, thiourea counteracts print background yellowing; in addition, it facilitates dye formation during development and improves the brightness of the azo dye.

Thiourea has also some negative aspects: it reduces the stability of the diazo compounds in general, and it promotes precoupling with some blue couplers.

Solubilizers

Solubilizers are necessary to increase the compatibility of different chemicals in the sensitizing solution. Many diazonium salts have limited compatibility with certain couplers, particularly in the presence of zinc chloride, and give rise to insoluble dark tarry products that cause coating defects such as black or white spots. To prevent this situation, chemicals with solubilizing properties are incorporated in the sensitizer preparation; these compounds have either a general effect on all systems or a selective effect on a particular combination of a diazo and a coupler. The following are the main solubilizers used:

Caffeine is an effective solubilizer in both blueline and blackline diazo preparations, in two-component as well as in one-component systems.

Theophylline is a similarly effective solubilizer when couplers of the resorcinol family are present.

Caprolactam is a general solubilizer with strong effect.

Acetic acid, in addition to lowering the solution pH, has a solubilizing effect.

Alcohols such as ethyl alcohol and isopropyl alcohol can be used in moderate amounts as solubilizers.

Acrylamide was at one time a popular solubilizer, but because of the severe health hazard it presents, its use in diazo papers has been completely discontinued.

1,3,6–1,3,7-Naphthalene trisulfonic acid, a sodium salt, is also frequently used as a solubilizer in one-component and in two-component systems.

Development Promoters

To reduce to a minimum the dwell time of a two-component diazo paper in an ammonia-developing chamber, development must be as rapid as possible. Without the presence of traces of water, the coupling reaction between the diazo and the coupler would not take place; for this reason, the sensitized paper should have, after drying, a moisture content of between 3 and 5%. If the moisture content is below this range, the paper develops slowly; if it is above this range, the paper will spoil in a short time.

To retain moisture, humectants are frequently used. These are compounds such as ethylene glycol, diethylene glycol, triethylene glycol, glycerine, dipropylene glycol, and polyols; the amount and type of humectant affect the shade of the azo dye as well as the shelf life of the paper.

Other chemicals were also found to accelerate greatly the rate of development, but it is not clear why they have this effect. Among these chemicals, urea and its derivatives play an important role; widely used are urea, dimethyl urea, and 1-allyl-3- β -hydroxyethyl-2-thiourea, also known as AETH. In addition to promoting development, some of these compounds improve the compatibility of diazos and couplers; they also have a substantial effect on the azo dye shade.

Tetrahydrofurfural alcohol has occasionally been used as a development accelerator.

Flow Modifiers

Sensitizers and precoat solutions applied to paper must not only be chemically sound. They also must have the right physical properties to give the best results. Temperature, surface tension, viscosity, foam tendency, homogeneity, and other physical parameters are all important, and they must be adjusted to ensure that the solutions can be coated,

without problems, to give defect-free materials. As a consequence, many chemicals that act as flow modifiers are added either to the sensitizer or to the precoat. The following are among those frequently used.

Saponin

This natural product with spreading properties is an important ingredient of most diazo coating preparations. While used in only very small amounts, saponin increases greatly the uniformity of the liquid coating on the paper web before drying. Care should be exercised to avoid excessive solution agitation, because the chemical has a strong foaming tendency.

Wetting and Spreading Agents

These are used in conjunction with or as a replacement for saponin; they can be selected to have good compatibility and spreading properties and low foaming action. Particularly useful are the acetylenic glycols and the nonionic nonfoaming surfactants such as 3,6-dimethyl-4-octyne-3,6-diol. These chemicals must be used in very small amounts, otherwise they could cause penetration of the solutions into the fibrous structure of the base paper.

Antifoam Agents

Diazo solutions and precoat preparations containing dispersions of pigments and resins tend to foam when subjected to mechanical movement. During the coating operation, stirrers and pumps often introduce enough air to create foam problems. If foam is carried onto the paper, it causes coating streaks and other imperfections. One should minimize foam through the selection of nonfoaming systems. When foam does occur, antifoam agents should be used to eliminate it. Such chemicals must be selected carefully and used sparingly, since they themselves could be the source of white spot defects.

Wax Dispersions

These are used in precoats and in diazo solutions to lubricate the paper surface, hence to facilitate the handling of the diazo paper through the photoprocessing machines. The elevated temperature encountered in the ammonia-developing chamber of large machines softens the chemicals on the paper and could cause them to stick. High-melting-point waxes correct or reduce this problem.

Dispersing and antisetling agents are required to aid the dispersion of pigments in the solution and to prevent rapid sedimentation of the heavier particles of pigment.

Dyes

The print background of diazo papers contains slightly yellowish components resulting from the light decomposition products of the diazonium salts, their oxidation products, and the oxidation products of the couplers; this background discoloration increases from extended exposure to daylight.

To minimize any yellow cast and sometimes to tint the print background distinctively, dyes are added in minute amounts not only to the base paper but also to the coating solutions. The best compensating effects are obtained from mixtures of blue-violet and blue-green dyes or from single dyes generating both these hues. To be suitable, the dyes must also be water soluble, compatible with all the ingredients in the coating solutions, and lightfast.

Two of the most commonly used dyes are methyl violet and methylene blue; the first is blue-violet, and the second is blue-green. These dyes, however, do not have a

good stability to light or to pH changes, and other proprietary commercial dyes are often preferred.

Sometimes, to give the diazo paper a distinctive strong tint, larger concentrations of colored dyes are added to the sensitizer and to the backcoat solution; in such instances, the diazo paper becomes intentionally tinted in red, blue, green, or yellow.

Pigments

To maximize the quality of the azo dye image, insoluble inert materials of mineral or organic polymeric nature are added either to the sensitizing solution or, more frequently, to the precoat layer. Each particle of pigment acts as a receptor for the azo dye, which absorbs the incident light, and as a reflector for the nonabsorbed part of the incident light, to improve the total brilliancy of the print image.

The role of the pigment is also to create a more even surface for a finer image grain.

Among the many pigments that have been suggested are silicas, blanc fixe, uncooked rice starch and dextrans, aluminum oxides, silicates of calcium, magnesium, or aluminum, clays, and diatomaceous earths.

Particle size and surface area play an important part in the performance of the pigment, and those with particle sizes from 0.1 to 5 μm have given the best results.

Silicas and rice starch are among the most popular additives for azo dye enhancement. Colloidal silicas of low particle size and noncolloidal silicas of slightly larger particle size have a pronounced effect on image dye density, but care must be exercised when using them, because they increase solution viscosity and can cause coating difficulties. Rice starch produces less dye enhancement, but it can be used in large amounts with very little effect on coating preparation viscosity; it is preferred over silicas for one-component systems.

Binders

The role of binders is first and foremost to fix all the chemicals firmly to the paper and prevent them from coming off during processing and handling of the diazo paper. By forming a continuous layer, they also contribute to the azo dye enhancement and to the general quality of the coating.

Binders are used in the precoat layer, in the sensitizing layer, or in both. To be suitable, binders must be compatible with the chemicals used in each layer, have an affinity for the azo dye, be permeable to ammonia gas when used in two-component papers and to water in the case of one-component papers, and have a high softening point to prevent sticking problems during coating and processing through hot ammonia developing machines. In addition, they must be colorless and inert, have good binding properties for the pigments and other chemicals, and have good adhesion to the paper surface.

Appropriate binders that meet many of the requirements above are chosen from the class of natural proteins and the group of synthetic materials.

Among the most frequently used protein binders are casein, an animal protein soluble in the form of sodium or ammonium caseinate, and a vegetal protein extracted from soy that is also soluble in alkaline media.

Among the synthetic materials, every possible polymer and copolymer has been tested in diazotype preparations, and a vast number of synthetic resin dispersions and solutions have been suggested with various degrees of success. The most commonly used are stabilized emulsions of polymers and copolymers of vinyl acetate, acrylic acid, vinyl chloride, styrene, and vinylidene chloride. Also frequently used are aqueous solutions of polyvinyl alcohol, fully or partially hydrolyzed, polyvinyl pyrrolidone, and methyl-, hydroxypropyl-, and other cellulose ethers.

Developer Chemicals

In addition to the essential coupling components, developers for one-component diazo papers contain a variety of chemicals whose functions are to create the best environmental condition for the azo coupling reaction, to wet the surface of the paper evenly, to reduce the spreading or bleeding of the azo dye, and to extend the useful life of the developing liquid.

Alkaline developers contain alkalis or preferably alkaline salts to set and maintain the pH value of the solution between 9 and 12. The following are commonly used in varying combinations: sodium or potassium hydroxide, sodium carbonate, potassium tetraborate, trisodium phosphate, borax, potassium metaborate, and similar salts.

Neutral or slightly acidic developers contain acids and acid salts to set and maintain the pH value of the solution between 5 and 7. The following are commonly used in varying combinations: citric acid, sodium formate, sodium benzoate, sodium acetate, sodium tartrate, sodium citrate, and similar salts.

Sodium or potassium hydroquinone monosulfonate is generally used to reduce oxidation of the couplers, and so are sodium thiosulfate, sodium hydrosulfite, and thiourea dioxide.

Sodium lauryl sulfate, sodium isopropyl naphthalene sulfonate, sodium dibutyl sulfosuccinate, and similar surface active agents are used to lower the surface tension of the developer for improved wetting of the paper.

Sodium sulfate is sometimes used to reduce spreading of the azo dye.

Miscellaneous Chemicals

Some chemicals that do not fall into any of the preceding categories are used in diazotype preparations for specific purposes; they have a unique effect on a single property and are effective only in a particular set of conditions. Many of these chemicals are directed at controlling the azo dye shade. For example, magnesium chloride is frequently used to increase the brightness of some blue azo dyes, whereas sodium chloride, sodium monophosphate, and calcium chloride have a beneficial effect on the shade of blackline papers by eliminating the reddish hue of some blue azo dyes.

3.4 FORMULATIONS, AQUEOUS SYSTEMS

Diazo paper manufacturers offer a wide range of materials that differ according to color, developing method, speed, substrate surface appearance, and application.

For instance, diazo papers are available in black, blue, red, and brown; in standard, fast, and superfast speeds; on opaque papers of basis weight from 45 to 220 g/m² or on translucent paper; for ammonia, amine, moist, or thermal development; with matte or glossy surface; for simple drawing reproduction or for continuous tone photographic duplication; and for proofing purposes or for the permanent record, with an almost endless list of applications.

Each type of paper necessitates a special formulation, and since many of the features and properties of diazo papers are judged subjectively, no single formulation for a given type of diazo paper can meet everyone's requirements. There are as many formulation possibilities as there are permutations of the major constituents. The role of the diazo paper formulator is to develop a recipe that is as simple and as economical as possible that will fulfill as many of the basic requirements as possible and have the minimum number of drawbacks.

A formulator, when designing a diazo paper, will aim at achieving optimum results with regard to the following properties:

- Coating evenness
- Shelf life
- Color shade in full tones and halftones
- Printing speed
- Optical density and contrast
- Development rate
- Actinic opacity (for sepia intermediate papers)
- Reprint speed translucency (for sepia intermediate papers)
- Background appearance and resistance to daylight exposure
- Coating smoothness
- Resistance to rub-off
- Freedom from curl
- Azo dye water and light fastness
- Azo dye resistance to color shift at different pH values
- Ease of azo dye eradication (mostly for sepia intermediate papers)
- Acceptance of pencil and ink lines
- Ease of paper processing through photoprinting equipment
- Handling characteristics

In addition, the formulator will have to take into consideration features relating to the coating solutions, such as compatibility with chemicals, solubility, viscosity, pot life, ease of coating, and drying.

Not least, the formulator will select chemicals that are readily available, not hazardous to health, ecologically safe, and economically acceptable.

Considering the complexity of the problems facing a diazo paper formulator, it is no surprise that few comprehensive recipes have been published outside the patent literature. Most diazo formulations are the result of extensive trials by companies trying to obtain a technical advantage over their competitors, and this explains why they are kept confidential.

The different formulations given in this section have been developed and tested in the laboratory of Andrews Paper and Chemical Corporation, a New York-based company not involved in the manufacture of diazo papers but in the supply of raw materials, paper, and chemicals to the diazo industry worldwide. Some of the chemicals in the formulations are mentioned by their Andrews code references; a complete explanation of the codes appears in the appendix to this chapter.

3.4.1 Precoat Formulations

Precoat D258

This precoat is suitable for all ammonia-developed diazotype papers on opaque base paper; it is an alkaline precoat.

Mix with a high-speed stirrer or a homogenizer for 30 minutes

Water	5	liters
Coating aid 200	3.5	g
Ammonia	35	cm ³
Pigment 2820	493	g

Add under moderate stirring

8% Antifoam A emulsion	13	cm ³
5% Antifoam T dispersion	130	cm ³
Resin VP	500	cm ³
Dispersion F	152	cm ³
Water to make a total of	10	liters

The pH value of this precoat is adjusted and maintained between 8.5 and 9.5.

Precoat D265

This precoat is suitable for all ammonia-developed diazotype papers on opaque base paper; it is an acid/neutral precoat.

Mix with a high-speed stirrer or a homogenizer for 30 minutes

Water	5	liters
Citric acid	11	g
Pigment 2820	515	g

Add under moderate stirring

5% Antifoam T dispersion	160	cm ³
Resin VN	680	cm ³
Dispersion F	160	cm ³
Water to make a total of	10	liters

The pH value of this precoat is adjusted and maintained between 5 and 7

Precoat D278

This precoat is suitable for all amine-developed diazotype papers on opaque base paper.

Mix with a high-speed stirrer for 30 minutes

Water	5	liters
Pigment 65	1500	g
Pigment R	750	g

Add under moderate stirring

Resin VN	1	liter
Dispersion F	150	cm ³
Water to make total of	10	liters

Precoat D261

This precoat is suitable for all ammonia developed diazotype papers on opaque base paper; it uses a protein binder.

Mix with a high-speed stirrer or a homogenizer for 30 minutes

Water	5	liters
Pigment 2820	493	g

Add under moderate stirring

5% Antifoam T dispersion	130	cm ³
Binder IQ	175	g
Ammonia	35	cm ³

Stir for 30 minutes; then add

Resin VP	175	cm ³
Dispersion F	150	cm ³
Salicylic acid	4	g
Water to make a total of	10	liters

The pH value of this precoat is adjusted and maintained between 8 and 9.

In this precoat, the vegetal protein Binder IQ can be replaced by the animal protein Binder C.

Precoat D316

This precoat is suitable for all moist-developed diazotype papers on opaque base paper; it is an acid precoat.

Mix with a high-speed stirrer or a homogenizer for 30 minutes

Water	5	liters
Citric acid	15	g
Dye AC-1	1.5	g
Pigment 2820	250	g
Pigment R	500	g

Add under moderate stirring

5% Antifoam T dispersion	150	cm ³
Resin VN	600	cm ³
Dispersion F	250	cm ³
Water to make a total of	10	liters

The pH value of this precoat is to be adjusted and maintained between 5 and 7.

Precoat D274

This precoat is suitable to produce a glossy finish on all ammonia developed diazo papers.

Mix under moderate stirring to avoid foaming

Water	2.5	liters
Resin VG	6.7	liters
Resin VP	500	cm ³
20% Antifoam L dispersion	75	cm ³
Dispersion F	100	cm ³
Water to make a total of	10	liters

Precoat D260

This precoat is suitable as a barrier layer for erasable ammonia developed diazo intermediate papers.

Mix under moderate stirring to avoid foaming

Water	2.5	liters
Ammonia	10	cm ³
Dye AC-1	2	g
Resin PS-75N	3.5	liters
Antifoam L	10	cm ³
Antifoam M	6	cm ³

Resin VK-2	1.7	liters
Water to make a total of	10	liters

The specific gravity and viscosity of all precoats must be kept constant during the entire period of coating by the continuous addition of a compensating solution containing water, ammonia, and resins in the case of alkaline precoats, and water with resins in the case of acid precoats.

3.4.2 Sensitizer

Blueline Formulations

Blueline Ammonia, Standard Speed, D7128

This sensitizer is to be used in conjunction with precoats D258, D265, D261, or D274.

Mix with a high-speed stirrer, in sequence

Water at 60 to 65°C	7.5	liters
Pigment 2820	25	g
Citric acid	100	g
Thiourea	400	g
Caffeine	100	g
Accelerator ST	600	cm ³
Coupler 111	200	g
Isopropyl alcohol	125	cm ³
Diazo 48NF	225	g
Zinc chloride	500	g
Wetter 27	5	g
Water to make a total of	10	liters

A faster printing version of this system is obtained by reducing the amount of Diazo 48NF to 150 g.

Blueline Ammonia, Standard Speed, D7120

This sensitizer is to be used in conjunction with precoats D258, D265, D261, or D274.

The shade of blue obtained is less violet than with Sensitizer D7128.

Mix with a medium-speed stirrer, in sequence

Water at 50 to 55°C	5	liters
Citric acid	50	g
Stabilizer TT	150	g
Accelerator LM	500	g
Thiourea	400	g
Coupler 111	175	g
Isopropyl alcohol	100	cm ³
Diazo 49NF	180	g
Developaid	100	g
Zinc chloride	600	g
Saponin	2.5	g
Water to make a total of	10	liters

A faster printing version of this system is obtained by reducing the amount of Diazo 49NF to 120 g.

Blueline Ammonia, Fast Speed, D7137

This sensitizer is to be used in conjunction with precoat D258, D265, D261, or D274. The shade of blue obtained is neutral blue with little or no red hue; this color is often referred to as "blueprint blue" in the United States.

Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	5	liters
Sulfuric acid (concentrated)	15	cm ³
Stabilizer AB	150	g
Solubilizer HI	300	g
Caffeine	100	g
Coupler 144	125	g
Dipropylene glycol	300	cm ³
Diazo 59S	175	g
Zinc chloride	75	g
Stabilizer CD	150	g
Wetter 27	5	g
Water to make a total of	10	liters

A superfast printing version of this system is obtained by reducing the amount of Diazo 59S to 125 g.

Blueline, Fast Speed, for Amine Development, D7122

This sensitizer is to be used in conjunction with Precoat D278. Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	5	liters
Citric acid	100	g
Stabilizer TT	50	g
Acetic acid	100	cm ³
Thiourea	100	g
Caffeine	200	g
Coupler 144	100	g
Isopropyl alcohol	100	cm ³
Accelerator ST	400	cm ³
Diazo 54S	150	g
Stabilizer CD	400	g
Wetter 27	5	g
Water to make a total of	10	liters

A superfast printing version of this system is obtained by reducing the amount of Diazo 54S to 100 g.

Blueline Ammonia, Standard Speed, for Use without Precoat, D7131

This sensitizer does not require a separate precoat. Density enhancement is achieved by adding the pigment and the binder to the diazo solution; such a system is often called a pseudo-precoat sensitizer or a one-pot sensitizer.

Mix with a high-speed stirrer for 20 minutes

Water at 30 to 35°C	7.5	liters
Pigment 2820	400	g
Citric acid	100	g

Reduce stirring speed and then add in sequence

Caffeine	50	g
Thiourea	200	g
Accelerator ST	300	cm ³
Coupler 111	200	g
Diazo 48L	180	g
Zinc chloride	250	g
Wetter 27	5	g
Resin VC-1	1	liter
Water to make a total of	10	liters

A faster printing version of this system is obtained by reducing the amount of Diazo 48L to 120 g.

Blueline Ammonia, Standard Speed, for Tropical Climate for Use Without Precoat, D132

This sensitizer, which does not require a precoat, is advocated when the paper is to be used in an environment of high temperature and humidity and when it is established that the water for the sensitizer, the base paper, or any of the other chemicals, contains iron at a level higher than 25 ppm.

Mix with a high-speed stirrer for 20 minutes

Water at 60 to 65°C	5	liters
Pigment 2820	400	g
Citric acid	200	g

Reduce stirring speed and then add in sequence

Water at 60 to 65°C	2.5	liters
Thiourea	300	g
Accelerator LM	200	g
Coupler O	125	g
Diazo 48NF	140	g
Zinc chloride	250	g
Wetter 27	5	g
Resin VC-1	1	liter
Water to make a total of	10	liters

Blackline Formulations

Diazotype blackline papers have gained enormous popularity in the past decade, and although blueline paper is still used more than blackline paper in the United States and in Japan, this is not the case in most other parts of the world.

Many single couplers give with diazonium salts blue azo dyes, but from a practical point of view, not a single coupler gives a black azo dye. To obtain a black image, it is necessary to use a minimum of two couplers, one blue and one brown, and more often three or more couplers chosen from those giving blue, brown, or yellow azo dyes, preferably at the same coupling rate. Each auxiliary chemical in the formulation could have an influence on the shade of the azo dye or the coupling reactivity of the couplers, thus affecting the final blackline color.

The main objective is to achieve a neutral black in the full tones as well as in the halftones of a gray scale image.

Blackline Ammonia, Standard Speed, D9156

This sensitizer is to be used in conjunction with precoats D258, D265, D261, or D274.

Mix with a high-speed stirrer in sequence

Water at 50 to 55°C	5	liters
Pigment 2820	25	g
Stabilizer AB	400	g
Thiourea	500	g
Sodium monophosphate	200	g
Accelerator LM	250	g
Coupler O	95	g
Coupler 950	100	g
Isopropyl alcohol	100	cm ³
Developaid	100	cm ³
Diazo 48NF	250	g
Zinc chloride	425	g
Wetter 27	5	g
Water to make a total of	10	liters

A faster printing version of this system is obtained by reducing the amount of Diazo 48NF to 180 g.

Blackline Ammonia, Fast speed, D9102

This sensitizer is to be used in conjunction with precoats D258, D265, or D261.

Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Citric acid	200	g
Sulfosalicylic acid	50	g
Thiourea	200	g
Accelerator LM	400	g
Caffeine	100	g
Coupler 166	100	g
Coupler 670	18	g
Coupler 690	60	g
Isopropyl alcohol	100	cm ³
Dipropylene glycol	150	cm ³
Diazo 59S	250	g
Zinc chloride	300	g
Saponin	2.5	g
Water to make a total of	10	liters

A faster printing version of this system is obtained by reducing the amount of Diazo 59S to 200 g.

Blackline Ammonia, Superfast Speed, D9155

This sensitizer is to be used in conjunction with precoats D258, D265, or D261.

Mix with a medium-speed stirrer, in sequence

Water at 55 to 60°C	3	liters
Stabilizer AB	200	g

Citric Acid	100	g
Theophylline	150	g
Coupler 195	50	g
Coupler O	100	g
Coupler 620	25	g
Coupler 690	165	g
Coupler 950	30	g
Thiourea	400	g
Aluminum sulfate	125	g
Isopropyl alcohol	100	cm ³
Dipropylene glycol	200	cm ³
Diazo 59NF	200	g
Zinc chloride	250	g
Stabilizer CD	250	g
Wetter 27	5	g
Water to make a total of	10	liters

Blackline, Fast Speed, for Amine Development, D9152

This sensitizer is to be used in conjunction with Precoat D278.

Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Sulfuric acid (concentrated)	15	cm ³
Stabilizer AB	150	g
Solubilizer HI	300	g
Stabilizer CD	150	g
Caffeine	100	g
Coupler 144	100	g
Coupler 195	5	g
Coupler 690	250	g
Coupler 620	5	g
Coupler 950	15	g
Diazo 59S	200	g
Developaid	100	cm ³
Zinc chloride	75	g
Wetter 27	5	g
Water to make a total of	10	liters

Blackline Ammonia, Standard Speed, for Use Without Precoat, D9-144

This sensitizer is a one-pot sensitizer that does not require a separate precoat.

Mix with a high-speed stirrer, in sequence

Water at 55 to 60°C	7.5	liters
Pigment 2820	400	g
Citric acid	100	g
Thiourea	200	g
Theophylline	100	g
Allyl hydroxyethyl thiourea	100	g
Coupler O	70	g

Coupler 111	20	g
Coupler 950	110	g
Isopropyl alcohol	100	cm ³
Zinc chloride	250	g
Diazo 48NF	250	g
Wetter 27	5	g
Resin VC-1	1	liter
Water to make a total of	10	liters

A faster printing version of this system is obtained by reducing the amount of Diazo 48NF to 150 g.

Redline Formulations

Redline Ammonia, Standard Speed, D1220

This sensitizer is to be used in conjunction with precoats D258, D265, D261, or D274.

Mix with a medium-speed stirrer, in sequence

Water at 50 to 55°C	7.5	liters
Sulfosalicylic acid	150	g
Thiourea	500	g
Coupler RG	150	g
Isopropyl alcohol	100	cm ³
Developaid	100	cm ³
Diazo 49L	130	g
Zinc chloride	500	g
Saponin	2.5	g
Water to make a total of	10	liters

Redline Ammonia, Fast Speed, D1228

This sensitizer is to be used in conjunction with precoats D258, D265, D261, or D274.

Mix with a medium-speed stirrer, in sequence

Water 70 to 75°C	2	liters
Stabilizer TT	175	g
Caffeine	25	g
Coupler 480	35	g
Coupler 166	40	g

Add

Water at room temperature	6	liters
Thiourea	200	g
Allyl hydroxyethyl thiourea	200	g
Isopropyl alcohol	100	cm ³
Developaid	100	cm ³
Diazo 88	100	g
Zinc chloride	500	g
Saponin	2.5	g
Water to make a total of	10	liters

Bicolor Formulation*Blue/Red Ammonia, D374*

This formulation is to be used in conjunction with precoats D258, D265, D261, or D274.

With this system, the fully opaque markings of the original are reproduced in blue by the coupling reaction of Diazo 59S and Coupler 144, whereas semiopaque markings, such as pencil or gray ink, are reproduced in red by the coupling reaction of Diazo 67 with its own decomposition product.

Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Citric acid	200	g
Sulfosalicylic acid	75	g
Caffeine	150	g
Coupler 144	100	g
Accelerator LM	100	g
Thiourea	200	g
Isopropyl alcohol	100	cm ³
Dipropylene glycol	300	cm ³
Diazo 59S	175	g
Diazo 67	125	g
Zinc chloride	400	g
Wetter 27	5	g
Water to make a total of	10	liters

Browline Formulations*Browline Ammonia, Standard Speed, for Opaque Base Paper, D1080*

This sensitizer is to be used in conjunction with precoats D258, D265, D261, or D274.

Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Citric acid	300	g
Sulfosalicylic acid	50	g
Thiourea	300	g
Accelerator LM	200	g
Theophylline	50	g
Coupler RX	150	g
Coupler 950	50	g
Isopropyl alcohol	100	cm ³
Dipropylene glycol	100	cm ³
Diazo 49L	225	g
Zinc chloride	300	g
Saponin	2.5	g
Water to make a total of	10	liters

Browline Ammonia, Standard Speed, for Natural Transparent Base Paper, D1081

This sensitizer requires no precoat.

Mix with a high-speed stirrer

Water at 30 to 35°C	3	liters
Pigment 2820	250	g

Reduce stirring speed and add, in sequence

Ethylene glycol monobutyl ether	1.6	liters
Isopropyl alcohol	1.6	liters
Stabilizer TT	125	g
Sulfosalicylic acid	40	g
Boric acid	150	g
Diethylene glycol	200	cm ³
Thiourea	90	g
Coupler RX	160	g
Chlororesorcinol	120	g
Coupler 320	22	g
Diazo 88	500	g
Zinc chloride	450	g
20% Polyvinyl alcohol solution	2	liters
Dispersion F	50	cm ³
Water to make a total of	10	liters

Brownline Ammonia, Fast Speed, for Transparentized Base Paper, D1089

This sensitizer is to be used in conjunction with precoats D258, D265, or D261.

Mix with a high-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Pigment 2820	25	g
Citric acid	125	g
Thiourea	400	g
Theophylline	200	g
Coupler 603	300	g
Isopropyl alcohol	100	cm ³
Dipropylene glycol	200	cm ³
Diazo 59S	350	g
Diazo 88	200	g
Zinc sulfate	200	g
Wetter 27	20	g
Water to make a total of	10	liters

Brownline Ammonia, Fast Speed, Glossy Finish, for Transparentized Base Paper, D1088

This sensitizer is to be used in conjunction with Precoat D274.

Mix with a high-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Pigment 2820	25	g
Citric acid	200	g
Acetic acid	200	cm ³
Thiourea	100	g
Coupler 950	250	g
Coupler 603	120	g
Coupler 111	20	g
Isopropyl alcohol	100	cm ³
Ethylene glycol monobutyl ether	250	cm ³

Theophylline	100	g
Diazo 59S	175	g
Diazo 10	100	g
Zinc chloride	100	g
20% Polyvinyl alcohol solution	500	cm ³
Wetter 27	10	g
Water to make a total of	10	liters

Brownline Ammonia, Fast Speed, Erasable, for Transparentized Base Paper D1098

This sensitizer is to be used in conjunction with Precoat D260.

Mix with a high-speed stirrer

Water at room temperature	3	liters
Stabilizer TT	150	g
Pigment 2820	300	g
Pigment 65	1500	g

Reduce stirring speed and add in sequence

Isopropyl alcohol	2.5	liters
Ethylene glycol monobutyl ether	1	liter
Thiourea	75	g
Theophylline	150	g
Coupler 950	250	g
Chlororesorcinol	75	g
Coupler 320	10	g
Diazo 59S	250	g
Diazo 88	88	g
Zinc chloride	150	g
20% Polyvinyl alcohol solution	2	liters
Saponin	5	g
Wetter 27	25	g
Water to make a total of	10	liters

Filter through 100 μ m polypropylene filter bag before use.

Moist Formulations

Sensitizer, Fast Speed, for Alkaline Development, D1431

This sensitizer is to be used in conjunction with Precoat D316. The line color depends on the developer used; black and blue are the most popular.

Mix with a medium-speed stirrer, in sequence

Water at 30 to 35°C	7.5	liters
Sulfamic acid	15	g
Caffeine	60	g
Diazo 54S	180	g
Ammonium oxalate	35	g
Aluminum sulfate	35	g
Solubilizer 1,3,6–1,3,7	50	g
Wetter 27	5	g
Water to make a total of	10	liters

A superfast printing version of this system is obtained by reducing the amount of Diazo 54S to 125 g.

Alkaline Developers

To be used with Sensitizer D1431.

Dissolve in water to make one liter of developer:

Potassium carbonate	35	g
Boric acid	17	g
Sodium hyposulfite	4	g
Sodium benzoate	12	g
Tetrasodium pyrophosphate	0.25	g
Potassium hydroquinone monosulfonate	0.5	g
Thiourea dioxide	0.2	g
Wetter 27	0.5	g

Add to solution above different coupler systems for different colors.

For black:	Phloroglucinol	4.8	g
	Resorcinol	4.2	g
For blue:	Coupler 122	4.75	g
	Coupler dinol	2	g
For red:	1-Phenyl-3-methylpyrazolone	4	g
For yellow:	Coupler EBA	10	g
For brown:	Coupler Dinol	4	g
	Resorcinol	6	g
	1-Phenyl-3-methylpyrazolone	1.5	g

Sensitizer, Standard Speed, for Neutral Development, D2060

This sensitizer is to be used in conjunction with Precoat D316. The line color is black with a standard acid/neutral moist developer.

Mix with a medium-speed stirrer, in sequence

Water at room temperature	7.5	liters
Tartaric acid	100	g
Stabilizer TT	200	g
Caffeine	100	g
Aluminum sulfate	100	g
Diazo 72	150	g
0.5% Methyl violet solution	50	g
Water to make a total of	10	liters

Sensitizer, Fast Speed, for Neutral Development, D2058

This sensitizer is to be used in conjunction with Precoat D316. The line color is black with a standard acid/neutral moist developer.

Mix with a medium-speed stirrer, in sequence

Water, at room temperature	7.5	liters
Tartaric acid	100	g
Stabilizer TT	100	g
Diazo 72	20	g

Diazo 78	90	g
0.5% Methyl violet solution	50	cm ³
Water to make a total of	10	liters

A superfast printing version of this system is obtained by omitting the Diazo 72.

Sensitizer, Fast Speed, for Neutral Development, D2065

This sensitizer is a one-pot sensitizer that does not require a separate precoat. The line color is black with a standard acid/neutral moist developer.

Mix with a high-speed stirrer, in sequence

Water, at room temperature	6.5	liters
Pigment R	850	g
Tartaric acid	100	g
Boric acid	45	g
Sulfuric acid (concentrated)	5	cm ³
Caffeine	50	g
Diazo 72	40	g
Diazo 78	75	g
0.5% Methyl violet solution	50	cm ³

Reduce stirring speed and add

20% Polyvinyl alcohol solution	500	cm ³
Resin VW-2	500	cm ³
Dispersion F	50	cm ³
Water to make a total of	10	liters

Sensitizer, Standard Speed, Neutral Development for Transparentized Base Paper, D2059

This sensitizer is to be used in conjunction with Precoat D316. The line color is black with a standard acid/neutral moist developer.

Mix with a medium-speed stirrer, in sequence

Water, at room temperature	7.5	liters
Tartaric acid	50	g
Stabilizer CD	400	g
Stabilizer TT	25	g
Diazo 72	160	g
Diazo 87	160	g
Wetter 27	25	g
0.5% Methyl violet solution	75	cm ³
Water to make a total of	10	liters

A violet-brown color is obtained with this system when Diazo 72 is deleted and the amount of Diazo 87 doubled.

Acid/Neutral Developer for Blackline

Dissolve in water to make one liter of developer

Sodium formate	60	g
Sodium benzoate	15	g

Sodium tartrate	5	g
Potassium bitartrate	1	g
Phloroglucinol	4	g
Potassium hydroquinone monosulfonate	0.5	g
Wetter 27	0.5	g

A blueline version of this developer is obtained by replacing phloroglucinol by a mixture of:

Coupler 122	4	g
Coupler dinol	2	g

3.4.3 Backcoats

The application of a precoat and/or a sensitizer on one side of the paper causes the paper to curl strongly toward the coated side after drying. The cellulosic fibers on the surface of the paper first swell and expand upon contact with the aqueous solution, then shrink and contract upon removal of the water by drying; this creates an imbalance between the coated and uncoated sides of the paper which makes a curl. To counterbalance this effect and to produce a flat sheet, it is necessary to apply a backcoat to the back side of the paper.

The backcoat can have functions other than controlling the curl; it can be designed to increase the shelf life, to decrease absorption of a moist developer, to increase slippage through processing machines, to improve drawing properties of the back surface, or to color the back side of the paper for identification purposes. In one rare instance, a backcoat was designed to supply ammonia for the thermal development of two-component papers.

Whatever other function is to be served, the backcoat must, first and foremost, allow the production of a diazo paper that remains flat before, during, and after exposure and development.

The composition of the backcoat will depend on the degree of control required. Some base papers, such as natural tracing paper, tend to give very pronounced curl on coating, whereas other base papers, such as all-rag transparentized paper, show very little curl; opaque base paper for diazo coating gives in general a medium degree of curl.

The simplest possible backcoat is plain water. Although the liquid form is commonly used, steam has the same effect and is occasionally applied as a backcoat.

In general, the degree of back curl is proportional to the amount of water applied to the paper surface; it follows that if the minimum amount of plain water that can be applied still causes some back curl, it will be necessary to take further corrective action by the addition of various chemicals to the backcoat. It was established that glycols, humectants, zinc chloride, urea, and similar compounds relax the tension in the cellulosic fibers by moisture retention.

Backcoat formulations are arrived at by trial and error, varying first the amount of liquid applied and then the chemical composition.

A typical curl-control backcoat might contain one or more chemicals for the following effects:

To relax curl:	
Citric acid	0–3%
Zinc chloride	0–5%
Diethylene glycol	0–5%
Urea	0–5%

To increase curl:

Polyvinyl alcohol	0–1%
Stabilizer TT	0–0.1%

A backcoat to reduce the absorption of moist developer might contain

Polyvinyl acetate emulsion	0–5%
Polystyrene emulsion	0–5%
Polyvinylidene chloride emulsion	0–3%

A backcoat to facilitate print passage in processing machines might contain

Dispersion JB-1	0–3%

A coloring backcoat might contain one or more of the following chemicals:

Diazotint red	0–2%
Diazotint blue	0–2%
Diazotint yellow	0–2%

3.5 DIAZO FILMS

The making of intermediate prints on translucent or transparent materials plays an extremely important role in the safeguarding of original drawings and in the creation of new ones.

We have seen in Section 3.2.4 how diazo intermediate papers allow the production of “second originals,” which are used instead of the initial drawing to make copies and can be modified by the addition or deletion of further graphic information.

Paper, however, good as it may be, because of its fibrous structure, absorbs and diffracts light appreciably; it also has a limited physical strength, is often sensitive to atmospheric conditions, and is not dimensionally stable.

An early search to overcome many of the limitations of paper has led to the use of films as substrates for diazotype intermediates.

Even before World War II, cellulose acetate film was suggested for diazo coating. This film had excellent clarity and could be sensitized with solvent systems to give bright and dense images. Later, the film was made suitable for aqueous sensitizing and moist development by saponification of its surface, which rendered it hydrophilic. Although a great improvement in light transmission and in strength over paper resulted, this film had serious drawbacks: if unplasticized, the film was brittle and could crack or tear easily; if plasticized, the film was soft and the plasticizer exuded. Cellulose triacetate film, because of its improved physical characteristics, replaced for a while the earlier cellulose acetate film; but only in the middle of the 1950s, with the commercial availability of polyester film, was a major step forward made in the production of substantially improved diazotype films.

Polyester films are a range of biaxially drawn films made from polyethylene terephthalate polymer. The process for manufacturing polyester film involves first extrusion of the polymer through a slot die as a continuous sheet and cooling the sheet rapidly to prevent it from crystallizing. The next step consists of heating the film and drawing it equally in two directions at right angles; this has the effect of orienting the molecules of the polymer so that they lie in the plane of the film, but with no particular order in this plane. Finally the plane-oriented film is held under tension and heat set. These treatments

confer to the film's outstanding strength and a high degree of dimensional stability at room temperature. In addition, the film has good resistance to most common chemicals. Clarity, strength, and dimensional stability make polyester films an ideal candidate as a substrate for a diazo film intermediate. The following are typical physical and thermal properties of a general-purpose polyester film 25 μm thick:

Density	1.39 g/m
Tensile strength	$>1600 \text{ kg/m}^2$
Tear strength (Elmendorf)	$20 \text{ g} \cdot \text{cm/m}$
Fold endurance (MIT test)	$>200,000$ cycles
Elongation at break	60–110%
Refractive index	1.50–1.60 D
Water absorption after prolonged immersion	$<0.6\%$
Softening point	165°C
Melting point	$250\text{--}265^\circ\text{C}$
Coefficient of expansion	$27 \times 10^\circ\text{C}$
Coefficient of thermal conductivity	$4 \times 10 \text{ cal cm/m}^2 \text{ sec } ^\circ\text{C}$
Operational temperature range	-60 to 150°C
Change in dimensions with humidity per 10% change in RH at 20°C	0.007%

Changes in polymer formulation, surface treatment, and manufacturing conditions are made to produce variations in optical, physical, and surface properties for the different grades of polyester film available. In addition, polyester films for diazotype coatings are available in thickness gauges varying between 36 and 175 μm , with the most popular gauges being 50 and 75 μm for engineering films, and 75 and 125 μm for microfilms and microfiches. Although the thinner gauge general-purpose polyester films are quite clear, for the thicker gauges the films can present a certain degree of haze that is detrimental for certain applications (e.g., microfilm); special optically clear films are specifically made for these applications.

Polyester film is particularly inert to chemicals, with practically no absorption for water or solvents.

Whereas the fibrous structure of paper allows penetration of the coating solution within the fibers, in the case of polyester film, the coating solution remains on the surface of the film upon evaporation of the solvents, and the chemicals are deposited in the form of a coated layer; to ensure retention during handling, this coated layer must have cohesion and a good adhesion to the surface of the film. The inertness of polyester film frequently causes adhesion problems, and it is generally necessary to treat the surface of the film to promote the adhesion of coated layers. This problem has received much attention early, at the introduction of polyester film for diazo coating, and a number of imaginative solutions were offered. In particular, three different types of surface treatment have produced acceptable results.

1. *Chemical etching.* Polyester film is attacked by strong acids and strong alkalies, and when these are applied at the correct concentration and under the right conditions, the surface of the film is sufficiently modified to cause improved adhesion of subsequently applied resin layers.

Among the chemicals suggested for chemical etching are some phenols and chlorinated phenols, trichloroacetic acid (TCA) and chromosulfuric acid, sodium and potassium

hydroxide, hydrogen peroxide, and other oxidizing agents; of these, only TCA has found a wide application in this field. The TCA is dissolved at a concentration of 5 to 10% in a suitable solvent such as methyl ethyl ketone or xylene, applied to the film in a very thin layer, and dried to leave 1 to 2 g/m² of chemical.

It should be mentioned that this process presents handling hazards and causes severe corrosion of equipment, but it is nevertheless used when other alternatives are not available.

2. *Resin coating.* This method consists of replacing the polyester surface by a new chemically different surface with good adhesion properties. Various resins or mixtures of resins have been cited in the patent literature to improve adhesion to polyester film; they range from vinylidene chloride to acrylates, from epoxy to isocyanates, and from acrylonitrile to polyesters, with each system being most effective in a particular coating case.

Such a priming method was popular until polyester film manufacturers found a way to incorporate in their manufacturing procedure a step that results in a film with built-in adhesion promoting properties.

A resin composition is applied very thinly to the polyester film after it is cast, but before it is stretched to become biaxially oriented; the coated resin, which is now an integral part of the film surface, improves adhesion without affecting any other properties of the polyester film.

Special grades of surface-treated films are now commercially available and have found a large use in diazo coating.

3. *Corona discharge.* When polyester film is subjected to a corona discharge from high-potential electrodes, the polarity, frictional, and adhesion properties of the film surface change; possibly some polymer chain breakage takes place as well, with the formation of hydroxyl, carboxylic, and carbonyl groups, which would be responsible for adhesion promotion.

The treatment is performed either in line on the coating machine, prior to further coatings, or as a separate step, in which case the next coating must follow rapidly (within a few hours), so that the effect of the corona discharge is not lost.

The range of resins that adhere well to corona-pretreated film is more limited than the range of resins that adhere to polyester films pretreated at source by the manufacturer. For instance, although acrylic resins adhere well to both types of treated film, cellulosic ester resins adhere well only to the second type. In addition to the resins, the solvents in which they are dissolved play an important role in the level of adhesion reached.

3.5.1 Engineering Films

Diazo engineering films, also called diazo film intermediates, reproduction films, or simply diazo films, find their major application in the reproduction of engineering graphics, in the same way as diazo paper intermediates. They were born as a direct result of the shortcomings of the translucent intermediates, particularly the poor strength and lack of dimensional stability of the substrate and the poor definition of the image. Polyester film afforded all the superior properties of the base plus those conveyed by high-quality coatings. Diazo intermediate films have excellent tear strength and dimensional stability under varying temperature and humidity conditions; good handling characteristics; water, stain, and shelf resistance; and good printing and reprinting speeds. The prints have good line definition, visual density, and actinic opacity, with a clear background that resists oxidation and light

discoloration; the front and back surfaces of the film offer good drafting qualities. Finally, the diazo films possess prolonged shelf life before printing and, after printing, retain their performance for many decades.

With such features, diazo film intermediates frequently perform better than the originals they are meant to replace.

An extremely large range of diazo films are available worldwide. The vast majority of them are made for ammonia development, with a few rare instances of diazo films made for moist development and even fewer made for amine development.

The technical problems associated with the design of ammonia films are considerably simpler than those relating to making moist or amine development films. For an ammonia diazo film, the layer containing the diazo simply needs to be permeable to ammonia gas; appropriate resins give layers that meet this requirement in addition to all the other requirements expected from the layer.

In the case of moist and amine development films, a liquid is applied to the surface of the films. Whereas with paper this developing liquid can penetrate into the fibers of the paper and the fibrous structure can accommodate the different chemicals of the developer, with film, which is a totally nonabsorbing medium, the liquid must be absorbed by a thin resin layer containing the diazo chemicals, but without softening it prior to drying to the point at which damage by physical contact might occur during processing of the film. Very few resins come close to fulfilling the requirement for a suitable moist or amine development layer.

Diazo films are commercially available in different gauges. For a long time the gauge relating to the particular diazo film was that of the polyester film substrate, not that of the coated product. Today, manufacturers are less specific, and the gauge may be either that of the uncoated film or that of the coated film, which includes the thickness of the different layers applied. Because polyester film is relatively costly, the price of the finished product will greatly depend on the thickness of the film.

The thinnest diazo film gauge is 36 μm or 1.5 mils (thousandths of an inch); below this value, films are flimsy and difficult to handle, at both the manufacturing and the processing stages, and as finished prints.

Diazo films of 50 μm or (2 mils) are extremely popular; they have sufficient body and weight to be handled easily, and they offer economic advantage over thicker gauges.

For extra strength and dimensional stability, diazo films of 75 μm (3.1 mils) are chosen. Although they are more costly than the thinner gauges, their superior handling properties make them the choice of quality-conscious users.

Two thicker diazo films are also commercially available for special applications requiring extra rigidity, strength, or dimensional stability. They are 100 μm (4 mils) and 125 μm (5 mils). These thick films are used when true-to-scale reproduction of engineering drawings is called for; in these cases, printing is done on flatbed printing equipment to avoid the slight distortion caused by printing around the cylinder of conventional print machines.

Diazo films are also made with different surface finishes; the side of the film with the sensitized layer, which is generally considered to be the front side, can be matte, semimatte, deglossed or glossy; the first three types of finish contain pigments in decreasing levels, while the glossy finish contains no pigment at all. The choice of the surface finish depends on taste as well as on the intended function of the film. A matte surface is more suited for pencil and ink additions than a glossy surface, but it will also absorb and diffract light more, reducing look-through and reprint speed.

A deglossed surface has just enough pigment to make it appear hazy and has a very low degree of roughness; the infinitesimal surface irregularity allows better contact during printing between a smooth surface original and the diazo film. Upon exposure to ultraviolet light, the diazonium salt decomposes with liberation of nitrogen; the nitrogen gas is trapped between the original and the reproduction film, and if both films are perfectly smooth, they will be lifted apart by the gas, causing poor contact and therefore image blur. This, of course, takes place at a microscopic scale, which explains why a slight surface roughness accommodates the nitrogen gas formed and increases image sharpness.

The coating layer on the side of the diazo film opposite the sensitized side is called the backcoat. This side is, in general, matte, and is designed to have good drafting qualities. For a completely clear diazo film with maximum transparency, both sides of the film are glossy.

A drafting film is a non-light-sensitive material in which one or both sides of the film have a matte layer, which is conceived for its drafting properties.

For the same reasons mentioned in the case of diazo intermediate papers, diazo films are available in sepia or blackline colors; sepia covers a range of shades varying from yellow to chocolate brown, and blackline can appear through transmitted light very dark green, brown, or bluish. Sepia film is indicated for maximum UV absorption with reasonable visual contrast, whereas blackline is indicated for maximum visual contrast with reasonable actinic opacity. Blackline is also chosen when the prints have to be photographed for the generation of microfilms.

As second originals, diazo films are intended to be used for the production of multiple copies of the original. In this process, they are frequently exposed to ultraviolet light, which as we know degrades the azo dye and catalyzes the oxidation of the phenolic couplers and the decomposition products of the diazonium salts, thus causing increased background discoloration. The more the film is exposed to light, the greater the possibility for the image to fade and the background to discolor; this would result in lower visual contrast and poorer reproduction performance.

To overcome the problems above, diazo films with specific stability to ultraviolet light are made available; these are called UV-stable diazo films and are generally sepia.

Diazo films, irrespective of their color, are offered in two printing speed ranges qualified as standard and fast. Standard speed films are expected to have a higher actinic opacity than fast speed films because they use either slow speed diazonium salts, giving dense azo dyes, or a high concentration of fast speed diazonium salts. In both cases, the result is a slower printing speed.

However, the relationship between printing speed and actinic opacity is not always as indicated above: by judiciously selecting the diazonium salts and the couplers, fast speed films can show as good an opacity as standard speed films.

A number of diazo films are also made with an emphasis on a particular property or feature; among these films are erasable diazo films, nonreproducible blue-line diazo films, and bluebase diazo films.

Usually when a correction is needed on a diazo film, part of the layer containing the image is removed by physical or chemical action, leaving the clear polyester film visible underneath. Pencil or ink additions are applied to the reverse side of the film; for this purpose, it is common to print in reverse so that the image becomes right reading when looked through the back of the film.

In erasable diazo films, when the layer containing the image is removed by mechanical erasure or chemical eradication, instead of the clear polyester film, a matte layer, which

readily accepts pencil and ink lines, is bared underneath the removed image area. In this instance it is not necessary to print in reverse because the corrections and additions are made on the same side as the image. Erasable diazo films require that the diazo layer be coated on top of a drafting layer without intermingling with it.

Nonreproducible blueline diazo films give faint but distinctly visible blueline images that have such a low actinic opacity that they do not reproduce when reprinted on diazo papers. The blue image is used as a guide for outlining or modifying with pencil or ink lines some particular part of the image. Upon reprinting, only the drawn pencil or ink lines reproduce and are visible on the print.

The majority of diazo films show the image on a quasi-white background. Although dyes are used to tint the background, their aim is to mask any yellow cast caused by the chemicals or to give a more pleasing shade to the white background by making it appear bluish, greenish, or grayish.

In some instances, the background is deliberately given a pronounced blue color that does not affect any of the functional properties of the material. These films, described as bluebase diazo films, were popular in Europe because they simulated the color of traditional blue natural tracing paper and blue diazo lacquered paper, which existed before diazo films. They are still used in some parts of the world but are almost nonexistent in the United States.

3.5.2 Diazo Microfilms

The production of microfilms has long been an established practice in the world, stimulated by the need to preserve more and more records and the recognition that size reduction can lead not only to economies in storage space but also to the establishment of an organized record system having good accessibility, retrieval, and reproduction capabilities.

The originals that have to be microfilmed vary between small documents such as bank checks or printed pages of a book with dense black type on a clean reflecting background, to large engineering drawings sometimes having weak pencil lines on low reflectance paper.

The initial transference of graphic information to microfilm is done exclusively on silver halide films because of their high light sensitivity, which allows the formation of images through an optical reduction system at very short exposure times. To record the wide range of line densities, and thickness, the silver microfilm is designed to have a high contrast (a gamma value γ of more than 4) and a high resolution (fine grain); this last requirement follows from the fact that if the original is capable of separating 10 lines/mm, after an optical reduction of 20, the film should be able to have a resolution of 200 lines/mm for the enlarged image to be readable.

Diazo films, which because of their lack of sensitivity are not suitable for the initial recording of microimages from originals, have been found to be eminently suitable for the duplication of silver and other microfilms at lower costs per frame. The resolution of diazo microfilm is vastly in excess of that of silver halide films because the image is molecular instead of granular, and it can reach values in excess of 1000 lines/mm.

Positive working ammonia-developed diazotype films specifically intended for use in microreproduction systems are commercially produced by a relatively small number of companies in the world. Although in principle the manufacture of diazo microfilm is not much different from that of engineering film, in practice it involves more sophisticated

coating and converting equipment and a degree of cleanliness of a different order of magnitude. Since the smallest dust particle or impurity speck in the coating would be magnified to appear like a boulder on the reproduced image, such contaminants must be absent at every stage of the operation. The entire manufacturing and converting process must be conducted in a clean room air environment, which requires costly equipment and operational procedures.

Diazo microfilms are available in the same standard sizes as the silver halide microfilms they are duplicating; they are made in rolls, fiches, and aperture card microformats.

Rolls of diazo microfilm are supplied in widths of 16, 35, 70, and 105 mm and in varying lengths of 100 to 600 m. Diazo microfiches are supplied in standard size sheets of 105 mm $\times$ 148 mm or 180 mm $\times$ 240 mm and in packets of between 100 and 500 fiches.

The aperture card format is used mainly in engineering applications; in an aperture card, a single frame of 35 mm microfilm is mounted in a cutout window in the card.

Diazo microfilms are manufactured on different gauges of optically clear polyester film; these are 65 to 75, 100, 125, and 175 μ m. The thin and medium gauges are generally used for rolls or aperture cards, while the thick gauges are used for fiches.

The image color in diazo microfilms is predominantly blue or black. It is desirable to have high-density azo dyes both in the visual and in the actinic regions of the spectrum so that the film can be reviewed directly or reprinted onto other ultraviolet-sensitive materials. However, some diazo microfilms are manufactured that are not intended to be duplicated, and such films require only good visual contrast.

The properties of two commercial diazo microfilms are as follows:

Blueline Microfilm Suitable for Use in Readers Only

Maximum dye density	1.9 –2.0
Minimum background density	0.02–0.03
$\bar{\gamma}$	2.2 –2.3
$\bar{\gamma}$ ratio	0.7 –0.8

Blackline Microfilm Suitable for Use in Readers and for the Production of Further Generations of Diazo Duplicates

Maximum dye density	1.8 –1.9
Minimum background density	0.02–0.03
$\bar{\gamma}$	1.8 –1.9
$\bar{\gamma}$ ratio	1.4 –1.6

The γ ratio is the ratio of the $\bar{\gamma}$ of the second diazotype generation and the $\bar{\gamma}$ of the first diazotype generation.

Diazo microfilms fall in one of two groups: the first group is intended to be used as “work” or “use” copies and is generally found in libraries, record centers, or working environments. The value of these films lies in their being available for ready reference, and because of their frequent handling, they have a relatively limited life expectancy.

The second group is intended for use as medium- and long-term storage copies. Medium-term diazo microfilm is indicated for the preservation of records for a minimum of 10 years, when stored under proper conditions; long-term diazo microfilm is indicated for the preservation of records for a minimum of 100 years, when stored under proper

conditions. Of vital importance for satisfactory extended preservation is the control of light exposure, temperature, and humidity, and the protection of the film from dirt and impurities.

Diazo images, as is well known, show density changes after exposure to light; for equal exposures, the changes could be slight or severe depending on the chemicals used. In the case of diazo microfilms, density changes are critical, especially when copies are viewed in commercial readers for extended periods of time; this is because the microfilm is exposed not only to light but also to heat from the light source. The degree to which the image quality is retained under such usage conditions will determine the acceptability of the diazo microfilm. Light fading tests using a fadeometer are necessary during the formulating phase of diazo microfilms; low- and high-density areas of the image are placed in the fadeometer for a specific length of time (8 hours), and the changes in density are measured with a densitometer; the film is considered to be unacceptable if the optical density difference between maximum and minimum densities is less than 0.8.

3.5.3 Vesicular Films

The vesicular process is based on the use of diazonium salts in the same manner as the diazotype process, but the image generation relies on a light-scattering phenomenon, not on an azo dye formation.

The first commercial vesicular films were produced by the Kalvar Corporation (11) in 1959 on the basis of its U.S. Patent 2,911,299, but the principle of light-scattering photography was disclosed much earlier, by Kalle (12) in 1932 and by GAF (13) in 1955. In vesicular films, a thermoplastic resin layer containing a light-sensitive diazonium salt is applied very thinly to a transparent polyester film base. The thermoplastic layer consists of a random mixture of amorphous and crystalline polymer areas, which give the system a uniform index of refraction and make it appear transparent.

Upon exposure to ultraviolet light, the diazo compound in the thermoplastic layer photolyzes with release of nitrogen gas; when the exposed film is immediately thereafter subjected to heat, the gaseous nitrogen expands to form microscopic vesicles, usually spherical, with a high concentration of crystalline areas on the surface. These vesicles have an index of refraction different from the nonorganized surrounding media, hence they scatter the light incident upon them, causing an image pattern in the exposed areas. Figure 3.3 illustrates the vesicle formation. Since the light-sensitive diazonium compound is still present in the unexposed areas, a fixing step is required to obtain a permanent image. This is accomplished by exposing the entire film once more to ultraviolet light to decompose the residual diazo and allowing the nitrogen gas that is formed to diffuse slowly from the layer at room temperature.

In the exposed and developed vesicular film, image contrast is the result of incident light reflection, refraction, and transmission: when viewed in reflected light, the exposed areas in which there are light-scattering vesicles appear white, and the unexposed or clear areas appear dark. However, when viewed by transmitted light, the exposed areas, in which there are scattering vesicles, appear dark and the unexposed areas appear clear. It follows that the exposed and developed vesicular film gives a negative-mode image in all light transmitted applications—for example, when the image is projected on the screen of a microfilm reader.

A positive-mode image is also possible if a black layer is applied to the film underneath the diazo-resin layer; in this case, in reflected light, the black of the underneath

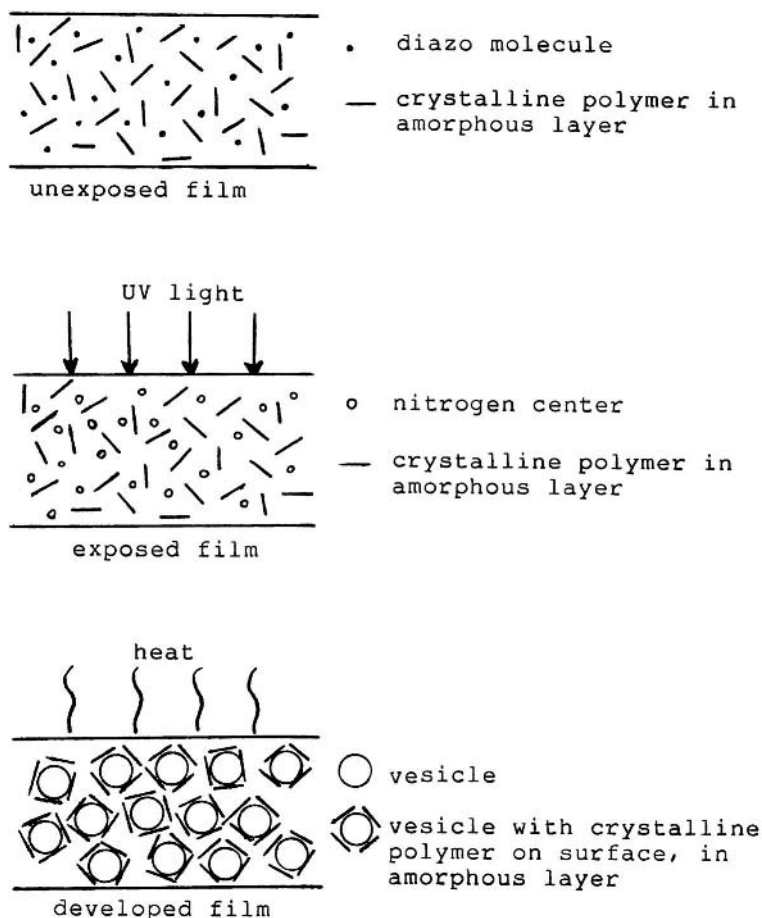


Figure 3.3 Principle of vesicle formation.

layer may clearly be seen through the unexposed transparent areas, whereas the exposed areas appear opaque white.

The sensitivity of vesicular films depends on the choice of the diazonium salt; it can vary with commercial diazo compounds between 350 and 420 nm. Exposure times are similar to those of engineering diazo films, but since the vesicular process is negative mode, images can already be obtained at very low exposure levels; as exposure time increases, more light-scattering centers are formed and a greater image density results. Above a certain point in the exposure scale, density is no longer directly proportional to the exposure time because the nitrogen gas generated diffuses during the prolonged exposure; the reciprocity law is valid over a range of exposure times from 0.05 to 60 seconds.

The temperature of the film during exposure should not be allowed to exceed 45°C, as this would result in premature development and a much higher rate of diffusion of the image-forming gas centers.

Development of the vesicular film is obtained by applying sufficient heat, for a short period of time, preferably by conduction or convection, to soften the resin layer and allow

the nitrogen gas nucleus to expand into a sizable vesicle, which can reach up to micrometers in diameter. Maximum development is a function of temperature and time, with temperatures ranging from 85 to 150°C and times ranging from milliseconds to a few seconds. Because the latent image decays rapidly through gas diffusion, development must follow immediately after exposure. After development and image formation, the residual unexposed diazonium compound is destroyed by the action of ultraviolet light, and the film is allowed to stand for several hours away from any source of heat to permit the gas diffusion process to take place.

To obtain reproducible results with so many parameters affecting the vesicular image quality, initial exposure and development temperature must be critically controlled in vesicular processing equipment, to a fraction of a second and to less than 1°C.

The resolution of vesicular films depends on the developing conditions but is in general higher than 150 lines/mm and can reach 500 lines/mm with special coating compositions. These high resolutions make vesicular film highly suitable for microfilm duplication.

Because they contain only the diazonium salt and no azo coupler, in a hydrophobic environment, vesicular films, when packed adequately, have a shelf life of many years, well in excess of diazo microfilms. In addition, a properly exposed, developed, and cleared vesicular image is stable under normal usage conditions and will withstand temperatures up to 90°C for extended periods of time; such a vesicular image will also show less density change after exposure to light than an equivalent diazo microfilm image.

The manufacture of vesicular films requires the same type of sophisticated equipment and clean environment conditions as diazo microfilms. Both types of film are made in the same formats and for the same applications; both are indicated for the preservation of records and for use as “work” copies. It appears, however, that diazo microfilm and in particular blueline diazo microfilm are gaining popularity for use as working copies, whereas vesicular film is still considered to be the standard for medium- and long-term storage duplicates.

3.5.4 Other Diazo Films

The simplicity and versatility of the diazo process has led to many other applications for diazo films; some are extensions of engineering film technology and others are extensions of diazo microfilm technology; all use polyester film base, require solvent coating, and are ammonia developed. Together, all other diazo films represent a commercially small volume of materials, either because of their limited industrial use or because, in some instances, better materials directed at the same application exist.

The following are the major specialty diazo films that can be found in the market.

Overhead Projection Films

The ability of diazonium compounds and coupling components to give different color azo dye images coupled with the possibility of producing these color images on optically clear film has given rise to the range of color films used in overhead projection. These films are designed to produce high-contrast color images on a completely clear background. By superimposing on the overhead projector two or more films, each with a different pattern in a different color, a composite multicolor image is progressively built up on the screen. Such a tool is extremely valuable in educational lectures, where most of the overhead projection films find their applications.

A careful selection of diazos and couplers allows the production of red, blue, yellow, brown, green, and black films. Each color film must be printed and developed separately, and the printing must be done in register to obtain perfect superimposition of the different images.

The production of overhead projection film is very similar to that of diazo microfilm, and although the magnification of the image on the projection screen is not as great as that of a microfilm on a reader screen, the same degree of cleanliness is required during all the manufacturing operations.

Color Proofing Films

Color proofing is a very well established technique in the printing industry.

Without entering into the details of color printing, it should be briefly explained that color photographs that are to be printed by a printing process are first converted into four screened color separation negatives, which are subsequently used to produce four printing plates: one for each of the primary colors (represented by cyan, magenta, and yellow), and one for black. Each plate is used to apply one of the four color inks to reconstitute the color photograph. The appearance of the final print will depend on the density and amount of each of the four inks applied during the printing process.

To assess the overall look of the final print, a color proof is made. There are different ways of producing this color proof and one of them is to make first a positive of each of the four color separation negatives and print the four positive films on a diazo film of the correct color, that is cyan, magenta, yellow, and black. The azo dye color of each diazo film must be of the exact density and hue to ensure that when the films are superimposed in register, the composite image will be a perfect color reproduction of the initial color image. It must be recognized that it is extremely difficult to find a combination of diazo and coupler that will give a good cyan or a good magenta color; it is easier to obtain a good yellow color. This limitation has prevented the wide use of diazo color proofing films; moreover, other, better materials are available.

Diazo Masking Films

One of the major requirements of an engineering diazo film is to produce an azo dye image of good actinic opacity, generally sepia, to give good reproduction prints on other diazo materials. In certain applications, an even greater opacity than that of an engineering film is necessary. In these applications, longer than usual exposures to ultraviolet light are needed to complete the photochemical reaction producing the image, as for instance, in the cases of photopolymerization or diazo-resin photomolecular rearrangement. The fabrication of printed circuit boards and the preparation of lithographic plates fall into such categories.

Silver halide films have proved most satisfactory for producing images having an almost total blocking power to ultraviolet light. Whenever possible, however, special diazo films, also called masking films, are made to substitute for silver halide films in these applications. The azo dye, which generally is yellow to orange, absorbs light almost completely between 320 and 450 nm but allows light of higher wavelengths (in the visible range) to pass through. This property is particularly useful when the masking film print is placed over an original drawing to view and check the image.

Diazo masking films are usually clear films of relatively thick gauges (125–175 nm) because of the need for high dimensional stability and accuracy in the printing step. The printing speed of such films is, most of the time, lower than that of diazo engineering

films because of the use of high concentrations of slow-to-medium-speed diazonium compounds.

The production of diazo masking films is similar to that of a clear diazo engineering film, but with a higher quality standard.

Adhesive-Backed Diazo Films

It is sometimes necessary in engineering graphics to transfer part of a drawing or image to another area and to make copies of this new composite drawing or image. It is also taken for granted that all the information to be reproduced is on translucent or transparent material. Adhesive-backed diazo films were specifically designed to meet the requirement of this particular kind of application.

A thin polyester film (25–35 μm) carries on one side a sepia or blackline reproduction diazo layer and on the other side an adhesive layer; this film is laminated to a silicone release paper to protect the adhesive layer during processing and handling. In usage, a print is first made on the adhesive-backed diazo film and developed; it is then cut out for transfer. The silicone release paper is peeled off the film, and the print is finally stuck down in its new place on the transfer film. The composite image is subsequently reprinted or photographed.

Manufacturers of diazotype materials do not in general involve themselves with laminating operations, and therefore they secure a film that carries the adhesive layer and is laminated to the silicone release paper. Their involvement consists in applying to the polyester film surface, from solvents, the diazo layer, which for all practical purposes is identical to the one used for diazo engineering films.

Opaque Diazo Films

All the diazo films we have seen so far were intended for use as reproduction materials. The base, of necessity, was either left clear or made slightly matte but still transparent to ultraviolet light. Visual contrast was always secondary to actinic opacity. For some applications, visual contrast is the most important criterion for the film, which is not meant to be reprinted but only viewed, or, in rare cases, photographed. Such films must have the densest possible image on the whitest possible background. They are usually intended for the production of display prints of engineering or architectural drawings.

The diazo light-sensitive layer is generally applied on one side of the polyester film base, while the opaque white layer is applied on the other side of the film. Diazos and couplers are selected to give optimal visual contrast and, in the case of a blackline, the most neutral tones. The whiteness and opaqueness of the back side of the film are achieved by the use of white pigments, such as titanium dioxide, bound by a resin matrix. Manufacture of opaque diazo film, printing, and developing are the same as for all other engineering diazo films.

3.6 CHEMICALS, SOLVENT SYSTEMS

The hydrophobicity of polyester film makes it very difficult to coat aqueous preparations evenly. In addition, water-soluble and water-dispersible resins do not possess all the properties required for a satisfactory coating layer, whereas many solvent-soluble resins do.

With almost no exceptions, all quality diazo films are produced from systems containing only organic solvents or a predominant amount of organic solvents. The di-

azos, couplers, and auxiliary chemicals used in the sensitizing layer must be soluble in solvents, such as alcohols, ketones, and glycol ethers; the resins and other ingredients must be soluble in the same polar solvents or in a mixture of polar and nonpolar solvents such as hydrocarbons. Pigments do not dissolve but should be easily dispersed in these systems.

3.6.1 Solvent-Soluble Diazos

Not all diazonium salts are soluble in the above-cited polar solvents. Some diazonium zinc chloride salts have sufficient solvent solubility to be used for film coatings, but most of the other have too low a solubility to be of practical use. Two zinc chloride diazos with acceptable solvent solubility are

1. 1-Diazo-4-*N,N*-diethylaminobenzene chloride; zinc chloride
2. 1-Diazo-2,5-dibutoxy-4-morpholinobenzene chloride, half-zinc-chloride

Among the diazo salts with increased solvent solubility are the borofluoride salts and the hexafluorophosphate salts. Both types of diazo salt are soluble in many polaric solvents at relatively high concentrations, the borofluoride salts being more soluble in alcohols and the hexafluorophosphate salts in ketones.

The commercially available solvent-soluble diazonium salts can be used for film coatings.

3. 1-Diazo-4-(*N*-ethyl-*N*-benzyl)aminobenzene borofluoride
4. 1-Diazo-2-ethoxy-4-*N,N*-diethylaminobenzene borofluoride
5. 1-Diazo-2,5-dibutoxy-4-morpholinobenzene borofluoride
6. 1-Diazo-2,5-diethoxy-4-morpholinobenzene borofluoride
7. 1-Diazo-4-*N,N*-diethylaminobenzene borofluoride
8. 1-Diazo-3-chloro-4-*N,N*-dibutylaminobenzene borofluoride
9. 1-Diazo-2,5-diethoxy-4-*p*-tolylmercaptobenzene borofluoride
10. 1-Diazo-3-chloro-4-(*N*-methyl-*N*-cyclohexyl)aminobenzene borofluoride
11. 1-Diazo-3-methyl-4-pyrrolidinobenzene borofluoride
12. 1-Diazo-2,5-dibutoxy-4-morpholinobenzene hexafluorophosphate
13. 1-Diazo-2,5-diethoxy-4-morpholinobenzene hexafluorophosphate
14. 1-Diazo-4-*N,N*-diethylaminobenzene hexafluorophosphate
15. 1-Diazo-3-chloro-4-*N,N*-diethylaminobenzene hexafluorophosphate
16. 1-Diazo-3-chloro-4-pyrrolidinobenzene hexafluorophosphate
17. 1-Diazo-3-methyl-4-pyrrolidinobenzene hexafluorophosphate

3.6.2 Solvent-Soluble Couplers

Many of the couplers that are soluble in water and are extensively used in aqueous diazo coatings are not soluble in solvents; such couplers include the sodium salts of dihydroxynaphthalene sulfonic acids, which are used for blue-line and black-line papers.

Other couplers that have little solubility or are totally insoluble in water are highly soluble in solvents and are most suitable for diazo film coatings.

A few couplers are soluble in both water and solvents.

The following commercially available solvent-soluble couplers can be used for film coatings.

Blue Couplers

1. 2,3-Dihydroxynaphthalene-6-sulfonic acid
2. 2-Hydroxynaphthalene-3-carboxylic acid ethanolamide
3. 2-Hydroxynaphthalene-3-carboxylic acid diethanolamide
4. 2,3-Dihydroxynaphthalene
5. 2-Hydroxynaphthalene-3-carboxylic acid-2'-methylanilide
6. 2-Hydroxynaphthalene-3-carboxylic acid-2'-methoxyanilide
7. 2-Hydroxynaphthalene-3-carboxylic acid α -naphthylamide
8. 2-Hydroxynaphthalene-3-carboxylic acid-3'-nitroanilide
9. 2-Hydroxynaphthalene-3-carboxylic acid-2'-ethoxyanilide

Yellow Couplers

10. Catechol monohydroxyethyl ether
11. *m*-Hydroxyphenylurea
12. β -Resorcylic acid
13. Bis(2,1-dimethylethyl)5-methyl-4-hydroxyphenyl thioether
14. Phenyl phenol
15. *p*-Dihydroxyphenyl thioether
16. Cyanoacetamide
17. Cyanoacet morpholide
18. Acetoacet benzylamide
19. Acetoacetanilide
20. Acetoacet-*o*-toluidide
21. Acetoacet-*o*-anisidide
22. Acetoacetoxyethyl methacrylate
23. 3,3'-Methylene bisacetoacetanilide

Brown Couplers

24. Resorcinol
25. 4-Chlororesorcinol
26. 4,6-Dichlororesorcinol
27. Methyl resorcinol
28. Diresorcinol sulfide
29. Diresorcinol sulfoxide
30. β -Resorcylic acid ethanolamide
31. Resorcinol monohydroxyethyl ether

Red Couplers

32. α -Resorcylic acid
33. α -Resorcylic acid ethanolamide
34. 1-Phenyl-3-methyl-5-pyrazolone
35. 4,4'-Methylene bis(3-methyl-1-phenyl-5-pyrazolone)
36. 4-Bromo- α -resorcylic acid
37. 4-Bromo- α -resorcylic acid amide
38. 4-Bromo- α -resorcylic acid methylamide

3.6.3 Auxiliary Solvent-Soluble Additives

Solvent diazo preparations for film coatings, like aqueous ones for paper coatings, require in addition to the diazos and couplers special chemicals to promote shelf life, development, background stability, and other properties. Many of these chemicals are the same as those used in aqueous systems because they are sufficiently soluble in solvents; some are suitable for use in solvent systems only (e.g., the solvent-soluble resins).

Acid stabilizers are necessary to ensure the stability of the diazo solution as well as to extend the shelf life of the film. The same acids used in aqueous diazo solutions can be used for solvent ones. In addition, acids are used as catalysts for cross-linking of thermosetting resins incorporated in the sensitizing coating or applied as separate coatings on the front or back of the film. Strong acids are preferred over weak acids because they can be effective in much smaller amounts. Among the most commonly used acids are 5-sulfosalicylic acid and *p*-toluene sulfonic acid.

Zinc chloride and thiourea are used for the same reasons as in diazo papers except that in general their levels are much lower in diazo films.

Stannic chloride, which cannot be used in aqueous diazo systems because it causes precipitation of the diazo, can be used in solvent because the diazo stannic salt is soluble in this medium. Solubilizers are very seldom necessary because few compatibility problems arise in solvents.

Development promoters are useful, and those mentioned for diazo papers, which are soluble in solvents, such as allyl hydroxyethyl thiourea and caprolactam, are frequently used. Humectants, like polyglycols, improve development but must be used only in moderation because their action tends to soften the resin layer adversely.

Coating aids such as wetting agents and defoamers, which are so important in aqueous coatings, are very rarely used in solvent coatings, since their effects on the coating performance of the solution are secondary to those of the solvents themselves.

Dyes play similar roles in diazo films and diazo papers. They are chosen for their solvent solubility and for their ability to mask the yellow cast in the print background. Methylene blue and methyl violet are two common dyes that are sometimes used in film coatings, but their sensitivity to pH changes and to ultraviolet light reduces their effectiveness; commercially available proprietary dyes are often required. Occasionally, blue dyes are used to give a distinct blue tint to the diazo film background, and they can be added either to the front coat or to the backcoat with similar results.

In addition to diazos, couplers, and other additives used in the sensitizer, three categories of chemicals are of critical importance for formulating film coatings: solvents, resins, and pigments.

Solvents

The choice of solvents affects the degree of solubility of each of the chemicals, as well as the viscosity, flow, and wetting properties of the solution, the evaporation rate of the system, the level of adhesion of the coated layer to the polyester film surface, and the overall physical quality of the finished product.

The solvents in film coatings are selected from the groups of alcohols, ketones, glycol ethers, and hydrocarbons. Table 3.1 lists these solvents with their main properties.

Low-boiling solvents have in general better solubility properties than high-boiling solvents, and they give lower resin solution viscosities. However, they evaporate too

Table 3.1 Properties of Solvents Used in Film Coatings

Solvent	Molecular weight	Specific gravity at 20/20°C	Boiling point range °C at 760 mm Hg	Evaporation rate (vs. but- Acet = (1)	Flash point tag, closed cup (°F)	Explosive limits (vol % in air)	
						Lower	Upper
Methyl alcohol	32.04	0.793	64–65	3.5	54	6.7	36.0
Ethyl alcohol, anhydrous	46.07	0.792	74–80	1.9	54	3.3	19.0
Ethyl alcohol 95%	46.07	0.812	74–80	1.7	58	3.3	19.0
Isopropyl alcohol anhydrous	60.09	0.787	82–83	1.7	53	2.0	12.0
Isopropyl alcohol 91%	60.09	0.818	79.7–80.7	1.6	61	2.0	12.0
<i>n</i> -Butyl alcohol	74.12	0.811	117–118	0.46	97	1.2	10.9
Acetone	58.08	0.792	55.5–56.5	7.7	–4	(100°C) 2.6	(100°C) 12.8
Methyl ethyl ketone	72.10	0.806	79–80	4.6	16	1.8	10.0
Methyl isobutyl ketone	100.16	0.802	114–117	1.6	60	1.2	
Ethylene glycol methyl ether	76.1	0.965	123.5–125	0.5	102		
Ethylene glycol ethyl ether	90.1	0.931	134–136	0.2	110		
Ethylene glycol <i>n</i> -butyl ether	118.2	0.902	169–172	0.1	143		
Ethylene glycol methyl ether acetate	118.2	1.005	140–147	0.2	120		
Toluene	93.13	0.870	110–111	1.5	45	1.2	7.0
Xylene	106.16	0.869	138–140	0.75	83	1.0	7.0

quickly before coating and during the drying process, causing viscosity changes in the solution and possible surface defects or adhesion failure. High-boiling solvents give high resin solution viscosities, which may make coating difficult, and they require higher drying temperatures; possible solvent retention after drying may cause softening of the layer.

Alcohols are good solvents for the diazo chemicals but are often poor solvents for the resins; the opposite is frequently the case with ketones and glycol ethers. Hydrocarbons are generally poor solvents for both the diazo chemicals and the resins, but in small amounts they have beneficial effects on the flow properties of the solution.

Because of the conflicting behaviors of the different solvents in relation to the various needs of the diazo system, it is very unusual to use a single solvent in a film coating solution. Mixtures of solvents are more common, with each solvent contributing one aspect of the total package requirement.

Drying conditions and application methods also determine the choice of solvents. Coating machines with high drying capacity allow the use of a greater amount of higher boiling solvents than machines with limited drying capacity or low oven temperatures. Multiple reverse roll coating applications require lower viscosity solutions than applications with a single roller followed by a wire wound rod metering device.

From a practical point of view, a mixture of 50% methyl alcohol and 50% acetone, which is frequently used in film coatings, can be considered to be a low-boiling solvent blend with excellent solvent power, giving low-viscosity solutions and having a very fast evaporation rate.

A mixture of 40% ethyl alcohol, 40% methyl ethyl ketone, 10% ethylene glycol monoethyl ether, and 10% xylene can be considered to be a medium-boiling solvent blend; such a mixture or similar ones are commonly used as general-purpose resin solution blends for wire wound rod metering coating systems.

Mixtures with predominantly high-boiling solvent blends are used only exceptionally.

The use of solvents in film coatings carries a severe fire and explosion risk, which should not be ignored or minimized. The flash point of a solvent is a measure of its flammability, and the lower the flash point, the greater the flammability risk. Table 3.2 relates the flammability risk to the flash point of liquids, or mixture of liquids or liquids containing solids in solution or in suspension.

The use of flammable volatile liquids also involves the risk of explosion when the concentration of solvent vapor in air is between a lower and an upper flammability limit; in this range, the application of a flame or spark of sufficient thermal intensity can ignite the vapor–air mixture and cause an explosion.

Table 3.2 Flammability Risk in Relation to Flash Point and Initial Boiling Point of Liquids

Flammability risk	Flash point, closed cup	Initial boiling point
Very high	<23°C (73°F)	≤37.8°C (100°F)
High	≥23°C (73°F)	≤37.8°C (100°F)
Medium	≥37.8°C	<61°C (141°F)
Low	≥61°C	<93.4°C (200°F)

It can be seen from Tables 3.1 and 3.2 that low-flash-point solvents, such as acetone and methyl alcohol, present the highest fire and explosion hazard, whereas high-flash-point solvents, such as the glycol ethers, have reduced risks.

A solvent-coating film operation requires extraordinary safety measures: all electrical equipment must be explosion proof, and all personnel must be thoroughly trained in the handling and use of flammable liquids. It is mainly for these reasons, and because costly special equipment is required, that the manufacture of solvent-coated products is limited to a much smaller number of companies than the manufacture of diazotype papers from aqueous solutions.

With the enhanced consciousness of health hazards and environmental pollution by volatile solvents, the use of many solvents has been restricted or even banned in some parts of the world; reformulating efforts aimed at the use of less hazardous solvents are constantly being made.

Resins

Resins are indispensable in binding the diazo chemicals or the pigments into a coherent, continuous film layer with good flexibility, hardness, and adhesion to the polyester base. The ideal resin layer must also be colorless, non-UV-absorbing, and permeable to the developing media (ammonia gas or liquid developer); it must have a high softening point, and it must be water insoluble, light stable, and resistant to oxidation. Resins must be easily soluble in the solvent blends chosen and must give reasonable viscosities at the required concentrations. Some resins must give crystal clear coatings (e.g., when intended for use in microfilm), some must be extremely hard (e.g., for use in drafting film), while others must be able to soften under heat (e.g., for use in vesicular film).

Few single resins, if any, meet all the different requirements of the various film applications, and a particular resin coating often consists of two or more resins, each contributing some specific property.

Thermoplastic as well as thermosetting resins have been used in film coatings. Thermoplastic resins are preferred for the diazo sensitizing layer because they are more permeable to ammonia gas; thermosetting resins are often selected for drafting films because of their final hardness.

Among the various thermoplastic resins available, the following classes of resins are the most frequently encountered in film coatings.

Polyvinyl Acetates. These resins give layers of good flexibility and adhesion but of relatively low softening point; the layers have also a good gas permeability. Free hydroxyl groups in the resins allow cross-linking and hardening of the layer. Many grades with good solvent solubilities and a wide range of viscosities are available.

Polyvinyl Butyrals. These resins give layers of good flexibility and adhesion with higher softening points than the polyvinyl acetates, but with lower gas permeability; free hydroxyl groups allow some degree of cross-linking. These resins are rarely used in diazo layers but are frequently used, with other resins, in drafting layers.

Polyvinyl Acetate and Polyvinyl Chloride Copolymers. These resins combine the properties of the two classes of polymers; they are sometimes used to improve adhesion to polyester film.

Cellulose Acetates. These resins have a high softening point, excellent clarity, good flexibility when properly plasticized, and good gas permeability, but unfortunately poor adhesion to the polyester film surface. They have an acceptable adhesion level to natural tracing paper. Cellulose acetate resins are easily saponified by strong alkalis; this

property has been utilized to render the surface of cellulose acetate layers water receptive for sensitizing or for the absorption of moist developers. These resins are mostly used in the preparation of moist developing diazo films and natural tracing intermediates.

Cellulose Acetate Propionates and Butyrates. These two classes of cellulosic ester resins are prominent in film coatings because they singly meet the greatest number of requirements for good results. They are clear and flexible, have adequate hardness and softening points, offer acceptable solution viscosity at the right concentration for diazo sensitizers, and have good adhesion, good binding properties, and good gas permeability. Their single main drawback is their tendency slowly to hydrolyze under the influence of strong acids and liberate unpleasant-smelling propionic or butyric acid; the butyric acid odor is found to be more objectionable than the propionic acid one, and as butyrates are more easily hydrolyzed than propionates, their use is also less recommended.

Cellulose mixed acetate esters are particularly popular for diazo film layers; they are manufactured by Eastman Chemical Corporation in the United States and are available in a number of grades, which vary according to the molecular weights, solubility characteristics, and viscosities. Three cellulose ester resins are commonly used in diazo film coatings:

Eastman Cellulose Acetate Propionate, grade 482-0.5

Eastman Cellulose Acetate Propionate, alcohol-soluble grade 504-0.2

Eastman Cellulose Acetate Butyrate, grade 381-0.1

A special type of thermoplastic resin is required for diazo vesicular films; such a resin must be sufficiently rigid and sparingly permeable to gas, and must exhibit some gas diffusivity. Four groups of resins are often cited in vesicular films:

Polyvinylidene chloride resins

Polyacrylonitrile and polymethacrylonitrile resins

Polystyrene resins

Epoxide resins

Among the thermosetting resins available, the following classes of resin are frequently used in film coatings.

Amino-Formaldehyde Resins. These urea-formaldehyde and malamine-formaldehyde resins, modified or unmodified, often are used as self-cross-linking resins or as cross-linking agents either for alkyd-type resins or for resins containing reactive groups such as free hydroxyl groups in polyvinyl acetates or polyvinyl alcohols. Their use in small amounts increases the hardness and softening points of thermoplastic resins, allowing these materials to find applications in drafting films.

Pigments

When added to resins in sufficient concentration, pigments produce matte layers; at low concentration, they simply reduce light reflection and glare by the film surface. Pigments also provide antiblocking properties to the coated layer without impairing its quality.

Pigments used in reproduction films or in drafting films must not absorb much ultraviolet light; they must be sufficiently hard to give pencil abrasive properties to the layer, but not hard enough to cause rapid wear of the pencil lead. They must have a surface area sufficient to give adequate ink absorption in the case of a drafting layer, but not so great as to allow ink line spreading and feathering. Particle size distribution must be as even as possible, with the ultimate particle size not too small (which would adversely affect viscosity) and not too large (which would adversely affect coating appearance).

Pigments must easily be dispersible in the coating solution medium without giving thixotropic conditions; they must have a low iron content for diazo layers.

No single pigment meets all the requirements for all film applications, and it is common to use mixtures of pigments, each contributing some properties to the final product.

Among the pigments most frequently used in film coatings are the natural crystalline and amorphous silicas, the synthetic amorphous silicas, and calcined aluminum silicates. In special applications, such as the production of white opaque film, titanium dioxide is used as an opacifying pigment.

The silicas, either natural or synthetic, are the major pigments used in engineering film coatings. The acceptable range of particle size of silica pigments for diazo or drafting films is between 1 and 10 μm ; the best results are obtained with particle sizes of 3 to 5 μm .

Commercial microcrystalline silicas, which are special grades of ground quartz, cristobalite, or tridymite, are available in 5 to 10 μm sizes with a relatively large particle size distribution; the larger size grades need to be further ground (e.g., in a ball mill) to reduce their abrasiveness. The popularity of crystalline silicas, which resulted from their low cost, has decreased considerably as a consequence of growing health consciousness; it is known today that crystalline silicas may cause lung damage (silicosis), and they recently have been classified as probable carcinogens.

Amorphous silicas are considered to be only mild irritants because of their drying properties; they are manufactured in a great variety of grades with different properties. Many commercial grades are available in the right particle size range (3–5 μm), the right surface area range (300–500 m^2/g), and with particular ease of dispersion. It is often found that two or more amorphous silicas with high and low property values give better matte results than a single silica with medium property values.

Diatomaceous earth, or diatomite, is primarily a form of natural amorphous silica that typically contains minor amounts of quartz. It has been suggested for use, with other pigments, in film coatings.

Calcined aluminum silicates, which are calcined clays, have shown interesting properties when used in resin systems for matte layers. They are easily dispersible and give adequate matte surfaces, but they also have a low hardness; they are frequently used in combination with harder silicas.

Titanium dioxide is rarely found in diazo films because of its opaqueness to ultraviolet light; occasionally minute amounts are used to increase the whiteness of the layer. Only in opaque films is titanium dioxide the pigment of choice.

3.7 FORMULATIONS, SOLVENT SYSTEMS

Many types of diazo film and drafting film are offered in the market for different applications, and manufacturers tend to specialize in particular fields, such as engineering graphics, diazo microfilms, or vesicular films. Basically, most diazo films for reproduction purposes aspire to excellence in printing speed, actinic opacity, visual density, development rate, reprinting speed, shelf life, background and dye stability, drafting characteristics, or other less important features.

Diazo films are available in different colors, different printing speeds, different surface finishes, and different gauges.

Since perfect adhesion of any coated layer to the film is expected, the first task of any manufacturer is to ensure that the film of his choice is surface treated for adhesion promotion, before applying a coating. The second task will be to decide whether the diazo layer is to be achieved in a single step or in two separate steps.

In the two-step method, the resins, which will act as binders for the chemicals, are first applied from a solvent solution in a well-defined layer, often called a lacquer or precoat lacquer, and dried. In a second step, the diazos, couplers, and auxiliary chemicals are applied from a solvent or mainly solvent solution on top of the resin layer, with the aim of combining with it after drying to form a single, homogeneous, light-sensitive layer. In the one-step method, the resins, diazos, couplers, and auxiliary chemicals are all mixed together, applied from a solvent solution in one operation to the film, and dried to give the final light-sensitive layer. Such a system is often referred to as one-pot film sensitizing, in the same way as the one-pot coating or pseudo-precoat in diazotype papers.

With the two-coating-layers approach, the formulator has more latitude in the choice of resins and solvents, and need have less concern for solubility problems or compatibility with the diazo chemicals. In addition, variations in the thickness of the precoat lacquer do not affect the functional properties of the sensitizing layer, such as printing speed and density, and greater manufacturing control of each layer is possible. The main disadvantage in this case is the higher cost involved in two applications instead of one.

With the one-coating-layer approach, the formulator has to ensure that common solvents for resins and diazo chemicals are chosen, and that the concentration and thickness of the resin layer remain constant from beginning to end of the coating operation, to avoid variations in print speed and other fundamental properties of the diazo film.

The coating method selected will determine the type of coating equipment to be used; the more sophisticated the coating machine, the easier it is to control the one-step application.

Whatever the coating method, the concentration of resin must be such as to bind perfectly all the other chemicals; in addition, some chemicals in the sensitizer, by a side effect, act as plasticizers for the resin and tend to lower its softening point. Care should be exercised to ensure, by a judicious choice of resins, a nonsticking condition of the surface of the diazo film, at room temperature as well as at the developing temperature. Sticking is promoted by solvent retention, and it is therefore necessary that all the solvents, particularly the high boiling solvents, be eliminated during drying.

To avoid surface tackiness or chalkiness caused by insufficient binding of the chemicals, it is generally accepted that the ratio of resin solids to all other chemical solids be at least 1.4 or 1.5.

For practical reasons, the solvent-coated layer applied must not be too thick or too thin; suitable results have been achieved with wet coating weights of 40 to 60 g/m² and dry weights of 8 to 12 g/m². Care should be exercised to avoid solution viscosity changes during coating, which would inevitably lead to variations in the amounts applied.

It is common in film coatings to distinguish between glossy layers in which no pigment is used and matte layers in which sufficient pigment is used to render the film visibly matte. Between these two extremes, depending on the ratio of pigment to resin, the surface of the film can have a deglossed, pearly, or semimatte appearance. Diazo films with all these degrees of surface finish are being manufactured. Most of the engineering diazo films have a matte-drafting layer on their backside.

A film with a glossy diazo layer on one side and a matte layer on the other is generally called a single-matte diazo film. A film with a matte diazo layer on one side and a matte layer on the other is known as a double-matte diazo film. A film with a glossy diazo layer on one side and no layer or a glossy layer on the other is generally called a clear diazo film.

When a film has a drafting layer on one side, but no diazo layer on the other side, it is called a drafting film. Frequently, drafting films have drafting layers on both sides.

Drafting films are used by draftsmen, architects, and engineers to produce the original drawing, either by hand or by computer-aided drafting (CAD) equipment. They play an extremely important role in the reprographic industry, and their development has been parallel to that of engineering diazotype films.

Drafting films have to meet stringent and varied requirements because of the many techniques used by those who draw. Ideally, a drafting layer must have all the following properties:

It must accept lead or plastic pencils of different hardness, from the softest to the hardest, without difficulty and without being damaged.

Pencil lines must be easy to erase without leaving a ghost line.

Pencil line corrections applied on an erased area must be accepted without loss of density.

Pencil lines must appear to be continuous and must retain the same thickness from beginning to end; the surface must not be too abrasive to wear out the pencil point too rapidly, but abrasive enough to cause a dense line.

A drafting layer must accept ink lines from a variety of inks without ink spread or feathering and with rapid ink drying.

Ink lines must have good adhesion, to ensure against removal by frequent handling or lifting by adhesive tape; they must also be easy to erase and to reapply on an erased area without loss of line quality.

A drafting layer must have a high ultraviolet light translucency.

It must have a resistance to water and to certain solvents used for cleaning or degreasing the surface.

A drafting film must be antistatic, to prevent the attraction and retention of dust and to facilitate separation from the copy film during printing.

Frequently, a drafting film that is eminently suitable for pencil work is less suitable for ink work, and it is common to apply a separate ink-receptive layer to a pencil drafting layer for optimum performance.

Most film formulators require an extensive knowledge and expertise outside the normal field of diazotype paper formulations. In addition, special equipment is required for solvent coating, and this explains why only a few of the many diazo paper manufacturers have ventured into the diazo film field.

The different examples of formulations given in this section have been developed and tested in the laboratory of Andrews Paper and Chemical Corporation in the same manner as the aqueous formulations. Some of the chemicals are mentioned by their Andrews code references; a complete explanation of the codes appears in the appendix.

All equipment for solvent coating must be explosion proof and grounded.

3.7.1 Glossy Lacquers

Glossy Film Precoat Lacquer, D4410

Mix with a high-speed stirrer or a homogenizer until completely dissolved

Methyl ethyl ketone	7.5	liters
Ethylene glycol ethyl ether	2.5	liters
Xylene	2.5	liters
Resin SB-10	1	kg
Resin SA-60	1	kg

Recommended dry coating weight is 9 to 11 g/m².

Glossy Film Precoat Lacquer, D4414

Mix with a high-speed stirrer or a homogenizer until completely dissolved

Methyl ethyl ketone	3	liters
Methanol	3	liters
Ethylene glycol ethyl ether	3	liters
<i>n</i> -Butyl alcohol	400	cm ³
Resin CP-50	1.35	kg

Dry coating weight is 8 to 12 g/m².

Glossy Natural Tracing Paper Precoat Lacquer, D447

Mix with a high-speed stirrer or a homogenizer until completely dissolved

Methyl ethyl ketone	6	liters
Ethylene glycol ethyl ether	3	liters
Isopropyl alcohol	3	liters
Resin CP-50	2	kg
Resin AY	250	g

Dry coating weight is 9 to 11 g/m².

3.7.2 Matte Lacquers*Matte Film Precoat Lacquer, D442*

Mix with a high-speed turbine mixer or in a ball mill

(A) Methyl ethyl ketone	1	liter
Ethylene glycol ethyl ether	1.5	liters
Resin AY	100	g
Amorphous silica, 5 μm	400	g
Pigment 65	200	g

Dissolve with a high-speed stirrer

(B) Methyl ethyl ketone	2	liters
Ethylene glycol ethyl ether	2	liters
Ethyl alcohol	2.5	liters
Resin CP-50	800	g
Resin AY	300	g

Add part A to part B and maintain under gentle stirring during usage. Dry coating weight is 9 to 11 g/m².

Matte Film Backcoat Lacquer, D2175 (Drafting Matte)

Mix with a homogenizer or any size-reducing equipment

Ethylene glycol ethyl ether	1	liter
Isopropyl alcohol	1	liter
Methyl ethyl ketone	0.5	liter
Resin CP-50	100	g
Amorphous silica, 9 μm	200	g
Amorphous silica, 4 μm	400	g

Dissolve with a high-speed stirrer

Methyl ethyl ketone	2	liters
Ethylene glycol ethyl ether	3	liters
Ethylene glycol butyl ether	0.5	liter
Isopropyl alcohol	2	liters
Resin SA-60	1	g
Proresin C8000	300	g
<i>p</i> -Toluenesulfonic acid	30	g

Maintain under gentle stirring during usage. Dry coating weight is 9 to 12 g/m²

3.7.3 Sensitizers

Sepialine Sensitizer for Glossy and Matte Lacquers, D4011

Mix with a high-speed stirrer for 30 minutes

Isopropyl alcohol	6	liters
Ethylene glycol ethyl ether	2.5	liters
Methanol	1.5	liters
Citric acid	100	g
Thiourea	50	g
50% Stannic chloride solution	100	cm ³
Chlororesorcinol	150	g
Coupler 950	100	g
Coupler RX	100	g
Diazo 55	280	g

Blackline Sensitizer for Glossy and Matte Lacquers, D408

Mix with a high-speed stirrer for 30 minutes

Ethyl alcohol	3	liters
Methanol	3	liters
Ethylene glycol ethyl ether	3	liters
Methyl ethyl ketone	1	liter
Acetic acid (glacial)	150	cm ³
Tartaric acid	300	g
Sulfosalicylic acid	50	g
Thiourea	100	g
Diresorcyyl sulfide	20	g
Coupler 122	60	g
Coupler 603	100	g
Coupler 670	200	g
Diazo 88	250	g
Zinc chloride	100	g

One-Pot Glossy Sepia Film Sensitizer, D401

Mix with a high-speed stirrer or homogenizer until completely dissolved

Methyl ethyl ketone	4	liters
Methanol	4	liters
Ethylene glycol ethyl ether	2	liters

Formic acid	100	cm ³
<i>p</i> -Toluenesulfonic acid	100	g
Thiourea	50	g
Resorcinol	180	g
Diazo 60	160	g
Zinc chloride	70	g
0.5% Methyl violet solution	10	cm ³
Resin CP-50	900	g

Dry coating weight is 9 to 11 g/m².

One-Pot Matte Sepia Film Sensitizer, D4031

Mix with a high-speed turbine mixer

(A) Methyl ethyl ketone	2.5	liters
Ethylene glycol ethyl ether	0.5	liter
Methanol	1	liter
Pigment 65	500	g
Resin CP-50	80	g

Mix separately with a high-speed turbine stirrer

(B) Methyl ethyl ketone	2.5	liters
Ethylene glycol ethyl ether	1.2	liters
Methanol	1.5	liters
Ethylene glycol butyl ether	300	cm ³
Formic acid	100	cm ³
Sulfosalicylic acid	20	g
Solubilizer HI	40	g
Coupler 615	70	g
Chlororesorcinol	70	g
Coupler 950	40	g
Diazo 55	160	g
Zinc chloride	75	g
0.5% Methyl violet solution	10	cm ³
Resin CP-50	720	g

Add part A to part B and maintain under gentle stirring during usage. Dry coating weight is 9 to 11 g/m².

One-Pot Glossy Blackline Film Sensitizer, D4025

Mix with a high-speed stirrer or homogenizer

Methyl ethyl ketone	4	liters
Methanol	4	liters
Ethylene glycol ethyl ether	2	liters
Citric acid	80	g
<i>p</i> -Toluenesulfonic acid	25	g
Thiourea	70	g
Solubilizer HI	50	g
Coupler 950	150	g
Coupler 1134	35	g

Coupler 122	30	g
Coupler 615	80	g
Diazo 69	160	g
Zinc chloride	50	g
0.5% Methyl violet solution	10	cm ³
Resin SA-60	250	g
Resin CP-60	750	g

Dry coating weight is 9 to 11 g/m².

One-Pot Matte Blackline Film Sensitizer, D4032

Mix with a high-speed turbine stirrer

(A) Methyl ethyl ketone	2.5	liters
Ethylene glycol ethyl ether	0.5	liter
Methanol	1	liter
Pigment 65	500	g
Resin CP-50	80	g

Mix separately with a high-speed turbine stirrer

(B) Methyl ethyl ketone	2.5	liters
Ethylene glycol ethyl ether	1.2	liters
Methanol	1.5	liters
Ethylene glycol butyl ether	300	cm ³
Sulfosalicylic acid	120	g
Citric acid	40	g
Thiourea	80	g
Coupler 660	80	g
Coupler 640	20	g
Coupler 1134	36	g
Diazo 54 (ZnCl ₂ salt)	120	g
Zinc chloride	30	g
0.5% Methyl violet solution	20	cm ³
Resin CP-50	720	g

Add part A to part B and maintain under gentle stirring during usage. Dry coating weight is 9 to 11 g/m².

One-Pot Glossy Sensitizers for Color Films, D2698

Mix with a high-speed turbine stirrer

(A) Methyl ethyl ketone	3.5	liters
Ethylene glycol ethyl ether	1.7	liters
Methanol	0.5	liter
Resin CP-50	700	g

Mix separately with a high-speed stirrer

(B.1) For magenta color		
Methyl ethyl ketone	1.5	liters

	Methanol	3	liters
	<i>p</i> -Toluenesulfonic acid	50	g
	Coupler 120	25	g
	Diazo 78	100	g
(B.2)	For cyan color		
	Methyl ethyl ketone	1.5	liters
	Methanol	3	liters
	<i>p</i> -Toluenesulfonic acid	20	g
	Citric acid	20	g
	Solubilizer HI	40	g
	Coupler 1167	40	g
	Diazo 39	40	g
(B.3)	Zinc chloride	20	g
	For yellow color		
	Methyl ethyl ketone	1.5	liters
	Methanol	3	liters
	<i>p</i> -Toluenesulfonic acid	50	g
	Coupler 601	100	g
	Diazo 76	100	g
	50% Stannic chloride solution	20	cm ³

Add part A to parts B.1, B.2, or B.3. Dry coating weight is 7 to 9 g/m².

3.8 DIAZO PAPER AND FILM MANUFACTURE

In the manufacture of diazotype materials, the initial step consists in selecting the appropriate formulation and the corresponding necessary raw materials. The next step involves mixing the chemicals according to the formulation, thus preparing the coating solutions, which are applied, with the use of a coating machine, to the chosen substrate. After coating, the resulting diazo material is converted from its mill-size roll into consumer-size rolls or sheets, which are stored for shipping to users.

Although the same sequence of activities applies to the manufacture of both diazo paper and diazo film, there are major differences in the equipment used and the handling conditions.

Diazo paper is a lower cost product with wider quality tolerances than diazo film. In the case of paper, the fibrous nature of the substrate minimizes coating irregularities, whereas with clear film the slightest coating fault becomes obvious and is generally unacceptable. For these reasons, more sophisticated equipment is needed for mixing and for applying solutions for diazo films and, since most of them are produced with flammable solvent systems, all equipment used must meet rigorous explosion hazard standards. In addition, the cleanliness requirements in film coating make it imperative to have a low-dust or dust-free environment.

Whatever the type of material produced, a diazo coating operation must have a plant layout that allows the raw materials to move conveniently to the unwind end of the coating machine and the coated products to be taken from the windup end of the machine to the finishing room, without crisscrossing or backtracking. A layout example for a two-machine coating plant for diazotype paper is shown in Fig. 3.4.

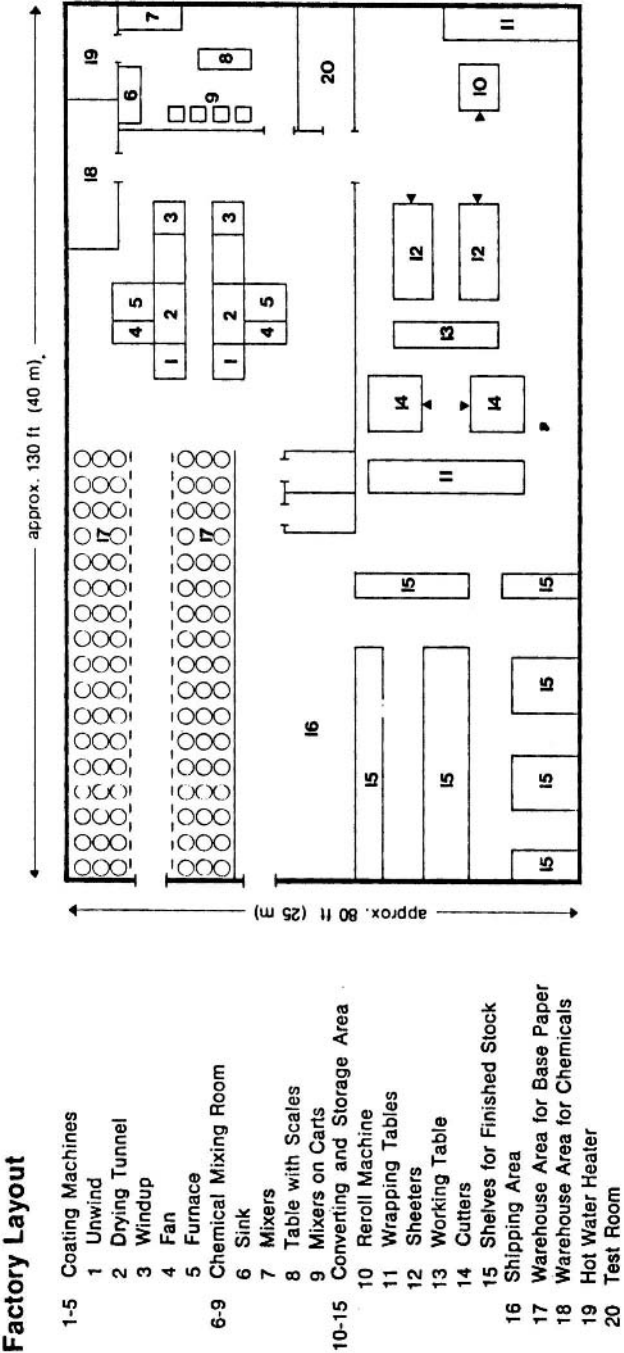


Figure 3.4 Layout for a two-machine diazotype coating plant.

3.8.1 Coating Equipment

At the heart of the manufacture of diazotype materials is the coating machine.

Aqueous Coating Machine

A coating machine is composed of different sections, each designed to perform a specific task. These sections are

- Unwind stand
- Precoat station
- Sensitizing station
- Backcoat station
- Drying tunnels after each coating application
- Windup stand

The diazo coating operation consists in placing a mill roll of diazo base paper on the unwind stand, threading the web through the machine, then applying to one side of the moving web, with a rotating applicator roller that is partly immersed in the coating preparation, an excess of precoat solution; after a short period of imbibition, the excess coating is removed with an air knife or other metering device. The operation proceeds with the elimination of the remaining water in the paper by passage through a drying tunnel in which the wet paper is subjected to a hot airstream. The web of precoated paper emerges from the dryer and meets the second coating station, in which an applicator roller applies, on top of the dry precoat layer, the sensitizing solution, followed by metering and drying, in the same manner as described for the precoat. Upon leaving the drying tunnel, the dry coated paper meets, face up, a third coating station; here the backcoat is applied to the backside of the material and dried. As the coated web leaves the drying tunnel for the last time, it may be cooled by contact with a water-cooled roller and wound up on the rewind stand.

Variations on the procedure above are frequent. On some machines, for example, the coating sequence is altered; the backcoat is applied after the precoat and before the sensitizing. Experience has shown, however, that better curl control is achieved when backcoating is done last. Occasionally, only two coatings are applied, the first being a combination of the precoat and the sensitizer (pseudo-precoat), the second the backcoat. This is often necessary when the coating machine has only two coating stations.

In designing and building coating machines, a balance must be struck between efficiency, automation, and cost. Aqueous coaters are made in different widths to handle mill rolls of paper from 90 cm up to 2 meters wide; the machines also run at coating speeds varying between 1800 and 9000 m/h, with the majority running at 4000 to 5000 m/h.

For a schematic description of the coating sequence of a commercial diazo aqueous coater, see Fig. 3.5. The roll of paper as received from the mill is secured on a metal shaft and mounted in the unwind stand; the shaft may be a simple bar with metal chucks or collars holding the roll in position or a more elaborate air shaft. The unwind stand may be of a single or double fixed position style; with such unwinds, the machine must be brought to a standstill or slowed down considerably to change rolls; manual splicing is frequently done at slow coating speed on a double-shaft unwind stand. For automatic flying splice at full machine speed, a two-position turret unwind is recommended. Tension of the web during unwinding of the roll is maintained by use of a manual, hydraulic, or electromagnetic brake on the unwind shaft. Too little tension reveals itself by a slack in

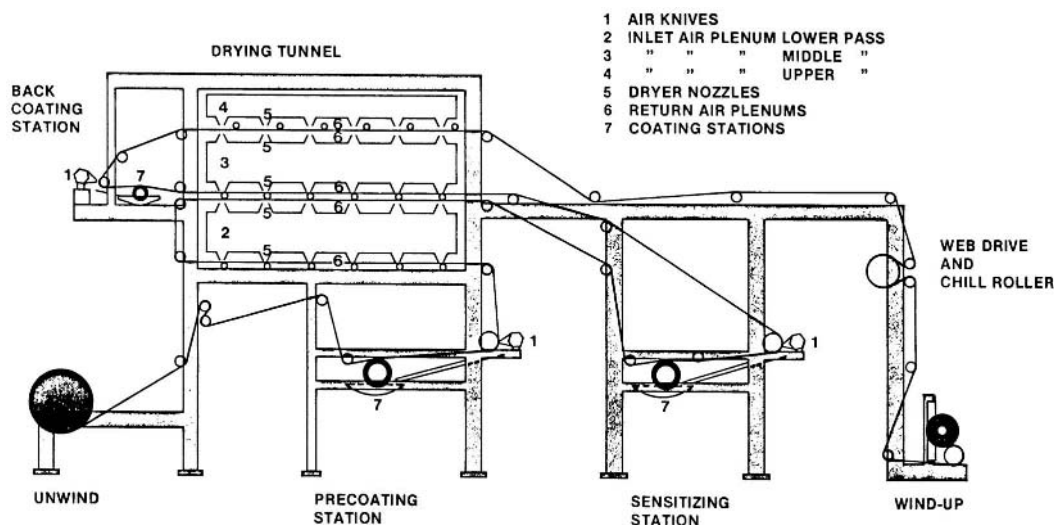


Figure 3.5 Coating sequence of a commercial diazo aqueous coater.

the web, while too much tension causes a taut web with eventual creases and possible break.

Each of the coating stations in an aqueous coating machine is composed of the following parts:

- Applicator roller with web contact control
- Coating pan, drip pan, and recirculation system
- Air knife with backing roller

The applicator roller picks up the coating preparation from the coating pan and transfers it, by contact, to the traveling web. To achieve an even contact along the entire width of the applicator roller, the web is held down by adjustable drop rollers kept absolutely parallel with it.

Large-diameter rubber-covered coating rollers of 8 to 10 in are preferred because they minimize the risk of solution penetration into the base paper and reduce the need for high revolution speeds, which could cause foam generation and coating defects. The variable speed applicator roller should be able to rotate with or against the web direction, depending on which way gives the best result with a particular type of coating.

The coating pan receives the solution to be applied, and its design has to meet a number of requirements such as

- Prevention of dead corners.
- Provision for solution movement at the bottom of the pan to minimize settling in pigmented coatings.
- Separation of the runback solution from the air knife to minimize foam generation.
- Feeding the fresh solution from the bottom of one end of the pan and overflowing both in front and back of the coating roller at the other end of the pan.

The coating solution is continuously circulated between a reservoir tank and the coating pan, with the aid of a recirculation pump. A larger holding tank feeds the reservoir. The

coating solution needs to be constantly adjusted for concentration and viscosity. The reason behind this is simple. In the coating pan, as the coating proceeds, the solution is enriched because of evaporation of water and mixing with the more concentrated runback from the air knife. If no countermeasures were taken, the solution in the entire recirculation system would become more and more concentrated. Therefore a diluted solution is fed from the holding tank into the reservoir tank. The section between the applicator roller and the air knife is called the runback zone, and as the web travels through this section, the coating solution diffuses partially into the base paper, while the runback solution from the air knife mixes with fresh solution. The imbibition period, which is the time the web remains in this section, is important because many of the properties of the finished material are influenced by this parameter. Imbibition periods of 1 to 2 seconds are in general satisfactory.

The excess solution applied by the applicator roller is metered by the air knife, which controls the wet coating weight left on the paper after the excess has been metered off. This wet coating weight is a function of the air knife pressure, the viscosity of the coating preparation, the web speed, and the absorptivity of the paper. Other factors, such as air knife angle, distance between air knife and web, and lip opening, affect the metering action. The aerodynamic design of the air knife lips provides for a nonturbulent airflow evenly across the total length of the air knife. A backing roller, generally Teflon coated to facilitate cleaning, keeps the web at a controlled angle and distance from the air knife lips.

After each coating station, the wet web enters the drying tunnel at one end and emerges dry at the other end.

In the process, dry hot air is passed through the tunnel, transferring part of its energy to the web, causing temperature rise and evaporation of water and/or other solvent, and removing the vapors from the drying web.

In modern coating machines, the drying efficiency is maximized by recycling the dryer air four or five times, raising its dynamic energy through powerful blowers to linear velocities of 5000 ft/min, and regenerating its calorific capacity by passing the air after each cycle through a direct-fired modulating gas furnace.

To accomplish this objective, the drying tunnel is equipped with plenum chambers to achieve even dryer air distribution across the web and to force the air through a series of spaced nozzles. The hot air jets impinge at short distances on the wet web surface, transfer caloric energy, and remove evaporated moisture from the web. Part of this moisture-laden air is then drawn into an exhaust stack by an extraction fan; the remaining part passes through the heater and is then recirculated into the plenum chamber.

The drying performance of the oven is governed by the velocity, volume, and temperature of the heated air. The temperature setting itself depends on a number of factors, such as ambient temperature and humidity in the coating room, width and basis weight of the web, linear speed of the web, and wet coating weight of the paper. The diazo paper is in general dried to a predetermined moisture content for optimum shelf life; such a moisture content averages 3 to 4% for two-component diazo papers, and 2.5 to 3% for one-component papers. Underdrying can cause poor shelf life and "pick-off" of the coating, while overdrying can cause diazo decomposition, loss of print contrast, and paper brittleness.

When the finished coated paper leaves the drying tunnel, it may be cooled by contact with a large-diameter water-cooled roller, which often doubles as a drive roller.

The paper is finally rewound in the windup stand on a cardboard core mounted on a metal shaft, of the same design as the unwind shaft. The windup can include single or

double fixed position stands, single-drum or double-drum surface units, or two-position center wind turrets, with or without automatic splicing. Many aqueous coating machines have supplementary features designed to improve quality, efficiency, and automation. Such features are in general very costly and are justified only when very large production volumes are possible. Among these features are automatic moisture control and web guide control systems.

Solvent Coating Machine

A diazo solvent coating machine is in many ways similar to a diazo aqueous coating machine, with unwind and rewind stands, coating stations, and a drying tunnel. However, each of these sections is specially designed for the handling of polyester film and of solvent solutions.

The unwind and rewind can be of the single or dual type, but in every case, center-winding is used, with fine tension control. Unlike paper, polyester film under excessive tension does not break and can cause serious equipment damage.

Probably the most critical part of a solvent coater is the coating station and in particular the coating head. Figure 3.6 shows a selection of coating heads for diazotype layers: 1, a kiss coating roller with scraper bar metering; 2, a kiss coating roller with air knife metering; and 3, a web feeder table with lateral flow and air knife metering. All three methods have been used for coating diazo paper, but the method of Figure 3.6(2) dominates the industry.

Solvent resin solutions are generally viscous and, polyester film being impervious, any amount of solution applied remains on the surface. Under these conditions, air knife metering is not suitable, and other ways of controlling the layer thickness become neces-

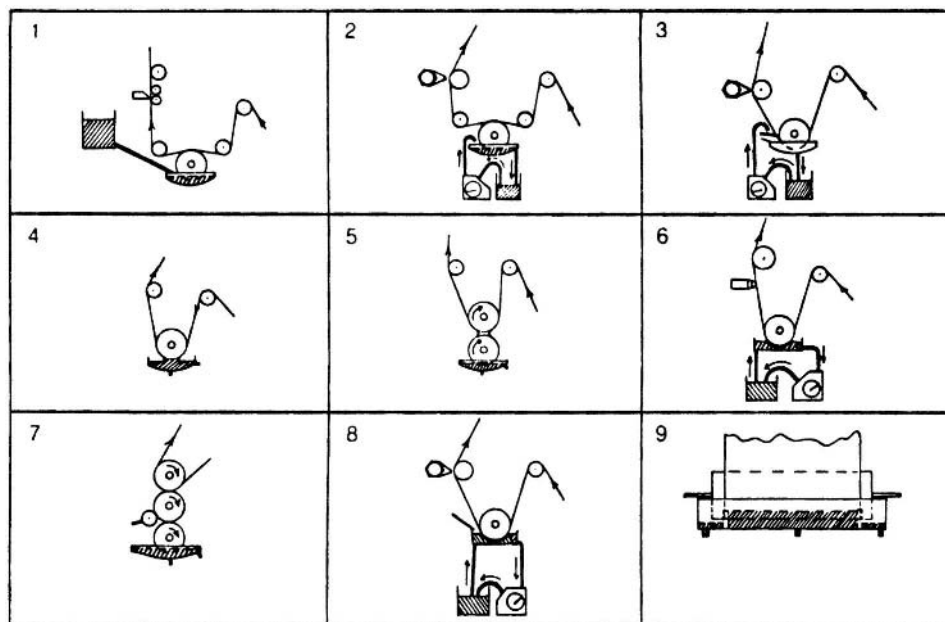


Figure 3.6 Coating heads for diazotype layers.

sary. One way, applicable for slow coating speeds, consists in creating a meniscus between the web and the solvent solution: as the web travels, it carries some of the solution with it. On the web, an equilibrium is soon reached between the fresh solution applied and the gravity flowback; no metering takes place after application, and the coating weight applied is controlled by the web speed as well as the solid content and viscosity of the coating solution. Figures 3.6(4) and 3.6(5) illustrate this type of application.

Increased production speed requirements have led to the introduction of wire wound bar and reverse roller coating techniques, respectively, Figs. 3.6(6) and 3.6(7).

In the wire wound bar method, the solvent solution is applied to the film web with an applicator roller dipping in it; the excess solution is subsequently metered with a rotating wire wound rod in close contact with the film. The amount of solution left on the film after metering is the amount that is allowed to pass the rod through the interstices or grooves between the tightly wound wire around the rod. A section of wire wound rod is illustrated in Fig. 3.7.

The coating weight of applied solution is controlled by the diameter of the wire used. The wire wound rods, often called Mayer rods or Mayer bars, are generally made of stainless steel and vary in diameter between $\frac{1}{4}$ and 1 in; the wire, also made of stainless steel, varies in gauge between 0.01 and 0.05 in. To ensure perfect contact with the full width of the web, the Mayer rod is supported by a rigid, low friction cradle, generally Teflon covered; the rod is rotated very slowly, with or against the web, to avoid wear in one spot and to allow any obstruction accidentally lodged in a groove of the rod to be freed.

The wire wound rod metering technique is frequently used in the production of glossy and matte diazo engineering films with viscous resin solutions. However, with low-viscosity solutions, as in the case of a diazo sensitizer containing no resin, the air knife metering method, shown in Fig. 3.6(8), is preferred.

For the production of microfilm, the use of a Mayer rod is not recommended because the film could be scratched by the wire pressing against the moving web. To avoid any physical damage of the film, a different coating technique is utilized. The solvent solution is metered onto the application roller before it is applied to the film; the metering is done by a multiplicity of rollers, accurately distanced from each other, transferring a controlled amount of liquid to one another and ultimately to the web. These coating techniques are called reverse roller coating, and a reverse three-roll system is illustrated in Figure 3.6(7).

Most solvent coating machines have two coating stations, one for each side of the

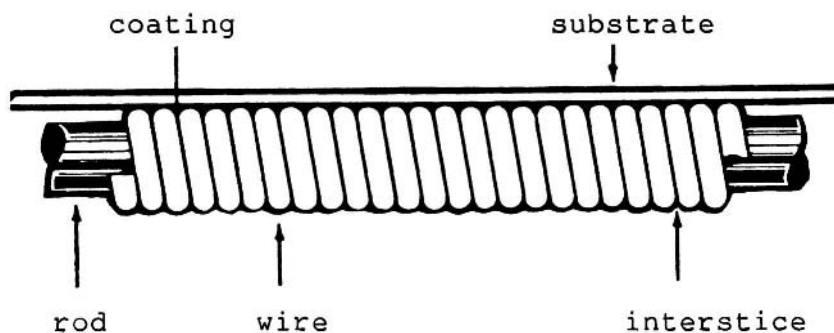


Figure 3.7 Section of a wire wound rod.

film or paper. Machines with only one station need two separate passes to produce a material that is coated front and back.

To achieve good coating results, it is important to maintain solution homogeneity by constant circulation, and concentration constancy by viscosity adjustments, during the course of the operation. Filtering the coating solution through cartridge filters is beneficial, especially in the production of microfilm. Drying conditions for solvent coating are also different from those for aqueous coating, since many solvents have a lower boiling point and a higher evaporation rate than water. The solvents must be eliminated during drying without disturbing the resin layer; impinging the wet web with high velocity hot air is not recommended because it is likely to evaporate the low-boiling solvents too quickly, causing surface defects. Larger volumes of air at lower velocity are preferred, in particular in the first drying phase. If resin curing or cross-linking is required after the solvent has evaporated, sufficient energy, in the form of convection or radiation heat, is supplied to the layer, taking care however that the transition temperature of the polyester film is not reached.

Substantial fire hazards and explosion risks are associated with the use of flammable solvents. It is imperative to prevent the buildup of static electricity and to eliminate it before it can cause an electric discharge near a flammable liquid or solvent vapor environment. The grounding of equipment and the fitting of antistatic devices in strategic positions is of critical importance in solvent coating operations.

Converting Equipment

Diazo coated materials are usually wound on the rewind stand in jumbo rolls as large as the original rolls; very occasionally they are wound on the coating machine into smaller rolls. For sale to consumers, the jumbo rolls must be converted into customer-size rolls or sheets.

Converting is an important part of the manufacturing process, and the various machines needed (rewinders, sheeters, slitters, cutters, prefolders, punchers, wrappers, etc.) account for a substantial part of the investment for a coating plant.

During converting, the diazo materials are exposed to the atmospheric environment for a longer period of time than during coating. For this reason, the areas of converting must be dry and cool, and not exposed to sun or other actinic light. Preferably, the areas should be air conditioned, dust free, and temperature and humidity controlled.

Rewinding or rerolling machines produce, from jumbo rolls, small rolls varying in size between a few meters and a few hundred meters. Rolls of 20 to 50 meters or yards are the most popular for use on manual operating photoprinting machines; larger rolls of 300 to 500 meters or yards are produced for automatic feeding photoprinting equipment.

Manually operated rewinders are used for a small volume output of rolls, such as a few hundred rolls per day, but for volume production, automatic rewinding machines can produce, nonstop, a few thousand rolls of diazo paper per day.

Diazo film is generally rewound on a cardboard core at a slower speed than diazo paper, to permit one more careful inspection for coating defects.

Sometimes rewinding into customer rolls is accompanied by an edge trimming operation, which produces rolls to an exact predetermined width. More often, the trimming is conducted separately by simultaneously rewinding and edge slitting the entire jumbo roll; this is particularly necessary when diazo film is not coated to the full width of the film, but is left with a few millimeters uncoated at both edges of the film.

Diazo microfilm is converted into narrow width rolls in one operation on slitter/rewinder machines, which can be semiautomatic or fully automatic.

A very large proportion of diazo material is supplied to users in sheet form. The material is first cut from jumbo rolls, by means of a sheeter, into large sheets of the same width as the coated roll, and stacked to piles of 100, 250, or 500 sheets. Then, with the aid of a guillotine cutter, the cut sheets are squared, trimmed, and cut to the required size in stacks.

In view of the infinite number of possible cut sheet sizes, standardizing efforts have led in Europe to the standard of the Deutsche Institut für Normung (DIN) for cut sheets; this German standard, which is followed in most countries of the world, excluding the United States, is based on a sheet size of 1 m^2 , being the area of a sheet $841 \text{ mm} \times 1189 \text{ mm}$; all succeeding sizes are half the larger sheet size, as shown in Table 3.3.

The American standard sheets for diazotype papers given in Federal Standard 00131E lists the following sizes, in inches: $8 \times 10\frac{1}{2}$, $8\frac{1}{2} \times 11$, 8×13 , $8\frac{1}{2} \times 14$, 11×17 , 17×22 , 18×24 , 22×24 , 22×34 , 23×25 , 24×30 , 24×36 , 24×40 , 28×40 , and 30×42 . Other sizes are also supplied on request.

For some special applications, diazo paper is used prefolded in continuous lengths; such a format is produced with specialized prefolding machines.

After being converted, the sensitized diazo materials must be protected against ultraviolet light and outside moisture. Wrapping materials opaque to actinic light and impermeable to moisture must be used. While formerly, multiple wrappers consisting of an inner liner and outer light and moisture barriers were used, today, single wrappers, either laminated or all plastic, are preferred. Black, red, or green thick pigmented polyethylene wrappers are popular and are used with manual or automatic wrapping machines.

3.8.2 Quality Control and Test Methods

Maintaining the quality standard of diazotype materials during manufacture is of primary importance, and systematic quality control must be performed in the course of each coating. Frequently, tests are made at the beginning and at the end of each mill roll to permit, if necessary, corrective measures before a new roll is coated. Some properties can be checked very rapidly, and the results allow operators to make immediate adjustments in the coating, while other properties require lengthy testing procedures, and the results cannot be used to make changes during the coating operation. Testing the first group of properties

Table 3.3 International Standards for Paper Sheet Sizes

DIN Number	Size (mm^2)
A0	841×1189
A1	594×841
A2	420×594
A3	297×420
A4	210×297
A5	148×210
A6	105×148

forms the basis of a comprehensive quality control procedure. The following immediate tests are routinely performed:

General Coating Quality

Using two large strips over the full width of the web, visual inspection of the coated material indicates obvious defects such as splashes, scratches, or holes. One strip is developed after being completely or partially burnt out by light exposure, and the other is developed fully without exposure; both are then checked for imperfections such as white or black spots, dark or light streaks, mottle, and uneven density. The cause for each imperfection must be found and eliminated.

Black or dark spots are often caused by pinhole penetration of the sensitizer into the base paper, by insoluble particles in the solution, or by tar formed through solution incompatibility. Better paper sizing, solution filtration, and the addition of solubilizers must be considered to tackle this type of defect.

White spots are generally caused by lack of wetting of the paper surface and local repellency; spreading or wetting agents, finely dispersed silica, and polyvinyl acetate resin additions often correct this type of defect.

Streaks are frequently the result of a dirty air knife or of foam in the solution; frequent cleaning of the air knife lips and use of antifoam agents usually solve these problems.

Producing visually defect-free coatings is every diazo coating operator's goal, and this requires a great deal of vigilance and experience.

Printing Speed

Using a reliable photoprinting machine and a control chart, a test print is made on a tear-out of coated material. Control charts, such as the Andrews Reproduction Control Chart, shown in Fig. 3.8, or the Kodak Projection Print Scale, are transparent film positives having a gray scale and other test designs.

A reference sample material is printed at the same exposure setting on the photoprinting machine and with the same control chart as the tear-out material. A comparison of the gray scale or step wedge on the two prints allow a judgment whether the newly coated material is faster, equal, or slower printing than the reference material. If faster or slower, corrective measures can be taken immediately by increasing or decreasing the concentration of diazo in the sensitizing solution. This is frequently done by adding a more or less concentrated diazo solution to the coating solution until a suitable match of the step wedge is achieved. A stock of reference material, made previously from a coating with correct printing speed, is usually kept in a refrigerator, when not in use, to reduce any potential speed loss on aging.

Primary printing speed standards are set by sensitometric measurements on calibrated and drift-free exposure instruments.

Color and Shade

The determination of the correct full tone and halftone color and shade is mostly done visually, on a print, against a control material; divergence from expected azo dye color is frequently an indication of an error in the making of the sensitizing solution, and corrective action can quickly be taken. A shift in the shade of a blackline material is often the consequence of an imbalance in the coupler ratios, taking place during continuous coating;

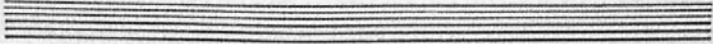
REPRODUCTION PAPER CONTROL CHART			
COATING (A)		COATING (B)	
Date		Date	
Stock		Stock	
Formula		Formula	
Machine N:		Machine N:	
Speed		Speed	
Remarks		Remarks	
PRINTING		PRINTING	
Date		Date	
Machine		Machine	
Speed		Speed	
Remarks		Remarks	
			
			
			

Figure 3.8 Reproduction control chart.

this is remedied by a readjustment of the coupler concentrations through addition of a certain amount of the coupler that has been most depleted.

Moisture Content

The final moisture content of a diazo paper has a great influence on its keeping qualities and its development rate. The moisture content must be kept within a very narrow range. Moisture reading or recording instruments allow a reliable measure of the moisture content either continuously during coating or by taking a measurement on a tear-out. If the moisture value found is too high, the drying temperature of the coating machine must be increased or its running speed must be decreased; the opposite action is taken if the moisture value is too low.

Density and Background

Maximum dye density and minimum background density of a print are both measured with a reflection densitometer; the values found must fall within the upper and lower values set for this type of material. Frequently, a visual assessment against a control material is sufficient to make a correct judgment. The density evaluation must be made under consideration of the printing speed, as a low density is often the result of a high printing speed; correcting one will immediately affect the other. Sometimes, a low dye density at the correct printing speed is the result of insufficient precoat application, which can easily be corrected by adjusting the precoat concentration. Minimum background density can be affected by overdrying, as the result of diazo decomposition, or occasionally by solution precoupling. A high background density can also be the result of iron contamination in the paper in water or in one of the chemicals, and all must be checked.

Rub-Off

Coatings that are poorly bound to the base paper are subject to powdering or rub-off. A simple way of testing the degree of rub-off, under either cold or hot conditions, is to rub a white paper towel or similar material, with a constant pressure, over the surface length of 20 to 30 cm of a fully developed sheet of diazo paper and observe on the towel the amount of dye transferred. Well-bound coatings give practically no removal of dye. To reduce rub-off, an increased amount of binding resin should be added to the precoat or to the sensitizer.

Coating Adhesion

The coated layer adhesion to the substrate must be excellent, especially in the case of film coatings. To test adhesion, the material is first fully developed (this is not required when testing a drafting film) and the layer is crisscrossed with a razor blade; this is done carefully, to prevent any cuts in the base itself. Then an adhesive tape is placed on the cut area and pulled away in a fast upward movement—no part of the layer must be removed and transferred to the adhesive tape. Poor adhesion is a serious defect, which might be caused by inadequate adhesion promotion treatment of the film base surface, and corrective measures are necessary.

Coating Weight

Coating weight is routinely tested in the case of film coatings, but not in the case of diazo papers. The amount of solids applied affects the final properties of the material as well as the cost, and it should be kept within a narrow range.

An uncoated and a coated sheet of film of specific size are weighed, and the weight of dry coating per unit area determined. If below standard, a thicker layer is applied, and vice versa; attention should be paid in this instance to printing speed and density, because these properties are affected by layer thickness.

Solvent Resistance of Cured Layers

To ensure full cross-linking in a film drafting layer, the resistance of the surface to attack by solvent is tested. A cotton swab moistened with methyl ethyl ketone is rubbed back and forth a number of times on the surface of the matte drafting layer; if cross-linking of the resins is complete, no removal of the layer is observed; if not, the drying temperature or the catalyst content might have to be increased, or the coating speed reduced.

Curl

An undesirable curl can lead to difficulties in print processing or in the use of the material. Curl, or curvature of the sheet, can be temporary—for instance, if disappearing within a brief time after emerging from the developing section of a machine—or permanent, if present at all times after equilibrium with the surroundings has been achieved. Curl is assessed by placing a sheet on flat impervious surface and, after equilibrium, measuring the greatest lift from the flat surface of any part of the sheet. Curl in paper coating is corrected by varying the amount or nature of the backcoat.

Miscellaneous Tests

The following tests are performed to evaluate other properties of the material. These properties can rarely be altered while the material is being made, but the test results can be most useful in changing the design of the product by reformulation of the coating solution.

Development Rate

Photoprinting machines have synchronized printing and developing sections; therefore, the diazo material must have a good development rate to develop at the same setting as its printing. Development rate is assessed in a comparative way by a test against a control material.

A whole sheet of sensitized material is developed at a speed many times its normal printing speed; then, while most of the sheet is protected by a light-absorbing cover sheet, a section is exposed to light to decompose any unreacted diazo. Thereupon, the sheet is developed again at the same fast speed as before, and a second section is similarly exposed to light, and so on. The result is a gradated print showing the effects of being developed once, twice, and more times, until no further gradation is noticeable at full development; the material with the densest gradation has the fastest development rate. This test can be performed on a machine set with hot or cold developing conditions, to give information on the hot or cold development rate.

Actinic Opacity

This property applies only to diazo paper or film intermediates. The actinic opacity determines the effectiveness of the reproduction material to produce dense images in reprints. To measure actinic opacity, a sheet of diazo intermediate material is fully developed; the developed print is half-covered with a light-absorbing cover sheet, printed on a diazotype paper, preferably slow speed blackline, at the printing speed of this paper, and fully developed. The covered part of the intermediate gives the maximum density obtainable on the print paper, while the uncovered part gives the density obtainable with the intermediate. Optical densities of the two areas are measured with a reflection densitometer, and the actinic opacity is determined by the percent ratio of reprint density and maximum density values.

Actinic Transmission

This property applies only to translucent or transparent materials. The actinic transmission measures the efficiency with which actinic light passes through a material. The reprint speed of a translucent material depends on its actinic transmission. A photoprinting machine, with a dial calibrated in linear speed, is used to measure actinic transmission. In a first step, a sheet of diazo paper, preferably slow speed blackline, is exposed and developed on the photoprinting machine, at a speed setting such as to leave a background

density of 0.05 above minimum density; this is represented by a slight dye haze in the background. The linear print speed used is recorded. In a second step, a sheet of translucent material (e.g., a drafting material or a completely exposed and developed intermediate material) is printed on a sheet of the same slow speed blackline diazo paper as before, with the photoprinting machine at various speeds, until a speed setting is established that leaves after development a background density of 0.05 above minimum density. The linear print speed used is also recorded. The actinic transmission is the percent ratio of the linear reprint speed of the translucent material and the linear print speed of the diazo paper.

Accelerated Aging Tests

These tests are designed to give an estimate of the period of time during which a diazotype material can produce satisfactory results. This period of time, also referred to as the shelf life, can be determined by forced aging of the sensitized material, to simulate within a relatively short time the effect of a much longer period of natural aging. The shelf life is evaluated by subjecting samples of sensitized material to an atmosphere of high humidity and/or an elevated temperature for a specific time.

Natural aging over several months (5–6 months at least) can be approximated by suspending a sheet of sensitized material in a closed container maintained at a relative humidity of 43% and a constant temperature of 50°C for a period of 24 hours; a saturated solution of potassium carbonate salt in contact with excess salt, in a closed container, will produce above it, at a temperature of 50°C, a relative humidity of 43%. Similar results would be obtained if a packet of sensitized sheets were wrapped in aluminum foil, sealed, and kept in an oven at 50°C for 7 days. A longer natural aging period (6–9 months at least) can be approximated by changing the saturated salt solution to one consisting of sodium chloride, which would give an atmosphere of 75% relative humidity at a temperature of 50°C.

A comparative assessment of the stability of diazo materials to general deterioration with age can be made simply and quickly by sealing sheets of material in aluminum foil and heating them at 80°C for 1 hour; this test, however, shows less correlation with normal aging at room temperature and should only be used when a fast evaporation is needed.

The effects of natural or accelerated aging on sensitized materials are partial decomposition of the diazo and/or premature formation of azo dye, which would give prints with lower maximum dye densities and higher minimum background densities; values for these properties can be measured before and after aging, and recorded for comparison purpose.

Light Aging

When diazo prints are exposed to light and air, the azo dye image tends to fade and the background tends to discolor. To determine the extent of loss of image density and increase in background color, light aging tests are performed.

For reproducible results, a fadeometer instrument, which emits a controlled amount of ultraviolet light, must be used.

Two sheets of diazo material are half-covered by an opaque material, exposed, and developed. One of them is then placed in the fadeometer and, after a given period of time, the maximum and minimum densities are taken and compared to those of the other sheet that has not been exposed to light.

Since the sun is a rich source of ultraviolet light, it can be used instead of a fadeometer, to make comparative light aging tests on different diazo prints.

In addition to the above-mentioned tests performed routinely or otherwise on diazo-type materials, many other properties can also be tested. Among these are water fastness for diazo papers, ink and pencil acceptance and erasure for drafting materials, chemical and physical eradication for intermediate materials, sensitometric characteristics for microfilms and vesicular films, static retention for all film products, and all physical properties of the base materials themselves.

3.9 CONCLUDING REMARKS

Diazotype materials have been in existence for more than half a century, and current Western production must be in excess of 1 billion square meters per year.

What is the future of the diazotype process?

In microfilm duplication, the diazo process is being challenged by electrophotographic imaging systems.

Until not so long ago, plain paper copiers existed only for the duplication of office documents; in the past few years, larger plain paper copiers, capable of reproducing large-size originals, have appeared and are replacing some diazo photoprinting machines. However, the higher costs of plain paper copiers and a certain lack of versatility has so far limited their acceptance in the marketplace.

The future of the diazo process is also being threatened by operational limitations imposed by environmental regulations. Restrictions on usage and disposal of chemicals considered to be hazardous (e.g., heavy metals, solvents, many organic and inorganic compounds) are making the manufacture of diazo materials more difficult and more costly. Sacrifices in quality and in the range of materials available will follow the eventual replacement of hazardous chemicals by nonhazardous ones.

Nevertheless, and as long as it remains economically competitive with other processes, the diazo process, because of its simplicity and versatility, is likely to remain popular and to be widely used for many years to come.

APPENDIX

Andrews code	Chemical description
Accelerator LM	Dimethylurea
Accelerator ST	Zinc methane sulfonate composite solution
Antifoam A	Proprietary mineral oil antifoam agent
Antifoam L	Proprietary acetylenic glycol antifoam agent
Antifoam M	Proprietary alkyl phosphate antifoam agent
Antifoam T	Proprietary fatty acids antifoam agent
Binder C	Casein
Binder IQ	Vegetal protein
Coating Aid 200	Hydrous magnesium silicate
Coupler 111	2,3-Dihydroxynaphthalene-6-sulfonic acid sodium salt
Coupler 120	2-Hydroxynaphthalene-3-carboxylic acid methyl ester
Coupler 122	2-Hydroxynaphthalene-3-carboxylic acid ethanolamide
Coupler 144	2-Hydroxynaphthalene-3-carboxylic acid-3'-N-morpholino propylamide
Coupler 166	2-Hydroxynaphthalene-3-carboxylic acid diethanolamide
Coupler 195	Proprietary composite blue coupler
Coupler 375	4-Bromo- α -resorcylic acid
Coupler 480	4-Bromo- α -resorcylic acid amide

APPENDIX (Continued)

Andrews code	Chemical description
Coupler 603	2,5-Dimethyl-4-morpholinomethyl phenol
Coupler 615	Bis(2-1,dimethylethyl)5-methyl 4-hydroxyphenyl thioether
Coupler 620	Proprietary composite yellow coupler
Coupler 640	3,3'-Methylene bis(acetoacetanilide)
Coupler 660	1-Hydroxynaphthalene-2-carboxylic acid-3'- <i>N</i> -morpholino propylamide
Coupler 670	Cyanoacet-morpholide
Coupler 690	1,10-Dicyanoacet-triethylene-tetramine, hydrochloride
Coupler 950	2,4-Dihydroxybenzylamine, alkyl sulfonate salt solution
Coupler 1134	2-Hydroxynaphthalene-3-carboxylic acid-2'-methoxyanilide
Coupler 1167	2-Hydroxynaphthalene-3-carboxylic acid-3'-nitroanilide
Coupler Dinol	2,3-Dihydroxynaphthalene
Coupler EBA	1,4-Bis(acetoacet-ethylenediamine)
Coupler O	2,7-Dihydroxynaphthalene-3,6-disulfonic acid disodium salt
Coupler RG	α -Resorcylic acid ethanolamide
Coupler RX	β -Resorcylic acid ethanolamide
Developaid	Polyglycol
Diazo 10	1-Diazo-4-(<i>N</i> -ethyl- <i>N</i> -benzyl)amino benzene chloride, half-zinc-chloride
Diazo 39	1-Diazo-2-ethoxy-4- <i>N,N</i> -diethylaminobenzene chloride, half-zinc-chloride
Diazo 48L	1-Diazo-4- <i>N,N</i> -dimethylaminobenzene chloride, half-zinc-chloride, 70% strength
Diazo 48NF	1-Diazo-4- <i>N,N</i> -dimethylaminobenzene sulfoisophthalate salt
Diazo 49L	1-Diazo-4- <i>N,N</i> -diethylaminobenzene chloride, half-zinc-chloride, 70% strength
Diazo 49NF	1-Diazo-4- <i>N,N</i> -diethylaminobenzene, sulfoisophthalate salt
Diazo 54	1-Diazo-2,5-dibutoxy-4-morpholinobenzene chloride, half-zinc-chloride
Diazo 54S	1-Diazo-2,5-dibutoxy-4-morpholinobenzene bisulfate, 80% strength
Diazo 55	1-Diazo-2,5-dibutoxy-4-morpholinobenzene borofluoride
Diazo 59S	1-Diazo-2,5-diethoxy-4-morpholinobenzene bisulfate, 77% strength
Diazo 60	1-Diazo-2,5-diethoxy-4-morpholinobenzene borofluoride
Diazo 67	2-Diazo-1-naphthol-5-sulfonic acid sodium salt
Diazo 69	1-Diazo-4- <i>N,N</i> -diethylaminobenzene borofluoride
Diazo 72	1-Diazo-2,5-diethoxy-4- <i>p</i> -tolylmercaptobenzene chloride, half-zinc-chloride
Diazo 76	1-Diazo-2,5-diethoxy-4- <i>p</i> -tolylmercaptobenzene borofluoride
Diazo 78	1-Diazo-2-chloro-5-(4'-chlorophenoxy)-4- <i>N,N</i> -diethylaminobenzene chloride, half-zinc-chloride
Diazo 87	1-Diazo-3-chloro-4- <i>N</i> -methyl- <i>N</i> -cyclohexylaminobenzene chloride, zinc chloride
Diazo 88	1-Diazo-3-methyl-4-pyrrolidinobenzene chloride, zinc chloride
Diazotint blue	Proprietary water-soluble blue dye
Diazotint red	Proprietary water-soluble red dye
Diazotint yellow	Proprietary water-soluble yellow dye
Dispersion F	Wax dispersion
Dispersion JB-1	Rosin aqueous dispersion
Dye AC-1	Proprietary blue dye
Pigment 65	Calcined silicate
Pigment 2820	Amorphous silica
Pigment R	Rice starch
Proresin C8000	Melamine-formaldehyde resin

APPENDIX (Continued)

Andrews code	Chemical description
Resin AY	Polyvinyl acetate resin
Resin CP-50	Cellulose acetate propionate
Resin CP-60	Cellulose acetate propionate, alcohol soluble
Resin PS-75N	Vinyl chloride copolymer dispersion
Resin SA-60	Acrylic resin
Resin SB-10	Vinyl chloride–vinyl acetate copolymer resin
Resin VC-1	Vinyl acetate homopolymer dispersion
Resin VK-2	Vinyl acetate multipolymer dispersion
Resin VG	Styrene polymer dispersion
Resin VN	Vinyl acetate copolymer dispersion
Resin VP	Vinyl acetate homopolymer dispersion
Resin VW-2	Vinyl acetate homopolymer dispersion
Solubilizer 136, 137	Naphthalene trisulfonic acid, sodium salt
Solubilizer HI	Aliphatic lactam
Stabilizer AB	Sodium salicylsulfonate
Stabilizer CD	Zinc toluenesulfonic acid
Stabilizer TT	<i>p</i> -Toluenesulfonic acid
Wetter 27	Dihydroxydialkyl hexyne

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4

A Brief Introduction to Electrophotography

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Much has been written about electrophotography since it burst upon the office-place scene in about 1960, and much development has occurred in all sorts of applications beyond simply copying a document onto one side of a piece of 8.5×11 " paper. The demonstration of the basic invention dates from 1938, and the first manual product, the Xerox Model A, came onto the market in 1949; the first automatic copier, the Xerox 914, appeared in 1959. The subject, then, is barely more than 50 years old. The sheer number of companies and people who have become involved in electrophotography due to its twin attractions of being a profitable business as well as an outstanding example of the need for a multidisciplinary approach to unravel the science behind the early empirical methods, has produced a strong competition for both markets and inventions. The number of identifiably different ways of practicing electrophotography is very large and is driven by both a search for improvement and a search for a path not covered by someone else's patents. The general approach is best summed up by a quote from the inimitable Mae West, "When faced by a choice between two evils, I always pick the one I haven't tried before!"

This said, it is apparent that any brief introduction to the subject must gloss over the many nuances in the differing ways of executing any particular function. It is also true that the majority of the readers of this book will have some passing familiarity with the subject. Accordingly, the subject matter will be reduced to its simplest terms and only passing mention given to alternative methods to the one described. It will be left to the reader to seek out much of the details by consulting the references. There will be very little discussion of image quality in terms of image digital image processing; only the

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major influences of some of the subsystems will be touched upon. This chapter will follow the order given below.

1. Overview of the process and main applications
2. Discussion of the subsystem elements
3. Applications to color
4. Major alternatives
5. Summary

4.1 OVERVIEW OF THE PROCESS AND MAIN APPLICATIONS

The original motivation of Chester Carlson was to find a simpler, cheaper way to reproduce documents in his work as a patent attorney. The mostly nontechnical history of the subsequent development can be found in Refs. 1–3. Today, the applications of electrophotography can be viewed as capturing some of the aspects of silver halide photography and magnetic recording in order to produce hard-copy output on mostly paper, since a piece of paper remains the single best method of displaying and viewing text and graphics under all circumstances. The resemblances to photography are that the image is captured and written to an intermediate medium optically, the output is on paper, and the image quality is quite high; the resemblances to magnetic recording are that the intermediate media can be constantly refreshed and overwritten, the image spends part of its time in digital form, and the process is fast. Unfortunately the electrophotographic process is not as compact as cameras or tape cassettes, but the economics of creating or displaying an 8.5×11 " image are highly favorable compared to photography or CRT monitors. The process can be used to copy an existing image or to print an image created or modified with a computer. The essence of this is shown in Fig. 4.1; on the left is a copier, and on the right a printer (which can be turned into a copier by the addition of a scanner). Externally they are indistinguishable. In the copier, the original image is coupled optically directly into the electrophotographic processor; in a printer, the "original" is indirectly coupled, which involves some digital transforms transparent to the user. Thus the process is used for copying and printing and to create multifunction machines that do at least both these functions and perhaps others, such as facsimile or internet communication. In the past, the process would turn colored originals into black-and-white hard copy; today, the process is quite capable of producing colored output from colored input, or coloring black-and-white input. The speed range available today for 8.5×11 " pages is from 6 pages per minute to in excess of 400 pages per minute (ppm). Reduction and enlargement from 50 to 200% is also readily available. The prices, at the time of writing, for machines using the electrophotographic process range from less than \$300 to more than \$500,000. The size (i.e., the floor space required) of the machines tends to become rapidly larger as the number of paper sizes handled by the machine increases, as the amount of paper stored in the machine increases, and as the variety of input and output finishing options increases. It is this, plus the greater amounts of internal computing power necessary at higher speeds, which drives the highly nonlinear rise in price as speed increases; there is, however, as with automobiles, a rough correlation between price and machine physical volume.

Turning to the internal workings of the machines, Fig. 2 shows, on the left, a schematic of all the process elements arranged for cyclic or repetitive hard-copy production, and, on the right, a simplified version of what each element is intended to achieve. The whole process operates in the dark; the only light allowed is strictly for imaging or re-

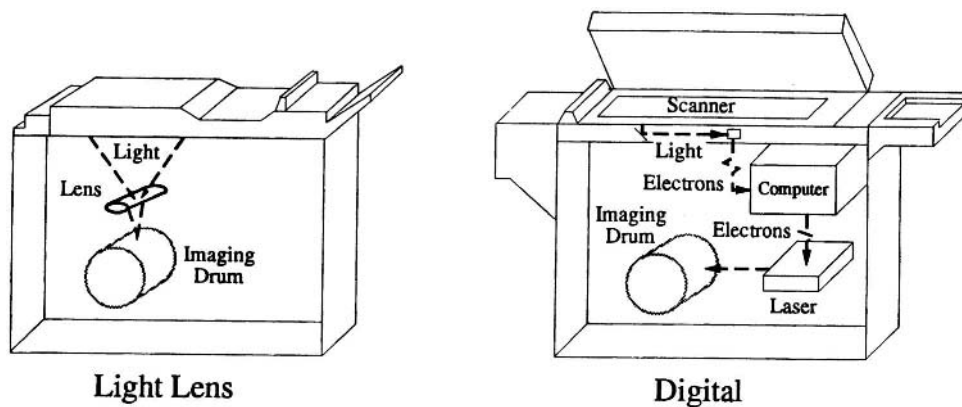


Figure 4.1 To the user these two copiers will look alike. The one on the left is a representation of a light lens copier; i.e., the original document is imaged through a system of moving lenses in a one-to-one or a reduced or an enlarged form directly on to the photoreceptor. The one on the right is a digital copier: the same original is imaged on to an electronic image capture device such as a CCD array, which subsequently processes the data for control of a digital imaging source such as a laser diode or an LED, which then directly writes the image on the photoreceptor. This latter scheme is capable of a much greater range of enlargement or reduction, and the image is accessible to the user for editing in various ways. Such a copier can also be readily connected to computers or modems.

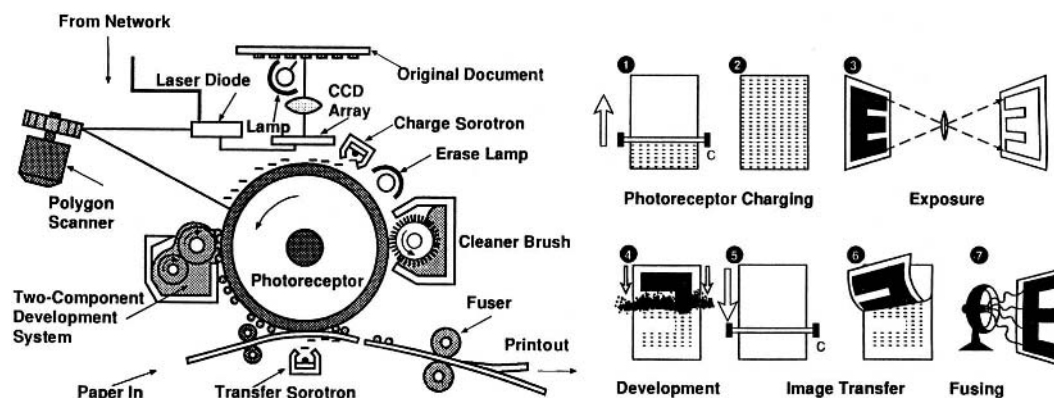


Figure 4.2 This figure shows the complete electrophotographic process. On the right, the steps in the process are displayed so as to illustrate the function of each. On the left is an example of how these various steps are incorporated into a machine; it also gives some idea of the physical cross section of the various subsystems. The steps in order are: charging the photoreceptor, developing the image, transferring the image to paper, fusing the image to the paper, and cleaning and refreshing the photoreceptor.

freshening purposes. The system is built to accommodate the width of the output media and there is no restriction on the orientation of the page. The paper can be in the form of cut sheets or a web fed from a roll. Each of the process elements shown in the figure will be addressed in more detail later, but first the way in which they interact will be discussed. As can readily be appreciated from Fig. 4.2, the overall process is a serial one. In effect, each subsystem sets the stage for the next one to perform its specific task. Consequently, understanding the limitations and sources of variance for each subsystem constitutes a large part of the R&D effort in developing new machines.

The first step is to achieve a uniform charge on the photoreceptor; for this to occur properly, the photoreceptor must act like a very uniform, ideal capacitor in the dark. Once charged, the photoreceptor can be discharged by shining light on it. This is done in an image-wise fashion either by reflecting light from an original document or by switching on and off a digital light source such as a laser to create a pattern of light and dark that simulates an original document. This, in turn, creates a pattern of charged and discharged areas on the photoreceptor that constitute a latent (i.e., undeveloped) *electrostatic* image. The electric fields above the surface of the photoreceptor are what interact with the development subsystem to dress this image with toner, which is a dry powder ink consisting of colored particles each of which is less than half the diameter of a human hair. Because the ink is dry we use the word *xerography* (*xero* from the Greek for dry and *graphy* from the Greek for writing) as an alternative term for electrophotography. The toner particles acquire the electric charge necessary for an interaction with the latent electrostatic image within the development unit. Upon exiting the development unit, a fully formed and visible image is on the surface of the photoreceptor. The remaining steps are to transfer this toner image to the media, fix it permanently to the media, and refresh the photoreceptor in preparation for the next cycle of imaging. The transfer is done by bringing a sheet of paper, say, in contact with the image and creating an electric field across the paper–toner–photoreceptor sandwich that is in such a direction as to attract the charged toner to the paper. The paper carrying the toner image, which can still be smudged or disturbed at this point, is then moved to the fusing unit. This unit applies sufficient heat and pressure to cause the toner to melt and coalesce, as well as to flow partially into the paper fibers. The paper is then passed to an output tray for collection by the user. The photoreceptor, now minus the toner image but still carrying the electrostatic image, rotates further to arrive at the erase station where the electrostatic image is removed, usually by shining light over the whole surface of the photoreceptor, which causes the remaining charged areas to discharge. This returns the photoreceptor to its uniform, ideal capacitor state.

The basic process that has just been described has, over the course of time, been applied first to copiers with fixed platens and speeds in the tens of pages per minute, then to duplicators intended for central reproduction departments operating at outputs well in excess of one hundred pages per minute, and moving on to printers both large and small, fast and slow beginning in about 1978. Duplex, or two-sided copying and printing was also introduced in this period. All these machines create predominantly black-and-white hard-copy output. In about 1974 the first color electrophotographic analogue copier showed up; by 2000, over 150 different digital color electrophotographic copiers and printers brands had been introduced representing about 12 different manufacturers and covering speeds ranging from 2 to 130 8.5" × 11" impressions per minute. The applications range from simple copying of documents, microfilm, and books, to printing from personal computers, to facsimile machines, to small office multifunction products, to printing from mainframe computers and large databases, to machines one meter wide that print on long rolls of paper, to emulations of four-color offset press output.

The foregoing implies printing on paper: the varieties of paper that can now be used is very large, covering the majority of basis weights and coatings encountered in the commercial printing world—roughly speaking from about 60 gsm (grams per square meter) to about 250 gsm. Besides paper, hard copy can be produced on overhead transparency materials, opaque white film, adhesive labels, card stock, tag and ticket stock, and transfer sheets, which can be used subsequently to transfer the image to textiles, ceramics, or even unwieldy three-dimensional objects. The imaging media that are used and the characteristics of the electrophotographic machine are determined by the customers' applications. Each special application requires some variant of the basic electrophotographic process. To appreciate the breadth of the machines available, consider that DataQuest publishes collections of specification sheets for copiers, printers, and facsimiles: each of these books is about 2 cm thick with one listing per page! (Refs. 4,5).

Another measure of the growth of the usage of the electrophotographic process is to examine the market size of the consumables as a function of time. This can only be done in a very approximate way by estimating the number of 8.5×11 " pages produced worldwide and applying algorithms based on toner page yields and photoreceptor lives to arrive at quantities per year (Note that toner page yields and photoreceptor lives are not constant over time!) This process yields compound annual growth rates in the range of 7 to 9% from 1985 to the present for millions of pounds of toner and for millions of photoreceptor units. This growth slowed to 3–5% beginning in 1999. In 2002, the worldwide production of toner is projected to be in the range of 330–380 Mlbs, of which some 25–35 Mlbs is projected to be color toner. Organic photoreceptor production is projected to reach 100 M units by this time.

4.2 DISCUSSION OF THE SUBSYSTEM ELEMENTS

The overall description of the process has been very brief. In order to gain a deeper understanding of black on white printing and copying, the reader is advised to refer to the items listed in Refs. 6–20, and the references to detailed papers contained within them. The references have been chosen with two criteria in mind: (1) that they be reasonably comprehensive from a system point of view, and (2) that they be relatively straightforward and uncomplicated but lead the reader to more detailed or complete specific references. Not all variations on the subsystems will be discussed; again, much more information is available in the references and the extant patent literature. To fix ideas, the discussion will be limited to printers or the digital form of the electrophotographic process. This is because another market trend for the copying function at the time of writing is that few if any clean-sheet, purely analogue or light lens copiers are in the R&D pipeline. The underlying electronic cost trends are such that the cost premium of digital over analogue is becoming vanishingly small. It should be added that another market trend is that the ubiquitous personal computer is causing a significant migration of what was once copied centrally to local printers. Hence the phenomenal growth of the sub-20 ppm printers over the last decade.

4.2.1 Charging

There are two basic methods, which both require the electrical breakdown of air by strong electric fields. Physically, these are very different schemes, however. Figure 4.3 shows the geometry of the *scorotron*, which is a noncontacting device for causing a well-defined electrical breakdown of air to occur immediately surrounding the central fine wire (about

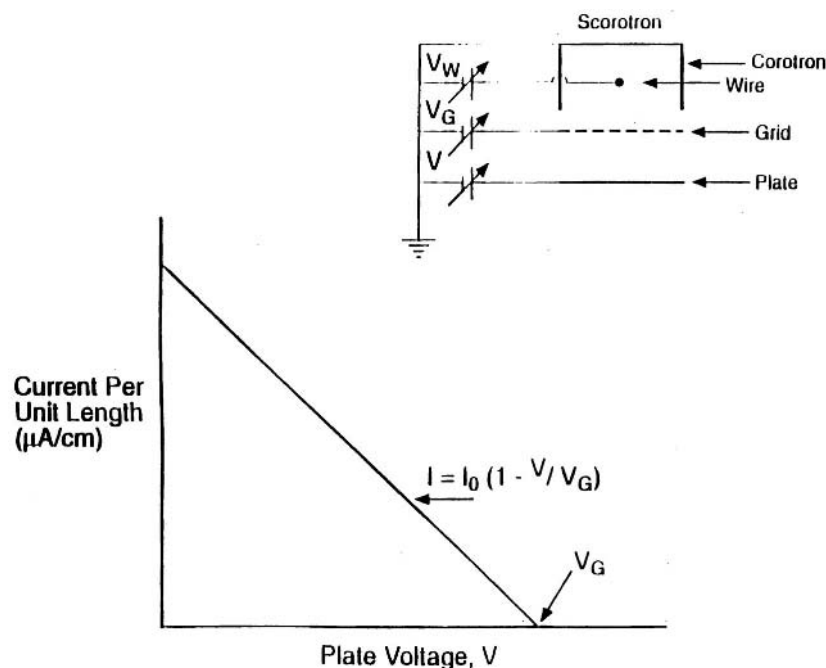


Figure 4.3 This figure shows a schematic cross section of a scorotron and a graph of its performance characteristic. V_W is typically in the range of 3.5–4.0 kilovolts, which causes an air breakdown or corona to be established around the central wire, which is typically 75 μm in diameter; V_G is typically in the range of 500–800 volts. The graph shows how the current decreases in a linear fashion as the voltage beneath the scorotron varies. Since this current ceases to flow at V_G for the ideal case, the photoreceptor will charge up to V_G . The grid is a thin-metal noncorrosible mesh with a typical transmission of 80%.

75 μm in diameter) from which the desired sign of charge is extracted and directed toward the photoreceptor by the application of suitable voltages to the wire and screen grid. For organic photoreceptors, which are the dominant type of photoreceptor in today's printers, negative charge is deposited on the photoreceptor surface producing a negative voltage in the range of -500 to -900 volts. When the electric field in the gap between the scorotron screen and the photoreceptor is zero, no more charge is delivered. Thus the screen voltage controls the photoreceptor surface potential. This is also illustrated in the figure.

The *primary charge roller*, or *biased charging roll* (Fig. 4.4) is a contact device that requires the application of both DC and AC voltages to achieve air breakdown in the nip-forming regions, and the separation and delivery of charge to the photoreceptor. In this case, the photoreceptor voltage is usually in the range from -400 to -600 volts; this voltage is controlled by the DC component of the applied voltages as is also shown in the figure. The roll itself is a multilayered composite of elastomers and other polymers tailored to provide the correct nip shape, electrical impedance, and wear properties.

Both devices produce oxides of nitrogen and ozone; the scorotron more than the biased charging roll. Some form of venting or filtering is required for the former. Both can have deleterious effects on the photoreceptor. The scorotron can deposit a surface conducting layer which in subsequent steps in the process can lead to image blur. The

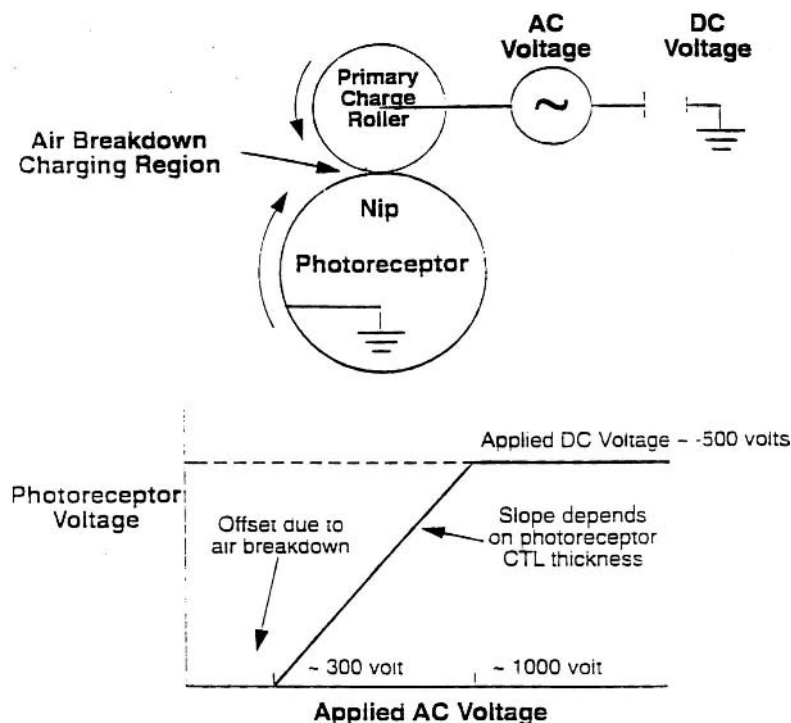


Figure 4.4 This figure shows an alternative charging scheme using a partially conducting elastomeric roller (primary charge roller) that has a typical diameter of 1 cm. In this case, the DC voltage plays the same role as V_G in Fig. 3: it governs the charged photoreceptor voltage. The AC voltage plays the role of V_w in Fig. 3: it creates a steady air breakdown in the nip regions. Typical values of the voltages are shown on the graph, which also shows how charging performance depends on these voltages.

primary charge roller (PCR) creates its discharge right at the surface of the photoreceptor; the reactive species in this discharge cause bond-breaking damage to the photoreceptors' topmost polymer layer, which results in excessive wear. The scorotron is capable of delivering more current but is less compact and so is most often found in the higher speed, larger volume machines. The biased charging roll is a common component in the print cartridges for desktop printers, where it is often called the "primary charge roller" or PCR.

4.2.2 Imaging

There are several types of image sources. If an original document is being copied, a scanning fluorescent or tungsten-halogen lamp is used to illuminate the document, and lenses are used to focus the image on the photoreceptor. This scheme has a speed limitation of some 80 ppm; beyond that speed flash lamps and lenses are used. This change means that a shift from drum photoreceptor architectures to belt photoreceptor architectures is practically mandatory.

In the case of printers, the two main digital image sources are *laser diodes*, whose light output is reflected onto the photoreceptor from a spinning mirror via focusing lenses,

and *LED image bars*. In both cases, the solid-state light source is switched on and off at about 35MHz. The LED image bar is a page-wide device consisting of a linear array of individual LEDs plus a focusing lens that is quite compact and is positioned close to the photoreceptor. Current capability is an addressability of 600 dpi (dots per inch). The laser diode systems are not compact, and the source is remote from the photoreceptor, as is shown in Fig. 4.5. The main drawbacks to the LED image bar are that it is expensive to achieve a pixel-to-pixel uniformity of light output greater than $\pm 2\%$, that careful alignment is required, and that one dead LED pixel will leave a black line on the image. The main drawbacks to the laser diode system are that it is prone to motion quality error due to polygon mirror wobble (and not all mirrors are the same) and that there is an inevitable nonuniformity of pixel size and positioning as the beam is swept across the photoreceptor.

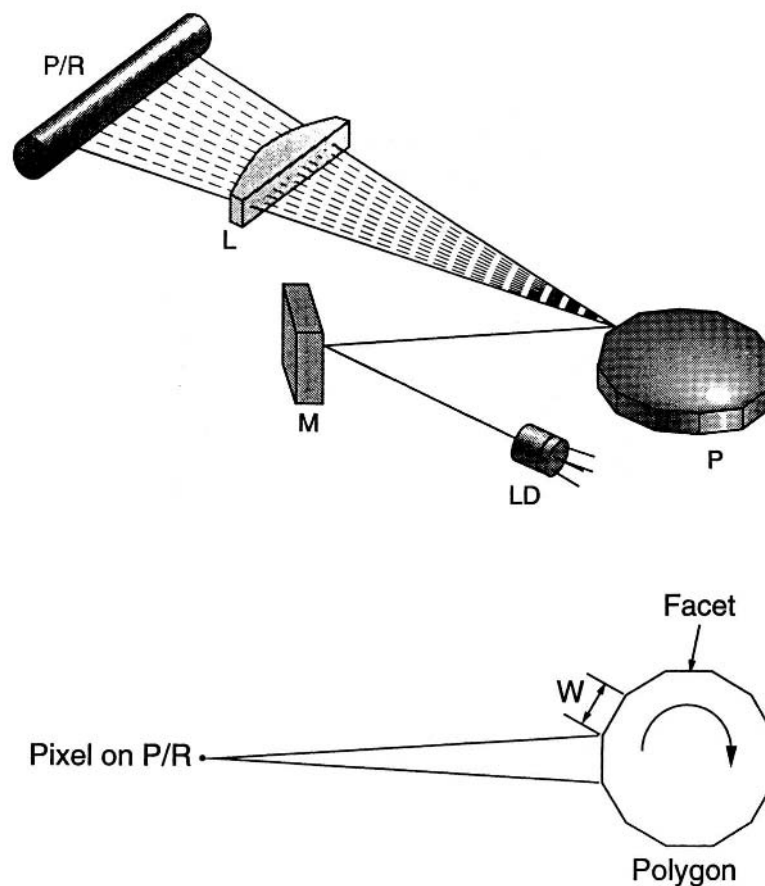


Figure 4.5 This figure is intended to illustrate only one of the possible digital imaging schemes. The main components are a laser diode emitting at a typical wavelength of 780 nm (in the near-infrared part of the spectrum), which can be switched on and off at very high frequencies, a system of lenses that focuses the beam to a spot (pixel) about $42\ \mu\text{m}$ in diameter at the half-power point for 600 dpi, and a rapidly rotating mirror (in the range of 30,000 rpm), which directs the beam across the photoreceptor parallel to its axis and perpendicular to its direction of rotation.

For low-end printers, only a single laser diode is required; for high speed engines, two or four beams that are interlaced are required. Laser diode systems have already reached the 1200 dpi capability plateau. For very wide printing systems, LED image bars are preferred for architectural reasons.

Being solid-state devices, both LEDs and laser diodes are most efficient in the wavelength band 635–820 nm, the most common wavelength in use being 780 nm. The shape of the spot of light from a single pixel, i.e., roughly 40 μm in extent, is such that the pixel is somewhat elliptical; the long axis is in the paper path (or process) direction, and the light intensity falls off from the center in a Gaussian (or bell) shape. This means that pixels have to overlap to achieve reasonable uniformity of exposure on the photoreceptor. This spatial overlap occurs at roughly the point where the light intensity has fallen by half from the central value. It is variations in this overlap that give rise to motion quality artifacts in prints, especially in halftones (or gray levels achieved by systematic patterns of pixels being on or off).

4.2.3 Photoreceptor

The action of the charging system and imaging system combined is to produce a charge pattern on the surface of the photoreceptor that constitutes the *latent electrostatic image*. In copiers, this pattern consists of charge where the original document is dark, and practically none where the original document is light, with variations in between these two states depending on the optical density of the original. This is known as *charged area development* (CAD) or “write-white.” In printers, for mostly historical reasons, the opposite convention is used—this is known as *discharged area development* (DAD) or “write-black.”

The photoreceptor must be designed to respond correctly to the wavelength of the exposure source; it must also be capable of repeated cycles of charge and discharge with no memory of any previous cycle; and it must be capable of supporting the required charge level and achieving the required discharge level over many hundreds of thousands of cycles without these levels varying significantly. The most important characteristic of the photoreceptor is its *photoinduced discharge curve* (PIDC). It is this response that determines the amount of light required to discharge it, and it determines the spatial shape of the charge pattern produced by a single pixel exposure. An example of such a curve is shown in Fig. 4.6. This curve can be approximately described algebraically: this enables computations to be performed of the resulting charge pattern shape when the photoreceptor is exposed to a single pixel, for example. Basically, as the exposure intensity increases, the single pixel charge pattern shape changes from being Gaussian to square. Coincidentally, the width of a line of single pixels will increase on the printed page. Basically, the intensity is set relative to the sharp bend in the PIDC, so that the effects of variations in the pixel overlap due to motion quality problems are minimized while the line resolution on the print is maximized.

The organic photoreceptor is composed of four basic layers as shown in Fig. 4.7. First comes the substrate, which is electrically grounded in operation; next is a *blocking layer*, or an *undercoat layer* (UCL), which prevents charge leakage from the substrate to the top surface; the *charge generating layer* (CGL), which is the layer in which charges are created by the action of light, comes next; and lastly comes the *charge transport layer* (CTL), which allows the movement of charge across the photoreceptor under the action of the electric fields created by the surface charge in order to effect discharge, and which must also support the surface charge in the dark. The top three layers involve various

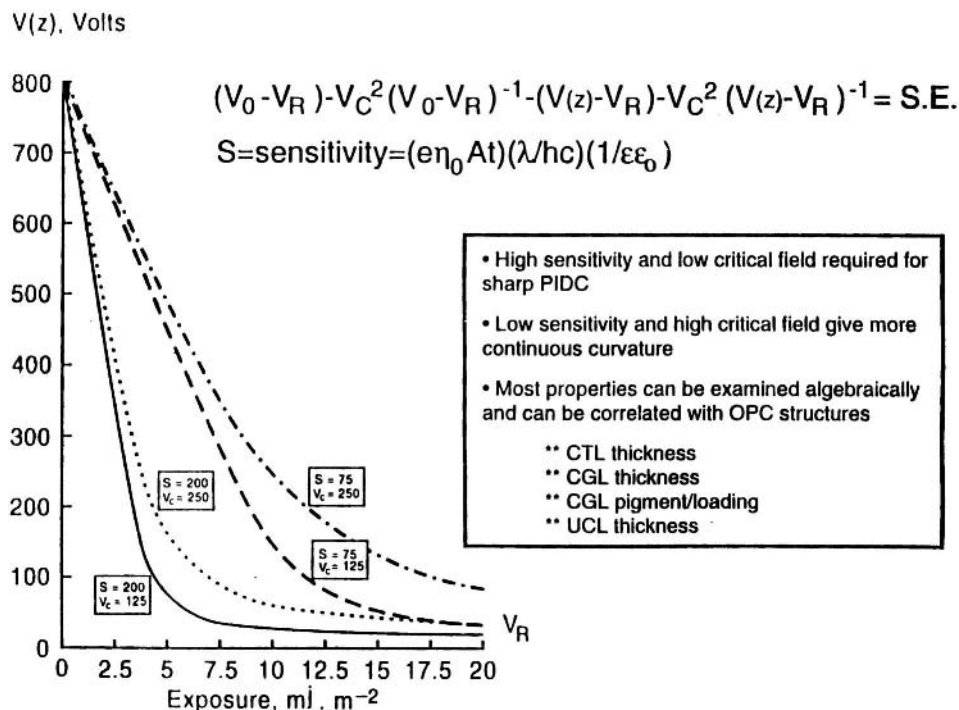


Figure 4.6 This figure shows a set of photodischarge curves typical of photoreceptors in the marketplace. As the exposure is increased, the photoreceptor voltage decreases due to the flow of charges created in the CGL by the action of light on the surface. The equation and the comments in the box illustrate how it is possible to set about designing a photoreceptor for a particular performance. The parameter S depends upon the photoreceptor thickness, t , the light wavelength λ , the dielectric constant ϵ , and the efficiency with which the light is turned into electric charge in the CGL, η ; the remaining factors are various physical constants. *Source:* A. Melnyk. In: Proceedings of the Third International Congress on Advances in Non-Impact Printing (1986).

materials embedded or dissolved in polymers. It is these materials that enable each layer to perform its special function. Typically, the photoreceptor will respond to a spectrum of light, not just a single wavelength, which is dictated by the charge-generating pigment used. For digital printers, this pigment is most often a member of the metallophthalocyanine family, since these pigments respond well to 780 nm light. The absorption of light in the CGL creates pairs of oppositely charged entities (electron-hole pairs), which the pre-existing electric field separates. Since an organic photoreceptor is usually charged negatively, the positive charge (the hole) flows to the surface, while its oppositely charged partner (the electron) leaks away to ground through the UCL. This scheme is shown conceptually in Fig. 4.8 for both CAD and DAD schemes.

These photoreceptors come in both drum and belt formats. The drums are dip coated, and the belts are web coated. Typically, the three top layers are coated in these ways in multiple pass operations. The dimensions of each layer are governed in part by the constraints of the coating process and in part by the electrophotographic system needs. For example, if higher voltages or very long life is required, the CTL tends to be about 30 μm thick. In order to avoid laser diode coherent light interference effects, the CGL is usually

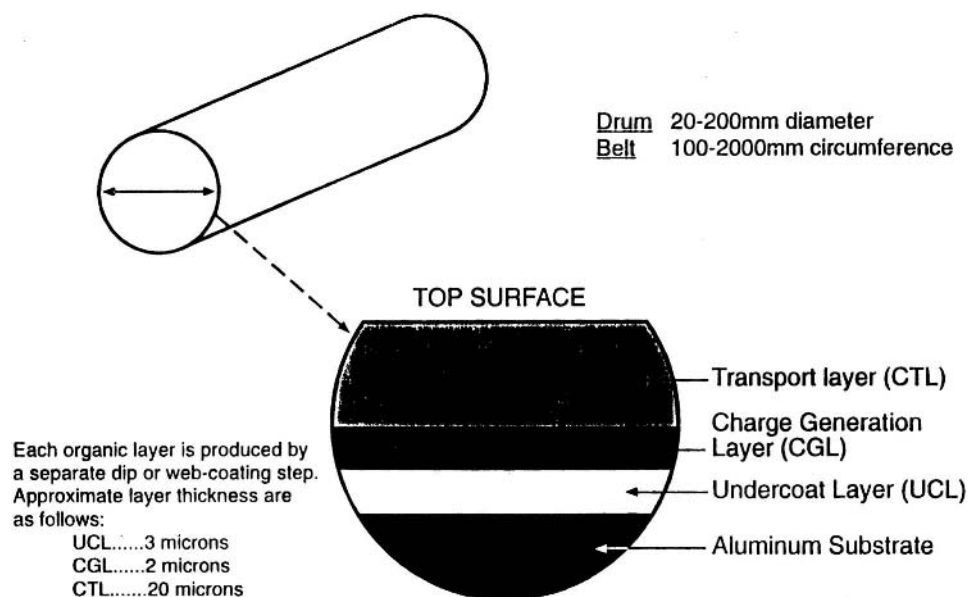


Figure 4.7 This figure illustrate a typical drum organic photoreceptor (OPC) structure; belt photoreceptor structures are quite similar. The UCL serves to block injection of charges from the metallic substrate; the CGL is where light is absorbed and creates electric charges; and the CTL is the layer that gives the photoreceptor its dielectric properties and simultaneously allows transport of one sign of the charge created in the CGL to flow to the surface to discharge the photoreceptor.

coated thick enough to absorb most of the incoming light. However, all photoreceptors generate some small amount of charge in the dark (dark decay), which often depends on the thickness of the CGL. The UCL must not be so insulating as to prevent the escape of charge from the CGL to ground.

The trends in organic photoreceptor development are to achieve longer life, greater electro-optical stability, and better overall coating uniformity. The drivers for these activities are the move toward faster, more robust machines and color printing.

4.2.4 Development

Referring to Fig. 4.8, we see that this step involves attracting the toner to the latent electrostatic image. In the case of typical printers (i.e., the right-hand side of Fig. 4.8), this means depositing toner in the discharged areas by making use of the fringe fields associated with the image. For this to happen, the toner must be negatively charged also. The development subsystem has two essential functions. One is to cause the toner to acquire the desired sign of charge. The other is to deliver the toner into close proximity to the image. There are two main schemes that are in use to achieve these twin goals. There are many variations of these schemes in existence; the reader is referred to Refs. 6, 10, 12, and 15 for additional details on some of these variations.

Figure 4.9 depicts an outline of a *two-component development* (TCD) method. The two components are a carrier and a toner. The carrier is a magnetic material such as steel grit or a ferrite, which is often partially coated with a polymer. The toner is a polymer

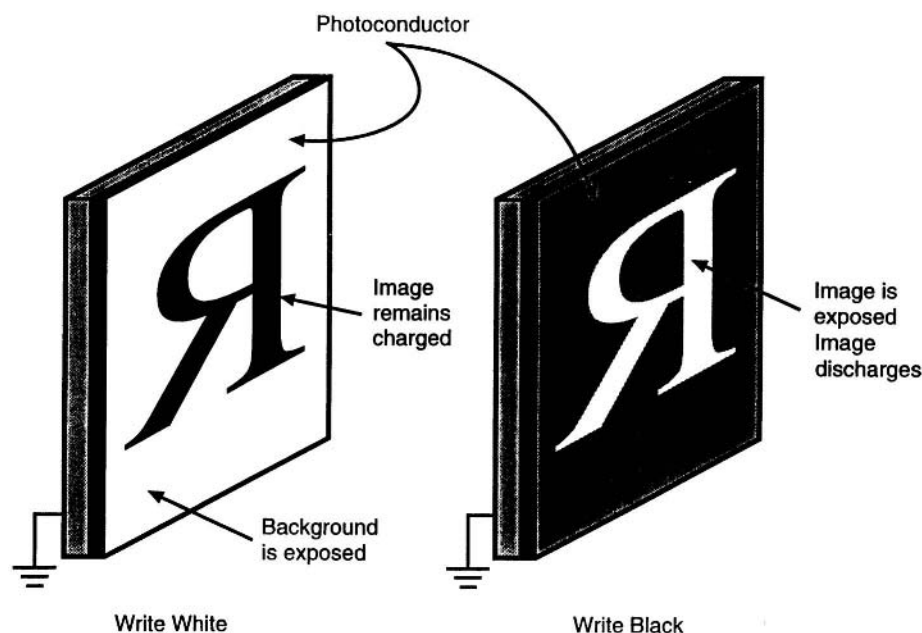


Figure 4.8 This figure shows the basic difference between charged (CAD) and discharged (DAD) area development. In both cases the electrostatic latent image, here shown in the shape of an R, has nonuniform fringing fields associated with it that will attract charged toner. In the write-black case on the right, which is typical of digital printers, the toner is the same sign as the electrostatically charged background areas, from which it is repelled, depositing in the uncharged image areas. If opposite sign toner is used, a reversed image will be developed; i.e. a black-on-white image will become a white-on-black image.

resin containing a colorant and other functional agents. The carrier-to-toner diameter size ratio is roughly 10:1. Feedback systems are used to keep the mass (or volume) ratio of toner to carrier, the *toner concentration*, at a reasonably constant ratio of roughly 3–5 wt%. The surface chemical properties of both the toner and the carrier are such that when they are tumbled together in the agitating area of the development housing, *triboelectric* interactions cause the toner to acquire a negative charge and the carrier to acquire positive charges. The figure shows the opposite situation, which would be true for a light lens copier CAD system. The magnetic forces created by the internal magnets plus the rotation of the shell around them cause the magnetic carrier to be transported into the region of the photoreceptor bearing the electrostatic image. The carrier is, of course, also transporting the toner, which is electrostatically bound to it by Coulomb forces. The magnetic field strengths are arranged so as to make the carrier beads form into hairlike structures as they approach the electrostatic image creating a *magnetic brush*. In order to complete the process, an additional voltage is applied to the rotating shell that is less negative than the image background areas, but much more negative than the image areas. This assures that the electric field in the background areas opposes the deposition of toner and simultaneously creates a stripping force toward the photoreceptor in the image areas. The strength of this electric field determines the quantity of toner deposited, which will in turn dictate the darkness of the final image on the page.

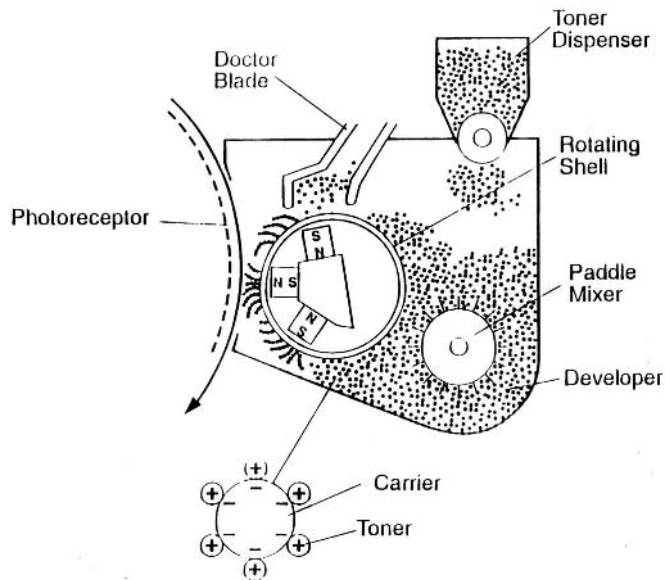


Figure 4.9 Cross section of a typical two-component development subsystem (TCD) showing the toner supply arrangement at the top right, the mixing area where the toner and carrier are blended together and triboelectric charging occurs, and the magnetic transporting scheme on the left. The toner dispenser is typically what the customer buys and replaces; the other component part of the system containing the carrier remains as part of the machine.

The other main scheme is called a single-component development (SCD) system. A schematic of it is shown in Fig. 4.10. SCD is much more compact than TCD. For this reason it is most often used in small printers. There is only toner in this scheme, which in order to be transported from a sump to the electrostatic image is itself magnetic. This is achieved by having small magnetic particles in the toner resin, which often serve as colorants as well. In order to charge the toner particles, some combination of rubbing contact with a triboelectrically active polymer and bias voltages is used. A separate development bias is used on the rotating shell, as for TCD, to ensure deposition of toner on the electrostatic image.

In both cases, the rotating roll that transports the toner from the sump to the development nip must be coated with materials that ensure proper electrical performance. That is, excessive current flows must be prevented, as must excessive accumulation of charge as toner is continually deposited on the electrostatic image.

As was mentioned above, the toner itself contains other functional agents. The role of these agents is severalfold: they help to ensure the acquisition of the correct triboelectric charge (*charge control agents* [CCA]); they help to assure good flow properties that are essential for preventing the toner from agglomerating or clumping (*flow agents*); they help to assure good release properties from the fuser rolls (*release agents*); and they can impart particular properties to the toner on the printed page such as enabling *magnetic ink character recognition* (MICR) for check-writing purposes. A typical SCD toner particle is shown in Fig. 4.11. Often, charge control, flow, and release agents are externally blended into the developer and are collectively known as *external additives*. The toner resin itself

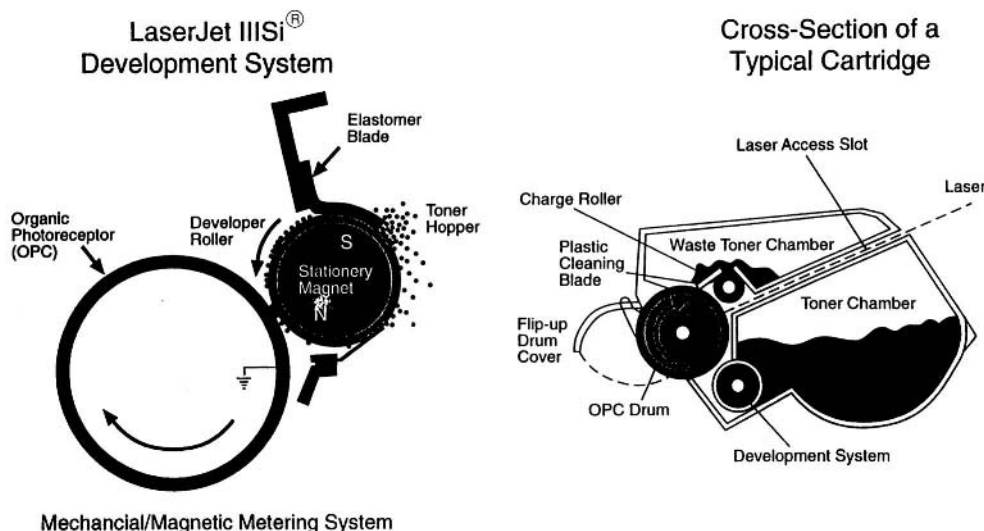


Figure 4.10 Cross sections of a typical single-component development subsystem (SCD) showing the toner supply arrangement, the area where the toner triboelectric charging occurs in conjunction with the magnetic transporting scheme on the lower left in the right-hand sketch. The whole cartridge containing an OPC, a charging system, and a cleaning blade as well as the toner is typically what the customer buys and replaces; the other components such as exposure remain as part of the machine.

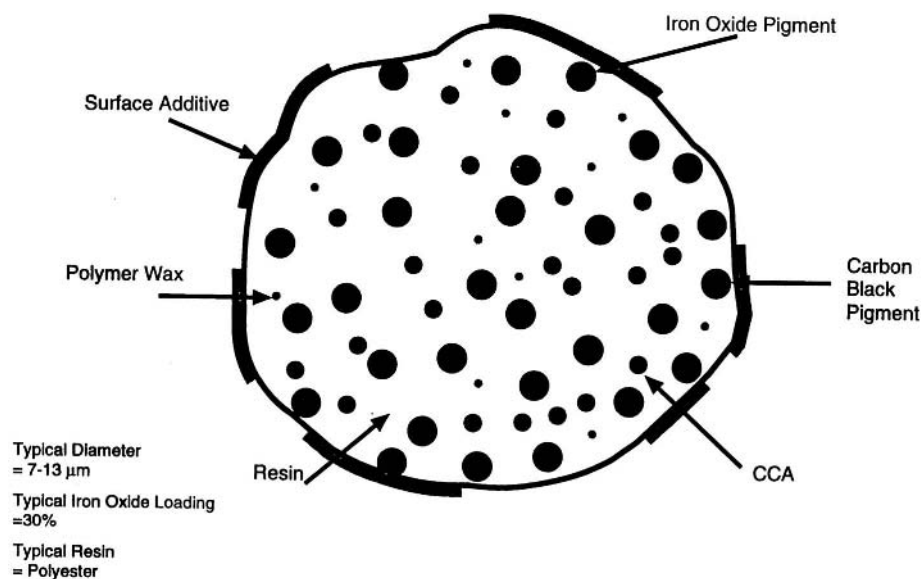


Figure 4.11 Shown in this figure is a typical SCD toner particle. Several of these components are also present in TCD toners. No iron oxide is present in color toners. The typical particle size is in the range of 7 to 9 μm , with a range about the average diameter of about 4 μm . The wax and the resin largely control the basic fusing properties, but the other additives modify the rheological behavior as a function of temperature. The surface additive, the resin, and the particle morphology largely control the flow properties. The CCA and the surface additives largely control the triboelectric charging properties, but the pigment and the resin modify this.

also must satisfy certain melt rheology requirements having to do with the fusing process. The toner particle size also influences the image quality—basically smaller is better—but there are limitations on what is possible that are governed by the manufacturing process, health considerations, and cost considerations. The typical average particle size for conventionally produced toner at the time of writing is between 6 and 7 μm . In terms of colorants, black presents no problem for either TCD or SCD systems. But since magnetic materials tend to be black or dark brown, SCD is particularly unsuitable for process color (or four-color) systems; the magnetic material makes all colors appear muted or even muddy. In order to have single-component development systems without magnetic transport, significant changes to the charging and delivery schemes have to be made (Ref. 15).

The trends in toner development are toward yet smaller particle sizes, toward lower cost manufacturing processes, and toward lower melting materials with good flow capabilities and improved environmental stability. The drivers for these trends are the need to improve color print quality and to decrease color per page costs with much improved reliability.

At this point it is useful to pause and see where in the electrophotographic process we are. Referring to Fig. 4.2, we have completed discussing steps 1–4 in terms of the right-hand side of the figure; and we have traveled about 200° counterclockwise from charging in terms of the left-hand side. Figure 4.12 summarizes the situation pictorially for achieving a single line as the image in both CAD and DAD processes. From this point on, the paper or other media enter the process.

4.2.5 Transfer

As with charging, there are two main approaches, which both involve the creation of an electric field across the photoreceptor–toner image–paper (or medium) sandwich. At the transfer step, the paper or medium must come into intimate contact with the toned image while moving at the same velocity as the photoreceptor; this is to minimize any possibility of image disturbance. It is a mechanical engineering matter beyond the scope of this introduction. Suffice it to say that this is readily accomplished so that upon contact no image disturbance occurs. The goal of the transfer step is to achieve 100% transfer of all the toner in the image areas from the photoreceptor to the medium without any disturbance to the image, while simultaneously preventing any stray toner in the background areas from transferring over. This is not as simple as it sounds, for two reasons. First, small charged particles, each of which has the same sign of charge, have to be physically moved a very small distance. Coulomb repulsion forces act so as to move these particles apart. These forces are significantly reduced when the particles are in contact with the smooth insulating photoreceptor. Second, at small distances, a molecular force, the van der Waals force, is stronger than the Coulomb force holding the toner to the photoreceptor. The Coulomb force itself increases as the particles get smaller. So in the transfer step the force created by an electric field must overcome these effects. The net result is that usually no more than 95% *transfer efficiency* is achieved; values as low as 85% have been reported. The last transfer problem is that the medium that will carry the final image, paper in particular, is not always well-defined electrically and that the electric impedance properties vary as the humidity changes. This means that performance in transfer depends on the local environment and on the paper type. If transfer efficiency is low, additional noise is introduced into the image, which degrades the print quality.

Figure 4.13 shows the first method employed to create an electric field: another corona device. It is essentially the same scheme as used for charging (Fig. 4.3). The

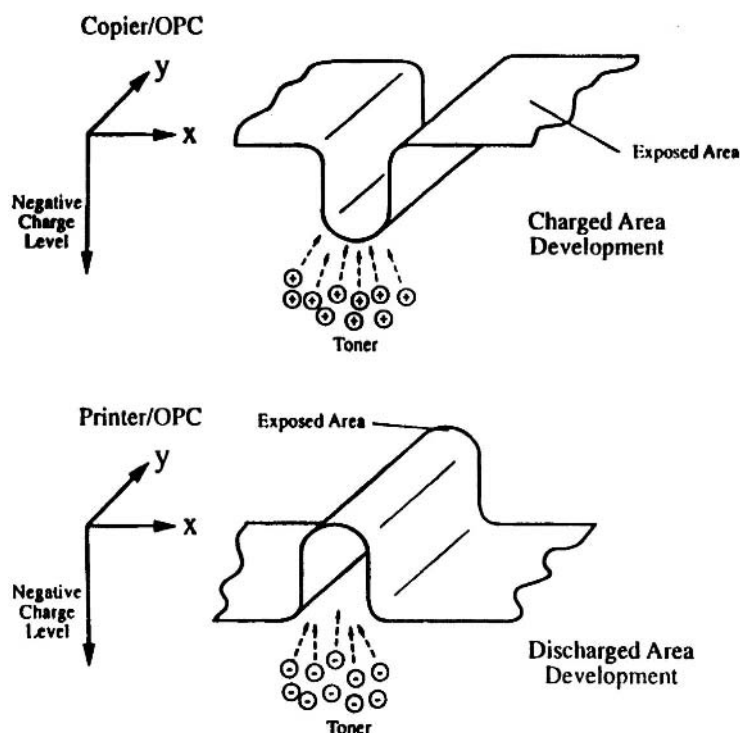


Figure 4.12 This is an illustration and summary of the two methods of creating and developing a latent electrostatic image in conjunction with an OPC. Both cases show the development of the image of a line. The upper drawing shows the situation for a copier wherein the OPC was initially uniformly negatively charged and the image area remains charged after exposure. This image area has electrostatic fringe fields that attract positively charged toner to it. The lower sketch is for a printer wherein the OPC was initially uniformly negatively charged and the image area is discharged after exposure. This image area has electrostatic fringe fields such that negatively charged toner is attracted to it.

charges deposited on the back side of the media for DAD systems using organic photoreceptors are positive, which creates an electric field directed so as to attract the negatively charged toner to the underside of the medium. This field has to be strong enough to attract much of the toner, but yet not so large as to create air breakdown in the small air gaps, which are ever-present due to the roughness of the paper. In practice this means electric fields in the range of 25–35 volts/ μm have to be created. The force of attraction between the charges on top of the paper and the ground plane of the photoreceptor are such that considerable pressure is created: this pressure helps to enhance the transfer efficiency and to prevent image disturbances. The other place where such disturbances can occur is in the act of removing the paper carrying the toned image from the photoreceptor. The electric field strengths are such that air breakdown can be encountered as the air gap during this stripping process increases. To counteract this, another corona device is often used in order to reduce the electric field strength during paper stripping from the photoreceptor.

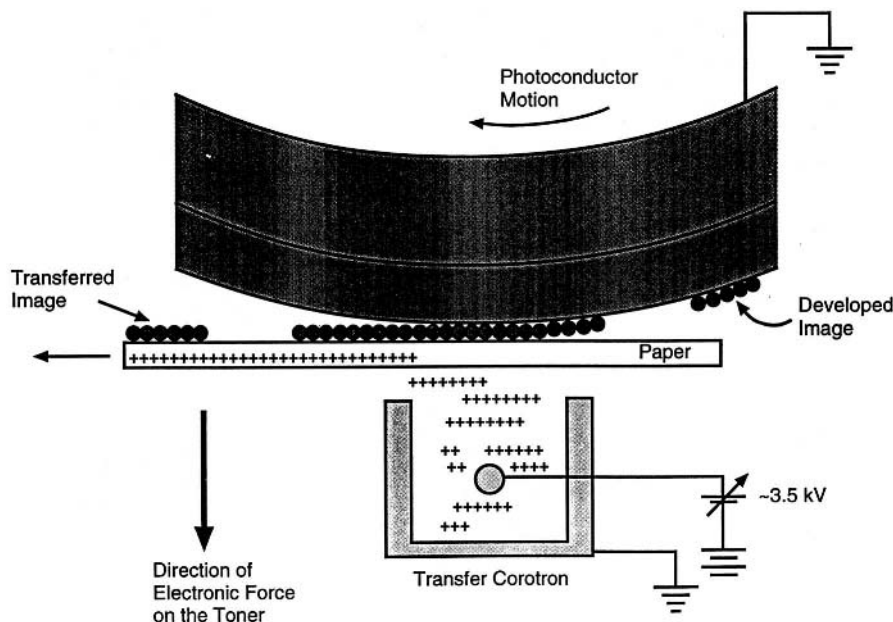


Figure 4.13 This is an example of a transfer charging scheme. It shows a charging device similar in concept to that in Fig. 4.3, which is used to create an electric field across the paper/toner/photoreceptor sandwich. The photoreceptor substrates provide the ground reference potential. In this example, the developed toner is negatively charged, and the charges deposited on the back of the paper are positive so as to create an electric field that creates an attractive force in the direction shown.

The other method for achieving transfer is similar to the biased roll charging scheme (Fig. 4.4). The same considerations as for scorotron transfer apply. In this case, though, additional pressure can be controlled by the loading on the *biased transfer roller*. The reasons for using this scheme are again compactness and less generation of oxides of nitrogen and ozone, plus somewhat better mechanical control over the media.

4.2.6 Fusing

The last step in the imaging path is to fix the toner permanently to the media. The toner resin is typically a thermoplastic. Moderate amounts of heat will cause it to flow and melt. If the respective surface energies of the molten toner and the media are correctly matched, the toner will flow into the fiber structure of the paper or simply adhere to smooth media like transparencies. So the function of the *fuser* is to melt and coalesce the toner, to cause it to flatten so that its final surface roughness profile matches the desired outcome (e.g., rough for a matte finish and smooth for a glossy look), and to create minimum image disturbance (e.g., no loss of resolution). As for the other subsystems, there are several ways to fix toner to the paper to achieve the required final print appearance. The principal methods are the contacting or the noncontacting application of heat. The noncontacting method is done either by flash fusing or by radiant fusing (e.g., as shown schematically on the right-hand side of Fig. 4.2, step 7). The contacting methods either use only pressure to squeeze the toner flat and into the paper, or employ a combination of heat and pressure,

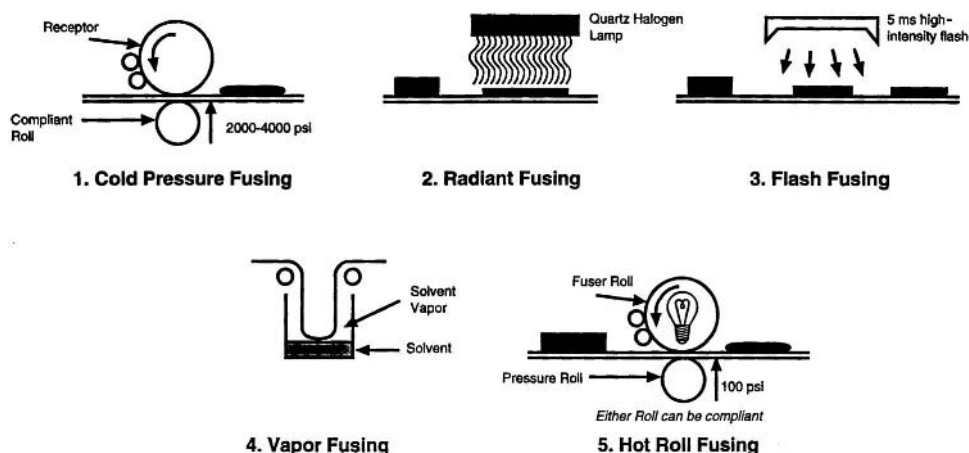


Figure 4.14 This figure shows sketches of the various kinds of fusing process that can be found in the marketplace. The selection of the fusing process depends upon such things as power consumption requirements, process speed, toner gloss requirements, and cost.

or exposure to solvent vapor to achieve coalescence. Only hot roll fusing will be discussed; the references give additional details about all methods.

Figure 4.14 shows a summary of the various methods. The lower right-hand picture shows schematically the standard hot roll method. Both rolls consist of at least two layers. There is a metal core covered by a conformable elastomer in order to be able to create a nip. In the case of the heated roll, it must have good heat-conducting properties. The nip width and the roll temperature are adjusted so that the toner is heated hot enough and for long enough to achieve the desired end. There is often another layer added to achieve good life and to achieve good toner or paper release properties for both of the rolls, since duplex operation is often a necessity. In some cases, the fuser rolls are lightly treated with an oil to aid in release; in other cases the toner has a waxlike release agent designed into it. This last is mostly true for low-speed black-and-white printers. The surface roughness of the heated roll, the nip pressure, the paper thickness and mechanical structure, and the toner pile height and melt rheology properties all combine to yield the degree of gloss and the fix level in the final image. From the foregoing, it can be realized that this is not a simple process. The toner is the intermediate agent between development and fusing. These two subsystems impose some stringent boundary conditions on the toner designer.

Figure 4.15 shows a typical time-temperature profile as the toner pile representing an unfused image passes through the fuser. As can be seen, the process of fixing the toner to the paper proceeds in three seemingly distinct steps: melting, coalescing, and flowing. In reality, since the toner is heated from above, the processes merge into one another throughout the toner pile. If the total quantity of heat applied is too low, the image fix is poor, and some toner adheres to the fuser roll because its internal cohesion is too low due to a lack of full coalescence (*cold offset*). If the fuser roll is too hot, the toner becomes too liquid and again sticks to the fuser because its internal cohesion is again too low (*hot offset*). The desired state is that the toner becomes hot enough to melt and coalesce and flow, yet not so hot as to have low internal cohesion. The adhesion to the medium must be greater than that to the fuser roll surface under these conditions, of course.

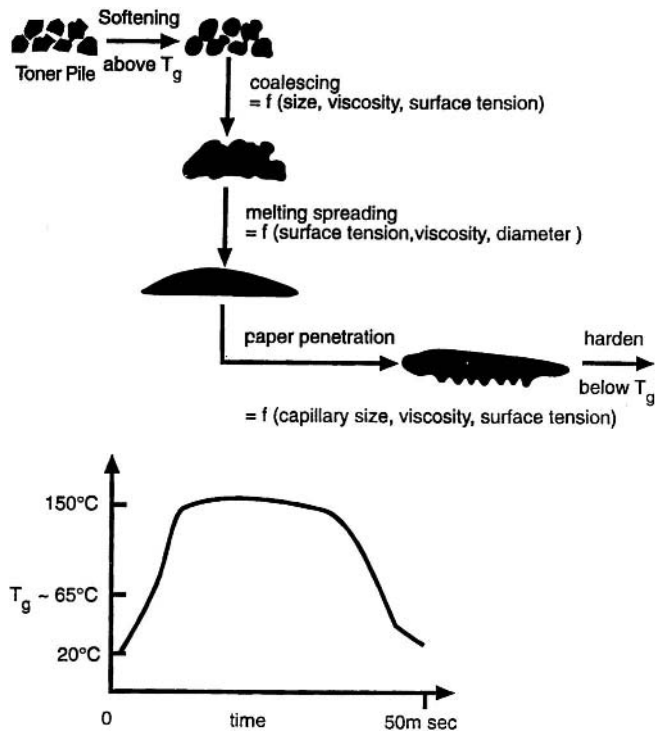


Figure 4.15 This figure shows schematically what is happening to the dry powder toner pile as it goes through the fusing nip. The graph at the left shows a typical time–temperature profile. As the toner softens, coalesces, and melts, various physical properties of the toner are controlling these processes, as shown at each step. These properties are all temperature dependent. The smoothness of the final toner layer also depends on the fuser roll surface properties. The final step is to cool the toner as it exits the fuser, by which time it has penetrated the paper fibers. The cooling step is by unforced convection and conduction.

4.2.7 Cleaning and Erasing

The final process step before the whole imaging cycle begins anew is to refresh the photoreceptor by removing any memory of the previous image; that is, to restore the photoreceptor to as close to a pristine state as possible. This means eradicating both the remaining electrostatic image and the traces of toner that were not transferred or that randomly found their way into the background areas. The electrostatic image is typically eliminated by flooding the photoreceptor with uniform illumination (*erase*), but it can also be done by recharging the photoreceptor uniformly. The former eliminates any possibility of a “ghost” image; the latter preferably requires the use of an alternating voltage corotron in order to create both positive and negative charge. The biased charging roll already uses both AC and DC voltages, so the erase lamp is usually omitted in this case.

The remnants of toner are removed either by mechanical means alone or with some form of reverse charging assistance that lowers the charge on the toner and consequently the adhesion force to the photoreceptor. The mechanical systems in use are brushes or blades or combinations of these. One such scheme is shown in Fig. 4.16 for a *blade cleaner*. It will be noticed that the waste or used toner is collected in a sump. In some

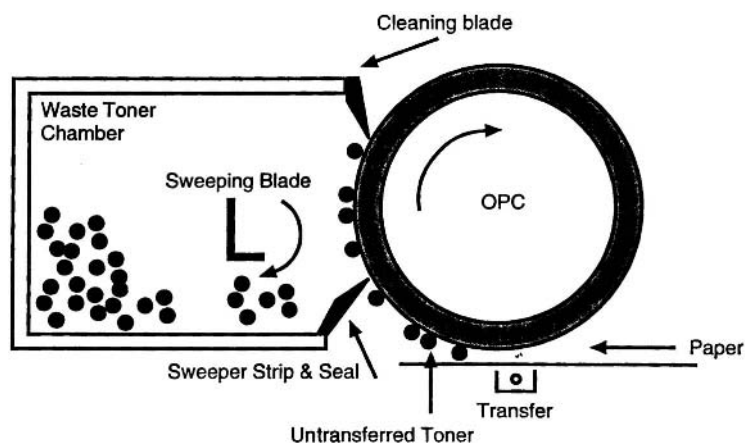


Figure 4.16 This figure illustrates perhaps the simplest cleaning system for removing toner from the photoreceptor. The blade simply scrapes off the toner into a waste hopper. Naturally, there is an art to designing the shape of the blade. Its effectiveness depends on this shape and the pressure exerted on it. Both the blade and the photoreceptor become damaged and worn during long usage.

systems, especially small machines, this toner accumulates until the sump is full. It must then be emptied or disposed of. In several larger systems, this toner is recycled within the system. The reason for this is understandable when one considers that if the transfer efficiency is 90%, 10% of the toner is being wasted.

4.3 APPLICATIONS TO COLOR

The first commercial color copier using the electrophotographic process was introduced by Xerox in 1973. This was a light lens device, not a digital printer. It took another 10 years or more before the digital versions appeared. This had as much to do with progress in computer technology as it did with progress in electrophotography. The method by which color pages are produced essentially mimics any printing process. The color image is broken down into four color planes, and each is printed separately and sequentially on the same piece of paper so that when the eye integrates the image it sees a full-color print. For information on the color process itself, see Refs. 17, 18, 19, and 21–29. These references are mostly general in nature and the additional criteria that they teach about color per se has been applied. The references used earlier for monochrome printing are still valid. Here we shall only address implications for the electrophotographic process. The four colors in question are cyan, magenta, yellow, and black (*CMYK*) since we deal with the so-called subtractive color process. What this means is that the whole electrophotographic process must be repeated four times within the confines of the same piece of hardware under the control of a microprocessor. The colors available from the process are determined by the specific pigments used in the toners, the media printed upon, and the method of digitally imaging and overlaying the four-color planes.

The same basic electrophotographic steps must still be accomplished. But first let us consider color in the abstract as compared to black-and-white documents. Primarily, black-and-white documents consist of text with some use of graphics; they are meant to convey information or communicate in mostly a verbal or arithmetic manner. Thus the

images must be above about 1.0 *optical density* with a matte finish, edges must be crisp, serifs or other small features must be resolved, the background must be clean, solid areas must be uniform, and graphics half-tones must be free from noise. In the United States, the typical black-and-white page is 8.5×11 ", is often duplex, is on plain (uncoated, nonglossy) paper, and has a toner area coverage between 3 and 8%.

Color documents, on the other hand, expand beyond many of these requirements and in other cases impose much stricter quality bounds. The primary changes are, first, the mechanical ones associated with large paper sizes and the handling of glossy or coated stock: these changes do not greatly affect the electrophotographic process. The major problem encountered is an engineering one of "stretching" all the subsystems to deal with a wider imaging path. Second, the requirement is to deliver uniformly glossy images at much greater toner area coverages, often up to 30% per color: these changes affect the design of the development subsystem, the toner, and the fuser. The changes to the fusing subsystem and development subsystem are often modifications to existing designs. Last, the issues related to print quality have to do with the fact that two or more CMYK toners are required to achieve a full *color gamut*: to achieve a uniform solid area of green, say, the yellow and cyan toners must be perfectly registered everywhere on the page; to achieve good definition in both highlight and shadow areas, single pixels need to be developed and properly fused; to achieve a sufficient number of gray levels with reasonable resolution to reduce graininess, at least 600 dpi is required; to get flat documents with no perceptible toner piles in dark areas, low developed toner mass is required; and to get a uniform level of gloss for different gray levels on glossy or coated stock, toner and fuser designs must be changed. The imaging system design is also impacted by these considerations, and the transfer subsystem often is as well. The systems that are largely left unchanged (but not unchallenged) are the charging, photoreceptor, and cleaning-and-erase subsystems. Usually, the first two are required to deliver more spatially uniform performance than for the monochrome case.

Precisely how this is accomplished is again to some degree a matter of choice. If the emphasis is to be on compactness and cost at the expense of a loss of speed and some degradation of print quality compared, say, to offset prints, then the same photoreceptor is used to image all four color planes. This results in a *multipass* system. But further choices are still to be made for the method where each color plane is stored before the final color image is complete, as illustrated in Fig. 4.17. The three choices are (1) on the photoreceptor as exemplified by the HP Color LaserJet®; (2) on the paper as exemplified by the Canon CLC® series and the Xerox Majestik/Regal®; and (3) on an intermediate as exemplified by the Tektronix Phaser 540/550® and the Xerox Xprint® series. There are further nuances within these boundaries depending on whether the CMYK developer stations are fixed or movable, and whether the photoreceptor is a belt or drum geometry.

If, on the other hand, the emphasis is on speed and productivity with excellent print quality but size and cost are secondary considerations, then a *single-pass* system is preferred. The choices in this case are illustrated in Fig. 4.18. The choices remain largely the same except that now the CMYK developer stations are always fixed. The currently preferred method is to use a separate electrophotographic engine for each color plane as exemplified by the Ricoh 8015®, the Xeikon DCP/32D®, the Xerox DocuColor 40®, and the Canon CLC1000® and their successor products.

In order to fix ideas more clearly, two examples only will be discussed—one each of multipass and single-pass architectures. Figure 4.19 shows the multipass examples. Most of the useful subsystem elements have been left out of the schematic to illustrate

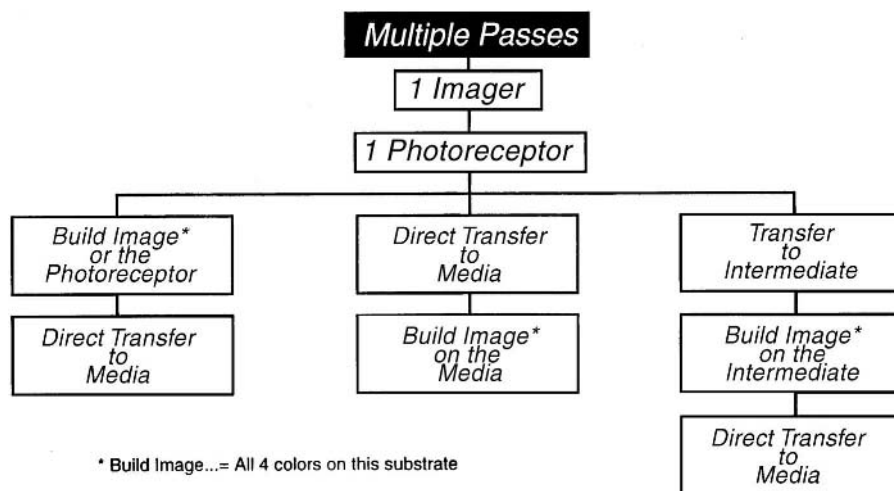


Figure 4.17 This figure shows the various pathways for implementing a multipass color electro-photographic process. There are many options, and the particular choice is dictated more by business, market, and patent access considerations than by technological ones. Examples of each path exist in the marketplace.

the features. The first is that the development stations have to be rotated to come into coincidence with their respective electrostatic latent images. This causes the development system to be the largest machine component. The second feature to note is that although the paper paths can be very different, the cut sheet of paper itself is stored on another drum (which is also larger in size than the photoreceptor) during the whole imaging process and

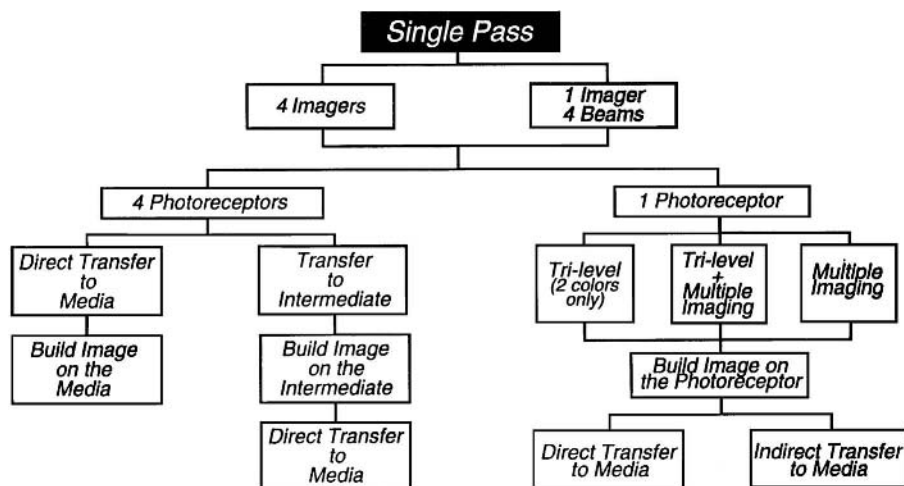


Figure 4.18 This figure shows the various pathways for implementing a single-pass color electro-photographic process. There are many options and the particular choice is dictated more by business, market, and patent access considerations than by technological ones.

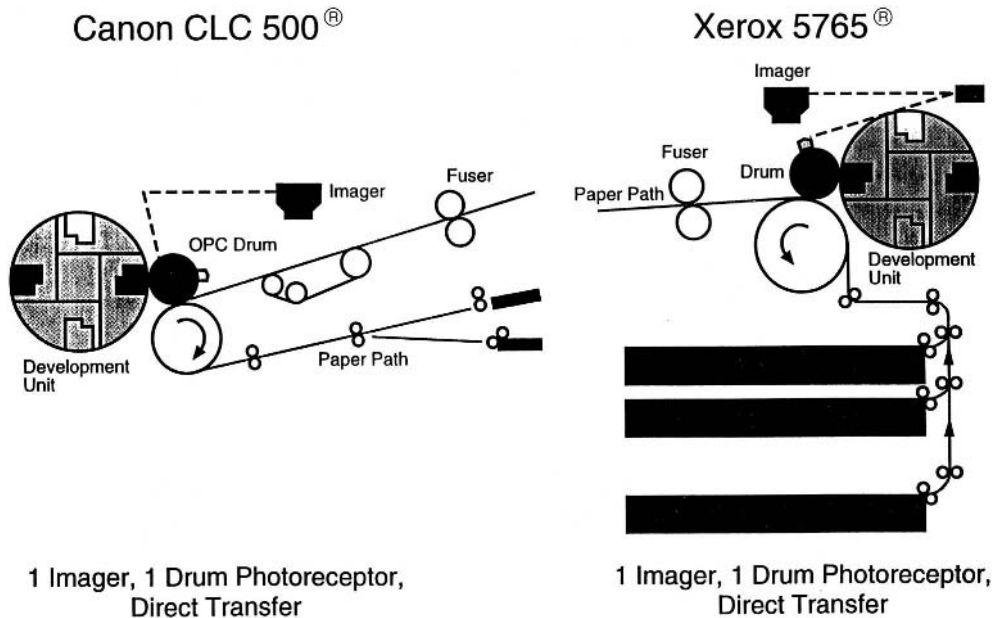


Figure 4.19 This figure shows two similar examples of a multipass color system. In both cases the paper is stored on a drum. Each color plane is imaged in sequence. As it is processed, it is transferred from the OPC to the paper on the drum. To develop the next color electrostatic latent image, the developer unit is rotated 90° to bring the next color into contact with the OPC. Both systems use laser diodes and spinning polygons for imaging, and hot roll fusing. The differences are in the details of the paper path and the image processing algorithms. Both units have built-in scanners for copying (see Fig. 1). Duplex printing or copying requires moving the media through the system a second time.

accumulates the image color plane by color plane. So compared to black-and-white printing, the complexity introduced by the need to keep four operations synchronous is considerable. This sort of scheme is capable of printing at the rate of 10 color pages per minute with OPCs no larger than 100 mm in diameter. To go faster, the size typically must increase somewhat and the development stations must be switched more quickly. The empirical limit to this scheme appears to be about 10 ppm.

Figure 4.20 shows the single-pass examples; again many of the details of the standard subsystems have been omitted from the sketches. The previous two examples were capable of duplex printing by having a convoluted paper path, since the image needs to be fused to each side separately. The single-pass example on the left suffers from this same difficulty; the one of the right overcomes this problem by having eight separate electrophotographic engines contained within it. There are other major differences related to choices the designers have made. The slower speed machine on the left uses laser diodes, in a rather complex imager, and relatively small OPCs, each of which is imaged with a separate laser beam. The system on the right is faster and uses larger OPCs, each of which is imaged by its own LED image bar. There remain two other distinctive differences. The machine on the left uses heated roll fusing and handles only cut sheet media. That on the right uses a radiant fuser and handles only a web of paper or other media.

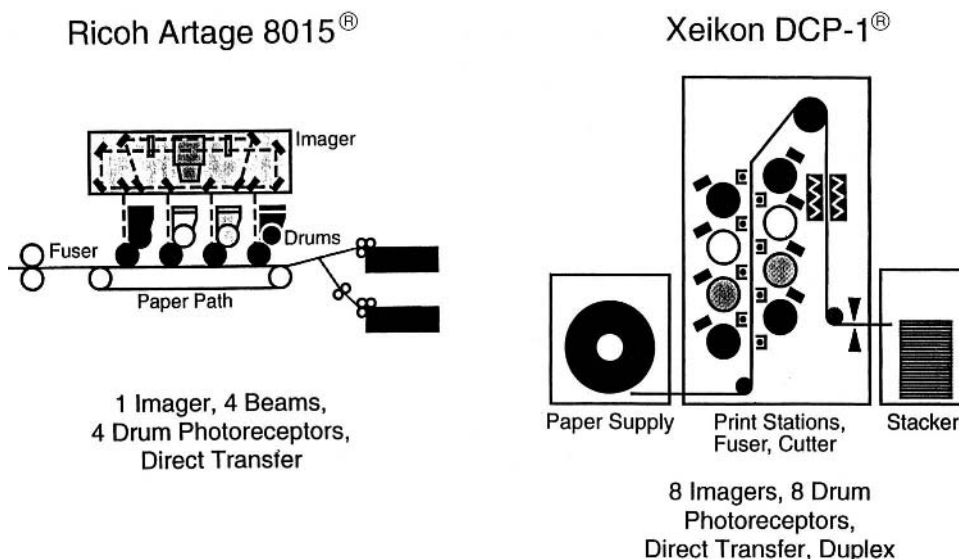


Figure 4.20 On the left of this figure is an example of a single-pass color system employing a single spinning polygon with optics to create four beams that image on four separate OPCs. Development, transfer, and fusing are all standard. Cut-sheet paper is “escorted” past each OPC on a transport belt before being delivered to the fuser, which is a heated pressure roll. Duplex printing requires the paper to be sent through the process yet again, so that duplex pages are produced at approximately half the speed of simplex pages. On the right of the figure is a more complex, higher speed design, which uses eight separate LED bars to image onto eight separate and somewhat larger OPCs. The medium in this case is fed from a roll and preconditioned before entering the process. Printing is simplex or duplex in the same pass through the process; the fusing in this case is by radiant fuser.

In both cases, however, the medium acquires each color plane in sequence by electrostatic transfer as it passes by each photoreceptor.

There are many more commercial variants on these themes. At present, all the color copiers and printers in production use digital imaging on organic photoreceptors with discharge area development and a CMYK toner set with an average size of about 7 μm . Nearly all use hot roll fusing and corotron transfer.

4.4 MAJOR ALTERNATIVES

This section will address briefly the three major alternatives to the xerographic version of electrophotography. Each of them utilizes several aspects of the basic process, so only the differences will be covered. Each of the systems discussed is in commercial use; for a more detailed discussion of them, the reader is again directed to the references. These brief discussions also illustrate the point made at the beginning of the chapter, that there are many ways to practice print-on-demand from a printing engine viewpoint (Refs. 5, 14, 15, 16, 19, and 20).

4.4.1 Ionography

The major difference in principle between ionography and electrophotography is that the optical imaging system of the latter is replaced by a direct charge writing scheme that is

imagewise capable; i.e., it can be turned on and off at the pixel level to write individual pixels. It has also been called “electron beam imaging.” Since no light is involved, no photoreceptor is required. This item is replaced by a simple dielectric member of suitable thickness and electrical properties; e.g., it must retain charges only on its surface with no leakage into the bulk, or image ghosting will result. The charge writing system still consists of a glow discharge in air, but now much more closely spaced multiple electrodes with apertures that control the pixel size are used to switch on and off the flow of current to create the images. The drawback to this scheme is that as the optical imaging techniques have moved on to 1200 dpi, this technology has found it harder and harder to keep pace. As practiced by Delphax, the development system is single component and the fusing has been done by simultaneous transfer and cold-pressure fixing. There is no intrinsic reason why this need be so: two component systems, standard transfer, and hot-roll fusing can be used, which opens up the door to color printing using this approach. This technology is fully capable of monochrome speeds above 300 ppm.

4.4.2 Magnetography

The major difference in principle between this method and electrophotography is that the optical imaging system is replaced by a magnetic writing head and the photoreceptor by a magnetizable receiver. The scheme bears some resemblance to tape recording in this regard. The system inevitably must use magnetic toner that is attracted to the magnetic latent image. This requirement makes this technology unsuited to color printing. As practiced by Nipson, transfer and fusing are done by using magnetic force and pressure, respectively. This technology is fully capable of monochrome speeds above 300 ppm.

4.4.3 Liquid Toner Development

The major difference in principle between this method and electrophotography is that the dry powder development system is replaced by a liquid ink system. The liquid “ink” consists of fine toner particles in a low molecular weight hydrocarbon solvent or carrier that also contains some additives that ensure that the toner particles acquire a net charge. Managing the carryout and mass balance of the carrier and ensuring a good fix level to most popular printing papers are two of the challenges for this technology. As practised by Indigo, an intermediate belt is used to prepare the image for transfer and fixing. The principal advantages of this technology are the low toner mass on the media, that toners can be mixed on line, and that exotic toners such as metallics can be fairly readily adapted to the system. This technology is fully capable of monochrome speeds above 200 ppm.

4.4.4 Electrography

This system is a combination of two of the above, ionography and liquid toner development, but with the simplification that the image is written directly onto the media by an array of niblike electrodes that may be switched on or off at the pixel level. As practised by Xerox ColorGrafx, this technology is quite slow and confined to wide format systems.

4.5 SUMMARY

This brief introduction has been intended to introduce the reader to the electrophotographic process as a system where all the serial process steps have to perform well in the context

of both the ultimate print quality and machine reliability, and the requirements set by the preceding and proceeding subsystems. It has deemphasized the copying function and focused on digital printing, because this is the direction the technology has taken and this is the path to color. It has attempted to point out the changes required of the basic monochrome process as a result of this shift. The references are not intended to be comprehensive, merely suitably more detailed for the reader who wishes to pursue the subject to find out more of the specifics related to variant ways of performing each process step, or to find out more about how to think about color. An attempt has been made in the figures to illustrate how the process works in principle rather than to indicate the best way to design each subsystem. There has been no attempt to be exhaustively technical; electrophotography is such a multidisciplinary process that only teams can successfully design a robust, reliable, and effective printer. The skills of many are required, and the team members learn best by doing and teaching each other. An introduction such as this can at best be only a preface.

Given the number of papers that are presented and the numbers of attendees from around the world at the IS&T's Non-Impacting Printing (NIP) Congresses (Ref. 15), the subject is a long way from being exhausted. Electrophotography has just begun to move out of the office into the commercial printing markets represented by offset presses and wide format printing, whether as a complete press or as part of some hybrid system. The miniaturization that occurred in the monochrome electrophotographic process and allowed printers on the desktop has now begun to occur in the area of color printing. The combination of multiple functions in a single machine is also now well established.

This brief introduction has also been meant as context setting for the chapters on toners, developers, and photoreceptors, and other materials that follow. In this regard, some allusions to the more important system level properties of these items have been made. It should be remembered that the design of these materials is done in conjunction with the subsystems, and even systems, in which they will be used. So, just as there are many different embodiments of the various process elements, so there are perhaps an even greater variety of materials used in conjunction with these process elements.

ACKNOWLEDGMENTS

This brief introduction is an outgrowth of a tutorial that I have presented at the Toner and Photoreceptor Conferences, organized by Diamond Research Corp.: I thank Art Diamond of that company for the resulting opportunity to have developed a broader knowledge of electrophotography. I also need to thank my many colleagues at Xerox Corp. who have answered my questions with patience and provided an atmosphere conducive to continuous learning.

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5

Dry Toner Technology

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5.1 INTRODUCTION

5.1.1 History of Xerography

The growth of xerography has been a classic example of the successful commercialization of an invention (Dessauer, 1971). Chester Carlson first used a photoconductive material to make an image on October 22, 1938. At the time Carlson was working with patent applications and was frustrated with the enormous labor involved in making copies of documents. The invention was the direct response to a perceived problem. Nonetheless it was almost 10 years before the Haloid Corporation saw the technology at the Battelle Memorial Institute and decided to commercialize it, and it was more than 10 years from that time before Haloid (now called Xerox) introduced the Xerox 914 automatic copier in 1959.

From this time the growth of Xerox was explosive, reaching \$1 billion in sales by 1968. Although Carlson had used sulfur as the first photoactive material, selenium metal was found to be much more practical, and this was the basis for Xerox's technology in the 1960s. The first commercial "dry inks" used with selenium were based on styrene methacrylate copolymers and had a negative electrical charge.

Other companies were eager to participate in the profitable business of xerography. Thus during the 1970s IBM and Kodak developed and introduced copiers based on organic photoactive materials and positive charging toners. With the 1075 copier, Xerox introduced its own organic photoreceptor and positive toner, while continuing to introduce products based on improved selenium photoreceptors and negative toners.

During the 1980s, Japanese manufacturers such as Canon and Minolta started introducing low-speed copiers based on selenium and cadmium sulfide photoreceptors and again using negative toner. They also introduced dry toner copiers using single-component development, eliminating the use of carrier beads.

Since the early 1980s, many combinations of single- and two-component development and positive and negative toner have been used in the industry. Presently companies are improving toner performance within the design options that they have chosen. None of the options has decisively shown itself to be superior in all applications.

The 1990s have been distinguished by the emergence of color copiers and printers as a major trend in the industry. This has been driven by computers in two ways: first, through creating the need for color output by the creation of color images at computer workstations, and second, through enabling sophisticated correction algorithms to achieve proper color in a given machine.

5.1.2 The Xerographic Process

Several books and articles on the xerographic process and its individual steps have been written over the years (Schaffert, 1980; Scharfe, 1984; Williams, 1984; Schein, 1996; Hays, 1998). The following summary places the role of toner in the context of the entire process. Each step in the process has been the recipient of considerable ingenuity over the years and has a multiplicity of options available. Typical realizations of a particular step are mentioned, but those given are by no means exhaustive.

While the xerographic process comprises many steps involving different materials technologies, the key phenomenon that enabled Chester Carlson to invent his copying process is the existence of materials that will hold a charge in darkness but conduct electricity when exposed to light. These electrically resistive substances, called photoconductors, typically work best when charged to a particular polarity. The photoreceptors (light-sensitive devices) based on the metal selenium used in the earliest xerographic machines are typically sensitized with a blanket positive charge, while later organic materials are negatively charged. These differences normally lead to a change in sign throughout the xerographic process when lenses are used to cast the image of a document on the platen onto the photoreceptor. In particular, they determine the sign of the dry toner used to develop the latent image. On the other hand, laser imaging allows us to discharge the photoreceptor either where we want the image to appear after development (discharged area development) or where we want blank areas after development (charged area development, as in light lens based copiers). The choice of either of the two options will change the charge polarity of the toner required. The choice is typically determined by many factors such as print quality or the availability of a suitable toner of the correct charge.

A practical copier based on photoconductivity goes through six basic steps in reproducing a document (Fig. 5.1): charging, exposure, development, transfer, fusing, and cleaning. A seventh step (erasure) is discussed below but not shown in Fig. 5.1. All the steps are repeated for each additional copy.

In the charging step, the photoreceptor is covered with ions of the appropriate polarity through the use of a wire or grid biased to high voltage.

In the exposure step, an optical system forms an image of the document on the photoreceptor. For a light lens copier, where the document is white, there is sufficient light to cause the photoreceptor to conduct charge and neutralize the image, but the dark lines of text leave the charge undisturbed when imaged on the photoreceptor. This process forms a latent image of charge, duplicating the original document.

In the development step, toner of the appropriate polarity is typically brought into contact with this image. As discussed above, this will vary with the choice of photoreceptor and imaging method. There is now an image of the document on the photoreceptor

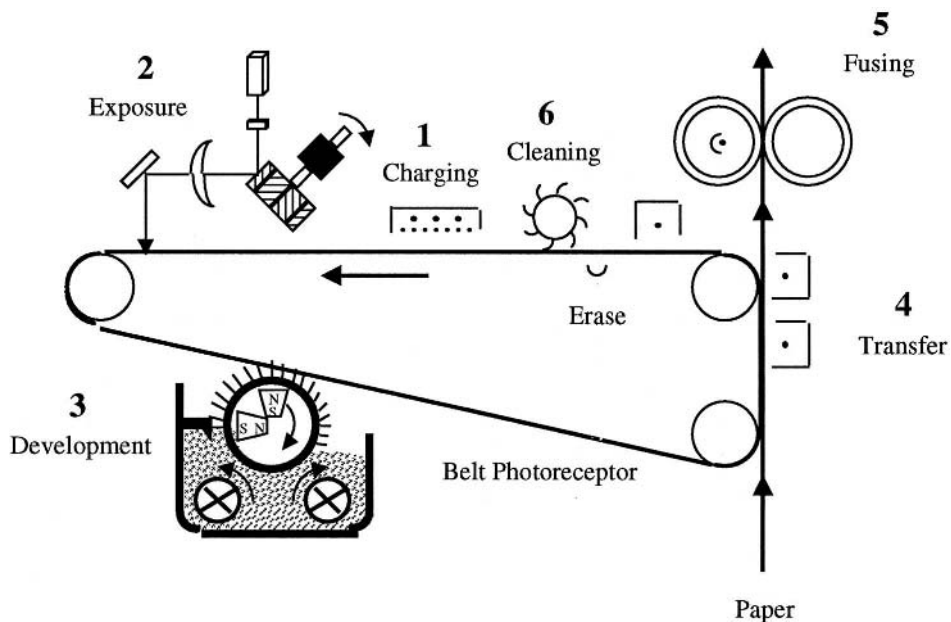


Figure 5.1 The basic steps in the xerographic process: (1) charging the photoreceptor, (2) exposing to form the latent image, (3) developing the latent image into a real image, (4) transferring the image to paper, (5) fusing the image to paper, and (6) cleaning residual toner from the photoconductor.

formed by individual toner particles held to the photoreceptor primarily by electrostatic forces.

In the transfer step, a piece of paper is brought into contact with the photoreceptor, and the back side of the paper is charged with ions opposite in polarity from the toner. This attaches the great majority of the toner particles to the paper. The paper is then removed from the photoreceptor and passed through the fuser.

In the fusing step, the toner is melted onto the surface of the paper. This is done either by running the sheet of paper between two rolls, at least one of which is heated, or by exposing it to radiant heat from a lamp. In an alternative arrangement called cold pressure fixing, high pressure is used without heat to force the toner into the paper.

In the cleaning step, the small amount of toner remaining on the photoreceptor after transfer typically should be removed if the photoreceptor is to be reused in its original condition. The toner is swept off the photoreceptor with a brush of furlike material, a brush of xerographic carrier beads electrically biased to remove toner, or a conformable rubber blade.

In the erase step, the photoreceptor charge is reduced to zero by exposing it to a lamp, which causes the entire width of the photoreceptor to conduct electricity. This erases any remnants of the latent image.

The entire process is then repeated as the photoconductive drum or belt returns to its starting point.

The steps that are most important to dry toner design are the development and fusing steps. The latter to a large extent determines the polymers that can be used in toner fabrication, since the toner should melt in the fuser and adhere to the paper without contaminating

the fuser itself. Similarly, cold pressure fixing has its special requirements for toner design (Bhateja and Gilbert, 1986).

Once a toner polymer has been selected and developed, most of the work of toner design goes into assuring that all the toner particles have the proper charge level to give sufficient development without background. This charge level will vary with the machine design.

In addition to these primary considerations, the effects of the toner design on the other steps in the process should be considered. The bulk of the toner should leave the photoreceptor during the transfer step; any remaining toner is typically removed during cleaning. Any microscopic toner constituents that are not removed by the cleaner should not degrade the charging properties of the photoreceptor, because this would affect subsequent charging, exposure, and erase steps.

5.1.3 Two-Component and Single-Component Developers

There are two primary methods of charging the dry ink and presenting it to the charge pattern on the photoreceptor to develop the latent image. The first, two-component development, was universally used in the early commercial applications of xerography. The charge is generated on the toner particles by mixing them with much larger beads chosen so that there is sufficient difference in the electrical nature of the toner and carrier materials to generate a charge of the desired magnitude on the toner. The mixture is then brought in contact with the latent image on the photoreceptor. A combination of impact and electrostatic forces strips the toner particles from the carrier beads, and the fields produced by the latent image attach them to the photoreceptor (Schein, 1996).

The earliest machines used nonmagnetic carrier beads and poured the developer over the latent image to bring the toner into contact in a process called cascade development (Schein, 1996).

Modern designs almost invariably have magnetic carrier beads and use magnets to control the flow of the developer and bring it into contact with the image. Since the magnetic fields in the contact zone with the latent image are typically designed to form a brush of carrier beads, this form of development is called “magnetic brush development” (Schein, 1996). Figures 5.2 and 5.3, respectively, show a typical two-component developer housing and a strand of the magnetic brush between the developer roll and the photoreceptor. Electrostatic forces drive the toner to image on the photoreceptor, while magnetic forces hold the carrier beads on the roll. Section 5.4 discusses toner properties for this application in more detail.

The use of carrier beads is not essential to xerography. The possibility of charging toner and then bringing it into contact with the latent image without using carrier has been mastered by many companies, with the introduction of successful products incorporating what is called “single-component technology” (Schein, 1996; Bares, 1993). A typical housing utilizing this technology is shown in Fig. 5.4 (Takahashi et al., 1982). Section 5.5 discusses toner designs targeted for this type of application.

At present both technologies play an important role in the marketplace. Single-component designs tend to be used mostly in smaller, slower machines where compactness, simplicity, and low cost are prime requirements, while two-component designs still dominate the high-speed machines, where clean copy quality and stability over long periods of time are most important. While the same toner technologies can be used for both types of application, the details of the toner design may be significantly different.

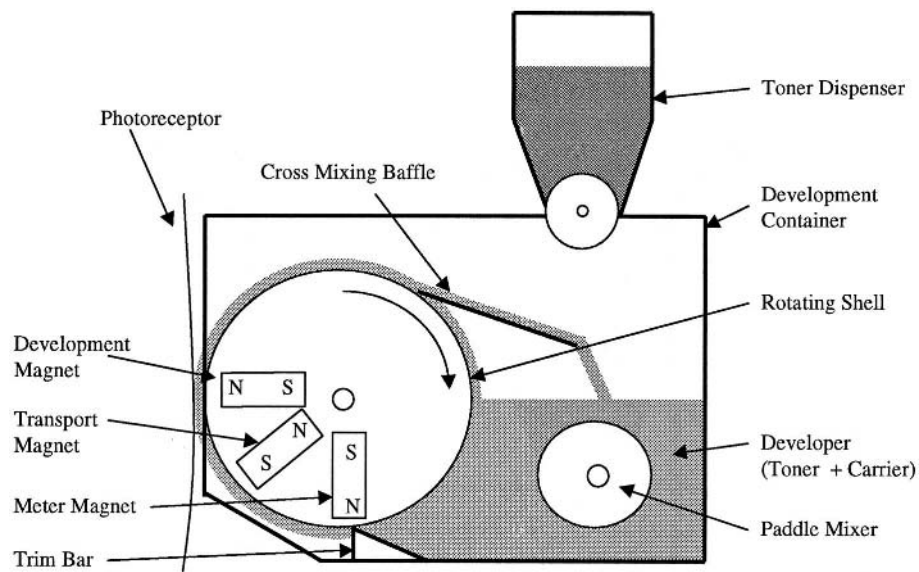


Figure 5.2 Structure of a typical two-component housing.

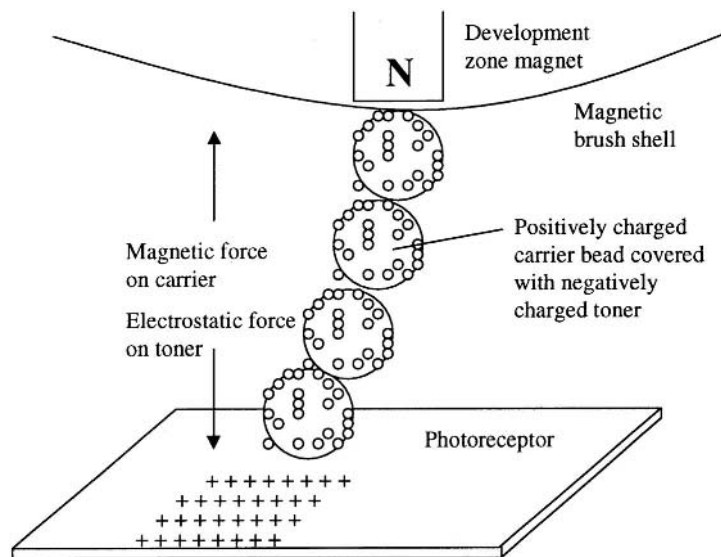


Figure 5.3 Schematic development, indicating direction of electrostatic force on toner and magnetic force on carrier above an image. (Adapted from Scharfe et al., 1989.)

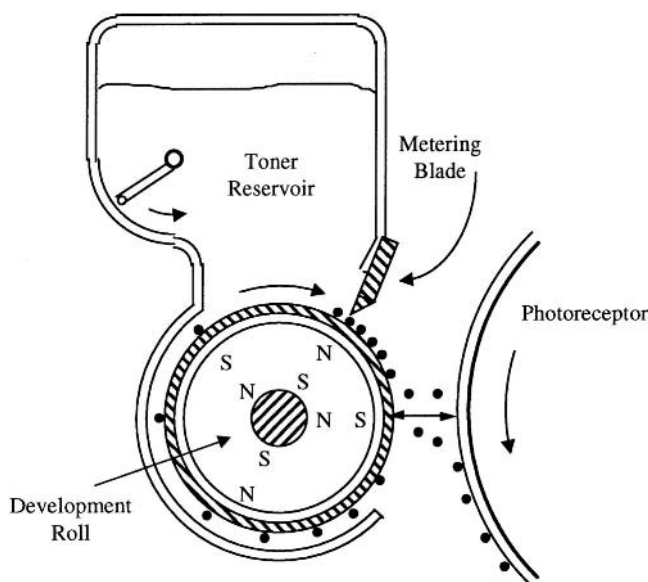


Figure 5.4 Single-component development unit with magnetic toner. (Adapted from Hays, 1998.)

5.2 TONER COMPONENTS

Dry xerographic toners consist of a colorant in a binder resin. Beyond these essential ingredients, a particular toner design may contain charge control additives to control the charge level, surface additives to control flow and cleaning properties, magnetic additives to aid in toner control, and waxes to promote toner release from the fuser roll. These components are introduced in the subsections that follow and are treated in more detail when the toner function they affect is discussed.

5.2.1 Resin

Several different families of resins (polymers) have found frequent application in xerography depending on the fixing technique selected (Table 5.1). The role of the resin in a toner is to bind the pigment to the paper or transparency material to form a permanent image. This is typically done by selecting a polymer that will melt at a reasonable temperature when heat is applied in any of a number of ways or one that can be forced into the paper fibers at high pressure without additional heat.

The materials for the last application are typically lower molecular weight polypropylenes, polyethylenes, ethylene–vinyl acetate copolymers, and mixtures of these materials. These cold pressure fix materials have the advantage of requiring low power in operation and no standby power (Bhateja and Gilbert, 1985a, b, 1986). They commonly have the disadvantage of producing high-gloss images that can be easily damaged by rubbing. However, they are perfectly acceptable for some applications, most notably computer printing (Rumsey and Bennewitz, 1986).

In other applications, a continuous radiant source of heat such as a quartz lamp or heated coil is used to melt the toner into the paper fibers. The viscosity of the toner usually reaches quite low values in flowing into the paper, but the time allowed for heating can

Table 5.1 Common Toner Resins

Polymer name or class	Morphology	Melt properties T_g or T_m (°C)	Molecular weight range ($\times 10^{-3}$)	Application
Polystyrene <i>n</i> -butyl methacrylate	Amorphous	T_g 50–60	50–60	Roll and flash fusing
Polystyrene <i>n</i> -butyl acrylate	Amorphous	T_g 50–60	50–60	Roll and flash fusing
Polyester	Amorphous	T_g 50–60	8–30	Radiant and roll fusing
Epoxy	Amorphous	T_g 60–100	1–10	Roll and flash fusing
Polyethylene	Crystalline	T_m 86–130	0.5–15	Cold pressure and roll fusing
Polypropylene	Crystalline	T_m 130–165	3–15	Cold pressure, roll fusing, and release agent ^a

^a Added to provide release between fuser roll and toner surface.

(Source: Adapted from Gruber et al., 1989.)

be up to 500 milliseconds. Here polyesters and epoxies are often used. In this application the molecular weight of these materials ranges from 5,000 to 50,000 and the glass transition temperature T_g , from 50 to 60°C (Palermi and Chatterji, 1971). A notable contemporary use of radiant fusing is the simultaneous duplex digital press developed by Xeikon (Tavernier et al., 1995).

In flash fusing, the toner is melted into the paper by a very short high-intensity flash of light lasting less than 5 milliseconds. Toner temperatures typically exceed 200°C in attaining the low viscosities required, and the thermal decomposition of the toner polymer is a significant problem. Styrene copolymers, epoxies, and copolycarbonates have all been used (Gruber et al., 1982; Narusawa et al., 1985).

The great majority of copier designs use hot roll fusers for fixing the image (Kuo, 1984; Prime, 1983; Lee, 1975). The paper with the unfused toner passes through a nip formed by a heated roll and a backup roll forced against the heated roll at fairly high pressures. This combination of temperature and pressure gives the best overall performance for most applications. Styrene copolymers such as styrene acrylates, methacrylates, and butadienes are used. Molecular weights range from 30,000 to 100,000, and glass transition temperatures range from 50 to 65°C (Nelson, 1984). Where lower melting temperatures T_m , are desired, polyester resins have been used (Fukumoto et al., 1985). When multiple layers of toner are fused, the low melt characteristics of polyester toners are especially important, and most contemporary full-color copiers and printers use polyester toners.

The above-named polymers can be specially modified for a particular application by incorporating monomers or side chains to accomplish such functions as charge level modification (Gibson, 1984). However, the primary role of the polymer resin is to fix the image, and polymer designs are developed with their fusing characteristics as the primary consideration.

Toners are typically manufactured by the attrition of the blend of the ingredients. Here the ease with which the polymer fractures has a very significant influence on the

rate at which one can produce toner. At the same time, the toner should not break up when subjected to the stresses within the developer housing (Ahuja, 1976). These mechanical characteristics are another essential consideration in polymer design.

Since usually 90% or more of the toner is polymer, its cost is very important in determining the cost of the final product. Polyester resins are typically more expensive than styrene acrylate resins and thus tend to be limited to color toners or to black toners intended to be used with the color toners. It is also possible to form hybrids of polyester and styrene acrylate, and these may have improved properties (Kawaji et al., 1995; Aoki et al., 1996).

Recently, chemical methods of producing toner have received increased attention from several manufacturers. These are discussed in more detail in Section 5.6.6. Polymers that are typically produced by suspension or emulsion polymerization methods have an advantage here, and much of the published literature is concerned with styrene acrylate type resins rather than those typically produced by bulk polymerization such as polyesters.

5.2.2 Colorants

The most common colorant for xerographic toners is carbon black (Julien, 1993). Most manufacturers offer a range of blacks that differ in such properties as tinting strength and acidity. Important properties of carbon blacks for xerographic applications are their dispersibility in the resin in hot melt mixing and their tendency to charge either positive or negative. Carbon blacks are usually used in toner at a loading of 5 to 15% by weight.

Besides carbon black there are several other materials that can be used to make black toners. Magnetite is often used in toners to allow for magnetic control of the toner. The substance is typically black and is seldom used as a pigment per se, but often the loadings for magnetic properties are sufficiently high that additional pigment is not necessary.

Some charge control additives such as nigrosine are good black pigments, and their use in a toner can lead to the reduction or elimination of the carbon black.

Pigments other than black are increasingly playing a role in xerography in two applications. The first is a color to be used in addition to black when there is a desire to highlight certain information. Typical colors used for this application are red, blue, green, and brown, made from either a single pigment or a blend of pigments.

The other major application is in the creation of full-color documents. Here the subtractive set of pigments, cyan, magenta, and yellow, is used. These pigments are chosen for colorimetric properties such as spectral purity and their ability to generate as broad a gamut of colors as possible when blended together. To give permanence to the color image, a degree of lightfastness is useful (Blaszak et al., 1994). This suggests that pigments are more useful than dyes. Usually organic pigments are used. Copper phthalocyanines are often used for cyans and blues, azo pigments for yellows, and quinacridones or rhodamines for magentas and reds (Bauer and Macholdt, 1995). Figure 5.5 shows graphically the color range accessible by the various chemical classes with typical pigments within each class. Color pigments are chemically active materials, and this can affect both their xerographic properties and their compatibility with existing chemical laws (Macholdt and Bauer, 1996).

5.2.3 Charge Control Additives

Charge control additives are often added to a toner when the pigment (chosen for its color) blended into the polymer (chosen for its fusing performance) does not give an adequate

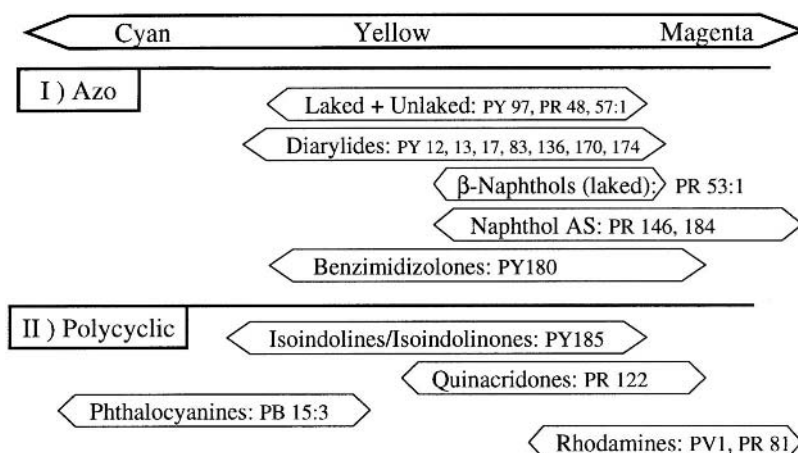


Figure 5.5 Pigments for full-color copying and printing; PY = Pigment Yellow, PR = Pigment Red, PB = Pigment Blue. (Adapted from Macholdt and Baur, 1996.)

charge level or rate of charging. This can occur in both positive and negative charging applications.

For positive applications, one family of charge control additives is the quaternary ammonium salts (Lu, 1981). These compounds are mostly colorless, allowing their use in color applications.

Nigrosine is an organic pigment that is effective in imparting a positive charge to toner (Guay et al., 1992). Because it is black, however, it is unsuitable for most color applications.

For negative applications, acidified carbon blacks have been quite successful as charge control agents in addition to their pigment qualities (Julien, 1993). In applications calling for transparent internal negative charge control, metal complexes have been found to be effective (Inoue et al., 1985; Birkett and Gregory, 1986). However, the oxide surface additives described in the next section have become increasingly important as charge control agents.

5.2.4 Surface Additives

The multifunctional benefits of surface additives such as silicas and titanias have received increased attention in recent years. When materials such as fumed silica are added to the surface of a toner, the flow properties often improve dramatically (Veregin and Bartha, 1998). The silicas can also improve transfer from the photoreceptor to paper by lowering the adhesion of the toner to the photoreceptor surface (Akagi et al., 1993) while improving the charge stability of the toner and carrier mixture (Nash and Bickmore, 1988; Stuebbe, 1991). The chemical treatment of silica surfaces has been found to have a profound influence on the properties of toners made with them (Julien et al., 1993; Veregin et al., 1997). In particular, amine treatments convert silicas from negative to positive charging materials (Takenouchi, 1986; Heinemann and Epping, 1993).

For blade cleaning, surfactant materials such as zinc stearate are often blended with the toner to lubricate the blade passing over the photoreceptor (Weigl, 1982). Fumed silicas may be used with the stearate to control the buildup of material on the photoreceptor.

5.2.5 Magnetic Additives

Magnetite is primarily added to toner in single-component applications, where it enables the transport of the toner through the developer housing and against the latent image under magnetic control (Button and Edberg, 1985). The additives are typically a few tenths of a micrometer in size.

It has been found that even in two-component development, where magnetite is not necessary for developer transport, this material offers advantages in controlling machine dirt (Knapp and Gruber, 1985). Here the typical loadings are about 15 to 20% as opposed to the 60 to 70% necessary for toner transport. Without magnetite, low charge toner often gives severe dirt and dusting problems.

If sufficient magnetic remanence is present within a toner formulation, the toner can be used for magnetic ink character recognition (MICR), a special xerographic application for check sorting, discussed in Section 5.4.3. Typically, a high-remanence magnetite is used at a loading in excess of 20% by weight.

5.2.6 Other Additives

Fuser rolls typically require the use of a release agent such as silicone oil to prevent the adhesion of the toner to the hot roll surface (Seanor, 1978). Hardware design is simplified if this release agent management system can be eliminated. This both lowers the cost of the machine and eliminates the need for the customer to handle fuser oil. It is possible to do this by incorporating a low molecular weight polyethylene or polypropylene wax into the toner itself (Gruber et al., 1986). This flows very readily at temperatures sufficient for toner fusing and fills the role of the silicone oil. Partial cross-linking of the polymer in the toner also helps prevent adhesion to the fuser roll (Inoue et al., 1985). This technology is now being used for color toners (Kawaji et al., 1997).

5.3 TONER REQUIREMENTS AND CHARACTERIZATION TECHNIQUES

The development of a toner involves the choice of the components described above, starting with the choice of polymer and proceeding through the selection of each component to fit the particular application. Techniques have been developed for each of the requirements to facilitate selection, and these are often unique to the xerographic application.

5.3.1 Rheology

There are three or four xerographically significant temperatures necessary to characterize a toner for xerography. The most obvious is the temperature at which the image is fixed to the paper. This will vary with the degree of fix required, but for an adequate fix level it is called the minimum fix temperature. Above this is a temperature at which the toner is so fluid that it simply splits apart when the paper leaves the fuser roll, leaving traces of the image on the fuser roll to contaminate the next sheet. This is called the hot offset temperature. Next, the toner should not sinter when left on a loading dock or in the machine toner hopper, even at an elevated temperature. The temperature at which significant sintering occurs is called the blocking temperature (Weigl, 1982).

For color printing, the gloss of the image is also very important (Dalal et al., 1991), and it is strongly affected by fusing conditions (Nakamura, 1994). Thus there can be a

fourth critical temperature for color toners, that is, the fuser temperature at which a toner reaches the desired gloss level, called the gloss temperature. Ideally, a toner should provide the desired gloss level at the minimum fix temperature, but this is not always true.

Adequate fix is a subjective judgment and can vary with the application. Measurements of fix level generally involve abrading an image on paper in a controlled way and measuring the amount of toner lost from the paper or the change in the density of the image (Bhateja and Gilbert, 1985a; Hayakawa and Ochiai, 1993).

The minimum blocking temperature allowable is determined by the highest temperature one expects the toner to see outside the fuser. It is often asked to be about 115°F. To a large extent this is a characteristic of the toner resin. However, it can be modified by the other ingredients of a toner. For example, carbon black can act as a reinforcing agent, raising all the characteristic temperatures including the blocking temperature (Ahuja, 1980c; Fox, 1982). Similarly, surface additives such as fumed silica will typically prevent sintering and hence raise the blocking temperature (Barby, 1976).

Even though additives can modify the results, the primary means for controlling the fusing properties of a toner is through the resin. The lowest possible minimum fix temperature is desirable, since this will typically minimize power consumption and maximize fuser life. For a given minimum fix temperature, the hot offset temperature should be as high as possible to maximize fuser latitude. The latter two temperatures in particular should be measured in the fuser of interest. More general rheological measurements can serve as an aid to polymer design, although they are not sufficient for final approval.

A commonly measured characteristic of a polymer is its glass transition temperature, T_g , where the polymer changes from a hard glass to a rubbery state. This is measured in a differential scanning calorimeter, which looks for the change in heat capacity at the transition. For adequate blocking, toners generally should have T_g values above 50°C.

Another relevant characteristic of the polymer is its melt viscosity, that is, its ability to flow at a given temperature. The rate at which this falls at and above T_g determines the temperature above the blocking temperature at which the toner flows into the paper and the temperature above this at which the toner splits, leaving residue on the fuser roll as well as on the paper.

These characteristics can be controlled by varying the composition and molecular weight of copolymers. This can be illustrated by examining one of the most common copolymers, styrene-butyl methacrylate. For a random copolymer, the T_g is given by

$$T_g = W_1 T_{g1} \pm W_2 T_{g2} \pm k W_1 W_2 \quad (5.1)$$

where W_1 and W_2 are the weight fractions of constituents 1 and 2 and T_{g1} and T_{g2} are the transition temperatures of the homopolymers (Manson and Sperling, 1976). The constant k allows for deviations from the ideal case. However, the transition temperature of the copolymer also depends on its molecular weight for lower molecular weights. This approaches an asymptote for high molecular weights due to chain entanglement. Figure 5.6 shows that the transition temperature for the copolymer decreases as the amount of *n*-butyl methacrylate increases (Scharfe et al., 1989). For any copolymer, the ratios are adjusted to obtain a T_g that corresponds to an acceptable blocking temperature.

The effect of molecular weight is shown in Figure 5.7 (Scharfe et al., 1989). T_g appears to reach a plateau at a molecular weight of about 23K. For a polystyrene homopolymer, the plateau is reached at about 34K. The plateau is reached earlier for the copolymer because its chains are more flexible, allowing earlier entanglement.

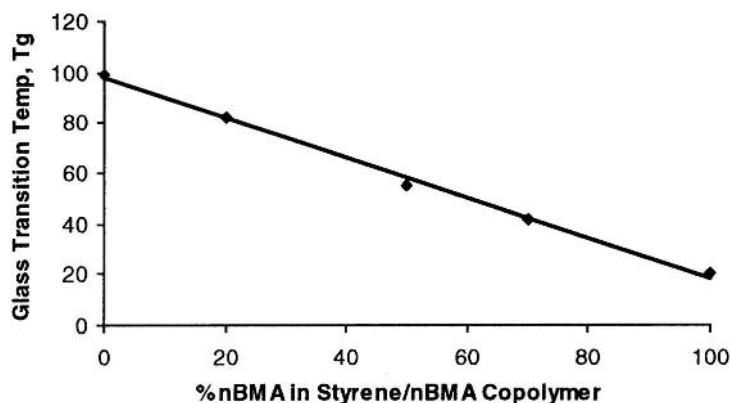


Figure 5.6 Effect of copolymer on glass transition temperature T_g of styrene-*n*-butyl methacrylate copolymers. (Adapted from Scharfe et al., 1989.)

The viscoelastic properties of polymers are measured in a viscometer. The viscosity of polymers typically depends on the frequency of the driving force as well as the temperature. It is found that time (the inverse of frequency) and temperature are interchangeable for typical (linear) polymers. Data often are expressed as viscosity as a function of reduced frequency $a_T\omega$, where ω is frequency, and a_T is the temperature-dependent shift factor.

Figure 5.8 shows the viscosity of styrene-*n*-butyl methacrylate toners as a function of reduced frequency (Ahuja, 1980b). Clearly the 399K molecular weight polymer has a higher viscosity, as well as a greater dependence of viscosity on temperature and time (which could be time in the fusing nip). When random copolymers of two different molecular weights (e.g., A = 29K and B = 371K) are blended, the mixture will have a viscoelastic response that is between that of the two original polymers and is monotonically dependent on the amounts of the two polymers, as shown in Figure 5.9 (Ahuja, 1980b). In particular, the addition of even 10% of the higher molecular weight material significantly raises the viscosity at higher times and temperatures. Blends of different molecular weights

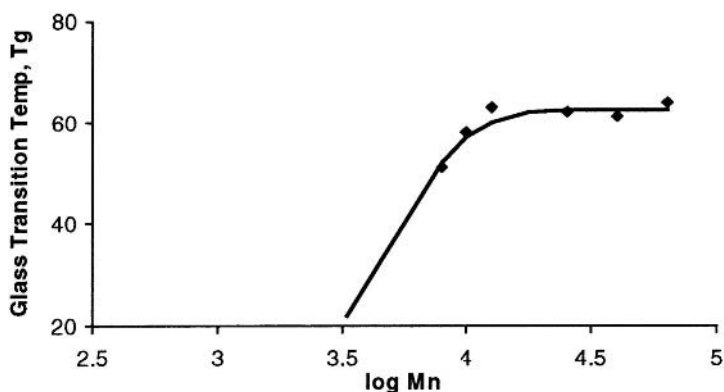


Figure 5.7 Effect of molecular weight on glass transition temperature T_g of styrene-*n*-butyl methacrylate copolymers. (Adapted from Scharfe et al., 1989.)

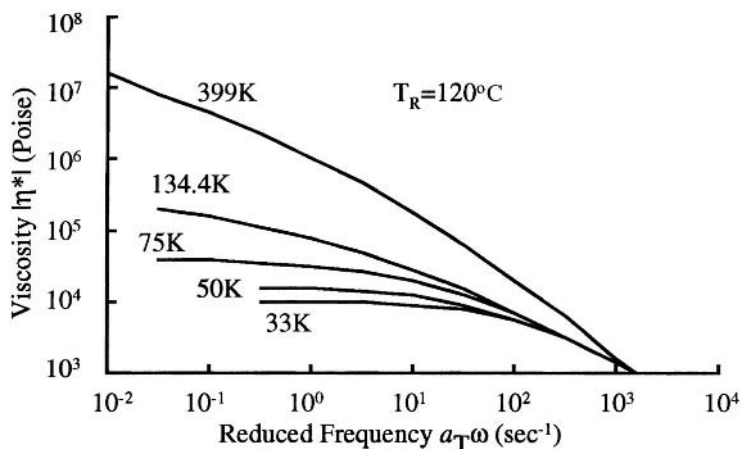


Figure 5.8 Viscosity as a function of reduced frequency $a_T \omega$ for various styrene-*n*-butyl methacrylate copolymers at reference temperature T_R in °C. (Adapted from Ahuja, 1980b.)

are a common method of modifying the fusing properties of a toner. For example, a broad molecular weight distribution or a blend of low and high molecular weight resins has been shown to allow high hot offset temperatures while retaining low minimum fix temperatures (Hayakawa and Ochiai, 1993).

The effect of the addition of carbon black to a particular polymer is shown in Figure 5.10 (Ahuja, 1980c). This effect is related to the reinforcement properties of the pigment, a property varying with the carbon black but controlled and characterized by the carbon black industry, particularly for rubber applications. In general, high surface area carbon blacks tend to raise viscosity more than low surface area carbon blacks. Similarly, high loadings of any color pigment can reinforce the pigment-polymer matrix, leading to higher fusing temperatures.

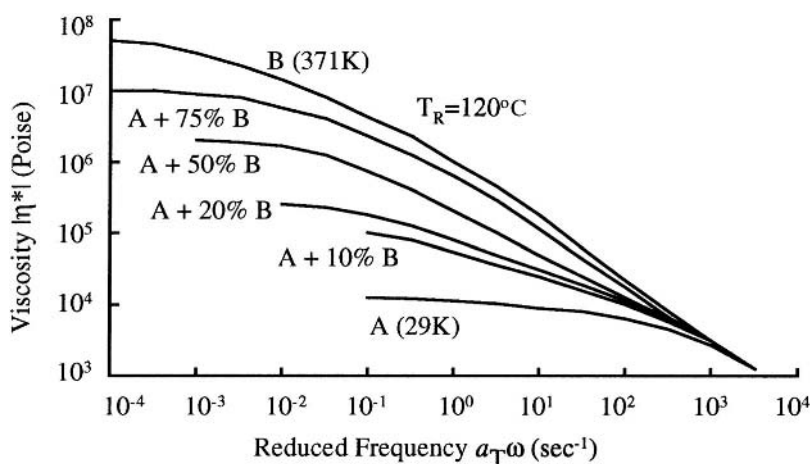


Figure 5.9 Complex viscosity as a function of reduced frequency $a_T \omega$ for styrene-*n*-butyl methacrylate blends. (Adapted from Scharfe et al., 1989.)

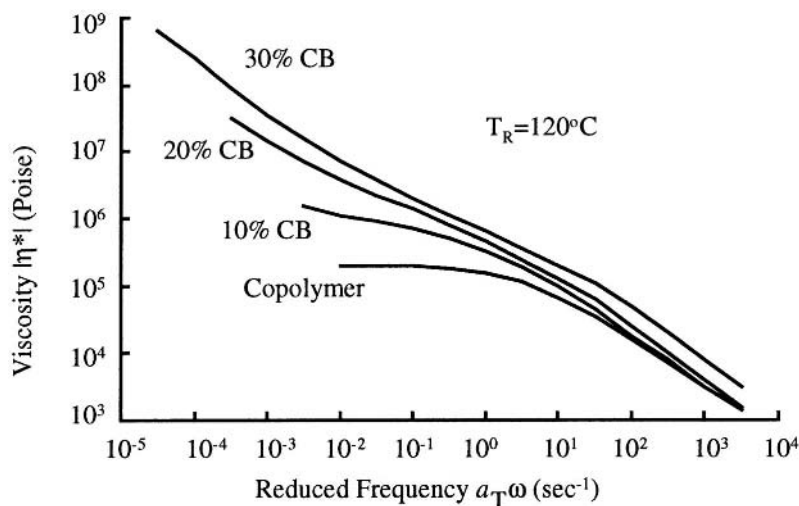


Figure 5.10 Effect of carbon black (CB) concentration on melt viscosity as a function of reduced frequency. (From Ahuja, 1980c.)

Molecular weight and copolymer ratio are also important in toner processing. Toners made from a molecular weight above a value called the brittle–ductile transition are very ductile and difficult to micronize. Similarly, copolymers such as styrene-butadiene with a large amount of butadiene are well known to be rubbers, hence are also very difficult to micronize efficiently. On the other hand, the more ductile polymers are less susceptible to fracture in a developer housing. In practice, polymer compositions are selected to effect a compromise between toughness and processibility. As discussed below, chemical toner preparation processes eliminate the need for micronization and thus may enable new or different classes of polymers to be used for toner application.

5.3.2 Colorimetrics

For black toners, the primary consideration is to generate sufficiently high optical densities with practical developed masses. In practice this has meant that the use of 5% or more of almost any of the available carbon blacks is quite sufficient.

For highlight color toners there is again a requirement to develop sufficient optical density of the color of interest. The amount of pigment necessary to do this will differ with the color strength of the pigment, which can vary quite significantly. Beyond the strength or chroma of the color, a hue that will be pleasing to the largest number of customers should be chosen. For example, the red for highlight color applications can be chosen from an infinite number of possibilities.

For process color developers the goal is to generate as wide a color gamut as possible from a particular set of cyan, magenta, and yellow toners. The range of colors possible depends on the detailed spectral absorption of the various pigments. As a result, a wavelength-scanning spectral densitometer is necessary. With this tool, the range of colors possible for a given pigment set can be calculated. Various combinations of pigments can then be evaluated to find the optimum set.

It is extremely difficult to find subtractive pigments that perfectly match any red, green, and blue filters used for optical color separation. To compensate for this, the image is completely converted to electronic information, adjustments are made to the strength of each color dot depending on the complete color signal, and the image is then reformed on the photoreceptor using a laser printer (Schein, 1996). In another application of electronic color correction, black toner can be added to the image to reduce the amount of more expensive color toner necessary.

Each of the candidate pigments is typically evaluated for lightfastness (Blaszak et al., 1994). If one of the pigments fades quickly, especially under office lights, this will distort the initial colors produced by the copier (Fujii et al., 1988). The degree of lightfastness necessary will depend on the application; however, since one wants to use a limited number of pigments, the goal is usually to obtain values sufficient for almost any possible application.

Pigment evaluation can only predict the largest gamut possible. The real color gamut a given set of toners will produce in a particular color copier is also affected by the smoothness of the image formed by the fused toner and the general quality of the image formed by the system (Nakaya et al., 1986).

5.3.3 Particle Size

Toner particle sizes have been slowly decreasing over the years and are now generally in the range of about 7 to 12 μm in diameter. Particle sizes significantly larger than this usually produce ragged lines and dots and thus degrade copy quality. As a result, smaller sizes have been found to be superior for color reproduction (Chiba and Inoue, 1988) and for noise reduction in general (Shigehiro et al., 1993). However, for a given resin the smaller sizes require longer grinding times in manufacturing and hence are more expensive to produce. Also, smaller sizes tend to produce more dirt at a given charge-to-mass ratio and to cause more rapid developer degradation (Nash and Bickmore, 1988).

Even if the average size is reasonable, a broad particle size distribution will introduce significant amounts of the small and large toner particles that cause dirt and copy quality problems. As a result, toner processing strives for the narrowest practical size distribution. This is typically done with well-designed micronization equipment followed by air classification and possibly sieving.

These limitations on the practical size of conventional dry toner are one of the attractions of the new chemical methods for making dry toner (Takezawa et al., 1997; Edwards et al., 1998).

The size distribution is measured by the use of the Coulter Counter (Beckman Coulter, Inc., Fullerton, CA) or similar instrumentation. This places the toner particles in a conducting fluid and examines changes in signal as the particles are passed through an orifice. The instrument is sensitive to the volume of liquid displaced by each toner particle and hence gives an accurate measurement of the volume size distribution of the toner. The distribution can be characterized in various ways, most typically by the geometric (logarithmic) standard deviation, the number fraction of particles below a certain size, and the volume fraction of particles above a certain size.

An optical image analyzer can also be used for toner size analysis if the particles are spread out on a microscope slide. This method looks at the projection of the particles in the object plane and can be used for linear or areal measurements. This method is often

used in conjunction with a charge spectrograph to make simultaneous measurements of toner size and charge as discussed in Section 5.3.4.

Since the electrolytic displacement and optical methods measure the size in quite different ways, there can be a significant displacement between measurements from the two techniques, and comparisons should be made using the same method (Julien, 1996).

5.3.4 Charging

To control toner in the electric field of the photoreceptor, the particles are given a well-defined charge. Much of the progress in the creation of clean, crisp copies and prints by means of xerography has come through increased control over the toner charge distribution. This in turn has been facilitated by increased sophistication in charge characterization methods.

The primary method of characterization of the charge on toner has been the measurement of the charge-to-mass ratio (Schein, 1996). For two-component development, this is typically done by putting the developer in a metal cage with screens on each end; the screens are large enough to allow toner but not carrier beads to escape. The mass of the developer in the cage is determined, and the cage is connected to an electrometer. The toner particles are then blown off, and the charge and mass differences that result are measured. The ratio of these differences gives the charge-to-mass ratio for the toner blown off. This quantity is called the tribo or blowoff tribo for that developer.

The same quantity can be determined for toner on a photoreceptor or single-component donor roll by drawing the toner into a chamber connected to an electrometer and weighing the chamber before and after. Because of size selectivity in development, the blowoff tribo measured for toner developed onto a photoreceptor will not necessarily be equal to that for the same toner when still mixed with carrier.

Another method of charge characterization that has become increasingly common in the industry is the charge spectrograph. In the embodiment of this instrument used at Xerox (Lewis et al., 1981a,b; 1983), the toner is drawn into an airflow while simultaneously exposed to a perpendicular electric field. The combination of viscous drag and electrical forces determines where each individual toner particle falls on a collection filter. Rather than the charge-to-mass ratio (q/m) that the previous technique measures, the charge spectrograph measures the charge-to-diameter ratio (q/d). The average charge-to-diameter ratio can be determined by eye from the trace on the filter very quickly, but the instrument also allows the simultaneous determination of the charge-to-diameter ratios and the diameters for all the individual toner particles. For the latter application, computer analysis of the collection filters is necessary.

Other, commercially available, realizations of charge spectra characterization are described in the literature (Tsujimoto et al., 1991; Epping, 1988).

It is important to realize that charge spectrograph measurements can be significantly different from blowoff tribo measurements. Most theories of toner charging predict that the charge will be proportional to the toner area (Gutman and Hartmann, 1995), and this is indeed the general result (Nakamura et al., 1997). This implies that q/d^2 is a constant as the toner size changes, and this in turn leads to the result that q/m (proportional to q/d^3) increases while q/d decreases as the toner size decreases (Julien, 1996). For different toner sizes with the same composition, one method of charge characterization will give higher charge levels while the other will give lower levels. Thus it is always important to keep toner size and characterization technique in mind when interpreting charging results.

Knowledge of the charge on an individual toner particle may still be insufficient to predict the behavior of the particles. Van der Waals forces can introduce irregularity into the adhesion of the toner particle to a carrier bead or to the photoreceptor (Schmidlin, 1976), but a nonuniform distribution of charge on the toner particle can lead to even larger variations in toner release characteristics (Hays, 1978; Lee and Ayala, 1985). Considerable work has been done in the last decade to investigate toner adhesion (Ott et al., 1996), and the results have generally been consistent with the nonuniform distribution of charge (Feng and Hays, 1998). The inability of the toner designer to control charge at this level contributes to the empirical nature of much toner formulation work.

For the 8 μm toner particles typical of modern color printers, the useful range of charge, using charge-to-mass ratios, is from 15 to 40 $\mu\text{C/g}$. Toner particles with higher charge are difficult to strip from the carrier and deposit relatively little mass for a given amount of charge neutralization on the photoreceptor. Since the amount of mass deposited on the photoreceptor for a given latent image voltage is a prime measure of development efficiency, one would like the largest mass for a given amount of charge on the toner particle and hence the lowest q/m . However, values below 15 $\mu\text{C/g}$ generally cause both dirt in the machine and background on the copy. As with so much else in xerography, the value used is a compromise between maximum development and minimum background for a particular hardware configuration.

Having the average charge level in the correct range is merely the first charging requirement that a toner faces. It should also reach this equilibrium charge level as rapidly as possible when added to the existing developer in a machine (Gutman and Matteson, 1998). Otherwise, it may still have little or no charge when the developer flow brings it into contact with the photoreceptor, and this can lead to background even though the bulk of the toner has adequate charge.

The charge on the toner should also be maintained as thousands of prints are made on the device. A design with initially excellent charging characteristics can rapidly lose its level in a period of time much shorter than the design intent of the copier or printer. Extensive work has been done on the aging mechanisms of two-component developers, particularly through the filming of the carrier by toner (Nash and Bickmore, 1988).

Furthermore, a toner or developer design is expected to retain its charge level through different environmental conditions. Moist air can have a dramatic effect on charge levels; very high levels such as 80 or 90% relative humidity can lower the charge, while very low levels such as 10 or 20% RH raise the charge. Hygroscopic additives in the toner can lead to very low charge levels at high humidity, but high charge levels at low humidity, and the resulting low developability can also be a problem. As a result, toners and developers should be tested early in a machine program on a bench scale and later in a full machine configuration at high, low, and moderate humidity levels.

5.3.5 Toner Flow and Adhesion

Toner flow and adhesion are related yet somewhat distinct properties. Toner flow describes how toner behaves in contact with itself (cohesion), while toner adhesion describes how toner behaves in contact with other materials, such as a donor roll or photoreceptor. Often, good toner flow is cited as an important toner property when the relevant process, such as transfer, really requires low toner adhesion (Tavernier et al., 1995; Sata et al., 1997). However, since low cohesion typically implies low adhesion, powder flow measurements are often a good guide for identifying toners with improved transfer.

There are many ways of measuring powder flow properties; most of them are static surrogate measurements for the dynamic properties of the toner. The angle of repose of a pile of toner measures how easily the toner slides, the bulk density or compressibility measures how easily it packs, and cohesivity measures how easily it passes through screens of various sizes. Hosokawa Micron manufactures a Powder Tester that can perform each of these measurements.

Toner adhesion as a unique property has received increased attention over the last decade. This is due to the increased presence of full-color copiers, where excellent transfer properties for all colors are essential to optimum copy quality, and to the increased presence of single component donor roll development, where low toner adhesion is required for high development efficiency. It is of course especially important for full-color non-magnetic single-component systems.

There are three common techniques for investigating toner adhesion (Ott et al., 1996). On a microscopic scale the atomic force microscope can be used to investigate the adhesion of individual toner particles to either other toner particles or to a substrate of interest. On a macroscopic scale the amount of toner transferred from one parallel plate to another as a function of the electric field can be monitored. Finally, centrifugal detachment can be used to measure the inertial forces required to separate a toner particle from the substrate upon which it is resting. The two macroscopic techniques are probably more common (Fukuchi and Takeuchi, 1998). The electric field detachment method is the closest surrogate to the actual development or transfer system itself.

Toner flow and adhesion are typically controlled by surface additives (Akagi et al., 1993; Sata et al., 1997; Veregin and Bartha, 1998).

5.3.6 Compatibility with Other Subsystems

The primary requirements for a toner concern the control of charge for development performance and the control of rheology for fusing performance. However, a toner should also be compatible with the other steps in the xerographic process, at times in ways that are not completely obvious.

The first subsystem the toner contacts after leaving the development zone is the photoreceptor. The toner should neither chemically alter the photoreceptor nor coat it with a thin layer of toner or toner constituents. A problem in this area shows up as a defect in the electrostatic image. For example, if the photoreceptor either cannot hold a charge or cannot be erased in an area where an image being used in testing contains a solid area patch, the root of the difficulty usually turns out to be a toner-photoreceptor interaction.

Ideally, the contact between the toner and the photoreceptor should be as gentle as possible to minimize the possibility of contamination. However, a typical cleaning system, whether a blade, a “fur” brush, or a carrier brush, effectively scrubs toner along the photoreceptor and hence has a tendency to smear it over the surface. With blade cleaning in particular, a lubricating film is often necessary for smooth blade action (Weigl, 1982). A soaplike molecule such as zinc stearate is often used for this purpose. This film should not alter the electrical performance of the photoreceptor.

In fusing, the obvious requirement is that the toner fuse to the paper without offset to the fuser roll. At the same time, the toner should not chemically attack the roll at the high temperatures encountered. Fuser rolls are often expected to last for hundreds of thousands of copies, and testing for interactions that can degrade ultimate performance is a very tedious but necessary part of any machine development program.

Once specific problems have been identified, either with the photoreceptor or with the fuser, quicker, more convenient bench tests usually can be implemented to assist in problem solving. Problems usually are first detected in full-scale systems tests, however, and any solution must eventually be verified in the same way.

5.3.7 Safety

The past 40 years, a period that has seen the xerographic industry reach maturity, has also seen greatly increased awareness of safety hazards and the corresponding development of means to detect them. This has in turn strongly affected the way materials are developed. In particular, as the concept of cancer-causing agents has become better known, the use of the Ames and related assays for mutagenicity has become an integral part of the toner design process.

There is nothing inherent in xerography that would require the use of dangerous materials, and the thrust in the industry is to make the materials as safe as any material a user would come in contact with. The safety of the various possible components that could go into a toner is considered before the research and development process is started. Often development of a particular compound is avoided even if mutagenicity tests have not been performed if related compounds have some form of toxicity. In the absence of detailed knowledge, xerographic evaluation is performed with reasonable precautions for personnel working with a comparatively unknown material.

Once a material has been identified as having promise, mutagenicity assays are performed, and any positive signal will disqualify the material. Acute toxicity tests and tests for skin and eye irritation are typically also performed. Assuming that the individual components of a toner pass all the safety requirements, the final toner design is again tested to assure that toner processing does not introduce new compounds that may be hazardous even though the initial ingredients were harmless. The results of the tests on the toners are summarized under the Toxicology and Health Information heading in Material Safety Data Sheets.

In addition to looking at the toner as a substance independent of its application, one can also carefully evaluate conditions (such as fusing) that can lead to the creation of hazardous substances from an otherwise benign toner. Any situation indicating a quantifiable (even if low-level) hazard can be examined to see whether there is a way of reducing the levels and hence minimizing the possibility of higher problem levels in the future.

It is prudent to monitor routinely even a material that has passed all safety requirements and has been introduced into the marketplace. The reason for this is that the source of an undesired substance is often a contaminated raw material. The use of a new processing technique or a new source of raw materials by a vendor of toner constituents can introduce mutagenic materials into the toner. The aim is to catch these changes as soon as they become detectable and eliminate the problem before it becomes hazardous.

5.4 TWO-COMPONENT DEVELOPERS

5.4.1 The Role of Carrier

The carrier in two-component systems provides two functions for the toner: charge generation and transport through the developer housing. First, the rubbing of the carrier against the toner generates the desired magnitude and sign of charge on the toner and a corresponding countercharge on the carrier bead itself, leaving a net neutral developer. Second, toner

particles attach themselves to a carrier bead through electrostatic forces and can be moved through the machine by the action of magnets on the magnetic carrier core material.

The ability of a carrier to control toner charge is very powerful, primarily because it is possible to coat the core with a selected polymer. In contrast to the toner polymer, which is typically chosen primarily for its rheology, the carrier polymer can be chosen primarily for its charge generation properties. An important requirement is that one must be able to coat it on the carrier bead, either from a solution or a suspension or as a dry powder that can then be fused onto the surface. It then should have sufficient integrity on the carrier surface to ensure that the resultant toner-carrier pair has long life in the machine. In practice, different carrier polymers can often be chosen to drive the charge level on a given toner from beyond the range of useful charge in the positive direction through useful charge levels both positive and negative to beyond the range of useful charge in the negative direction. Thus a methacrylate-coated carrier can charge a toner to $-40 \mu\text{C/g}$, while a fluoropolymer-coated carrier will drive the same toner to $+50 \mu\text{C/g}$. While this flexibility does not guarantee that the charging rate will be adequate for both signs, it is still a powerful tool.

The transport function of carrier is also useful. Almost invariably either rotating magnets or a rotating shell over stationary magnets are used to transport developer through the development zone and to create a "magnetic brush" to transfer toner onto the latent image. Thus magnets are used to control toner even though the toner itself is nonmagnetic. Most single-component systems retain the use of magnets for toner transport, but this requires the use of magnetic toner, which either is black or has a very limited set of magnetic color pigments. Through the use of carrier beads, magnetic transport is possible with all color toners.

5.4.2 Two-Component Charging

Toner charge is primarily determined by chemical composition. Since the typical toner charges involve only 10^{-4} or 10^{-5} of the surface atoms, charging can be extremely sensitive to impurities. Nevertheless, the industry has been able to design toners and implement development based largely on empirical knowledge of the charging properties of the toner components.

The most basic description of our empirical understanding of the charging of different materials is to rank them according to which gains a positive charge and which gains a negative charge when two materials are rubbed together. This generates a triboelectric series, with materials that acquire a positive charge at one end of the series and those that acquire a negative charge at the other. Isolated cases of a particular polymer, metal, or other substance may violate this ranking, presumably as a result of impurities or surface treatment, but the tribo series does provide general guidelines for developing materials for xerographic application.

The extensive experimental and theoretical work on charge exchange between polymers and between metals and polymers has been reviewed by Harper (1967), Seanor (1972), and Lowell and Rose-Innes (1980). Models of toner charging in particular have been discussed over the years by Anderson (1994), Gutman (Gutman and Mattison, 1998), Nash (Nash et al., 1998), Schein (1998), and Takahashi (Lee and Takahashi, 1998). The references cited are only the most recent presentations at "Non-Impact Printing" conferences conducted by the Society for Imaging Science and Technology (IS&T).

Duke and Fabish (1978) modeled the electronic structure of polymers based on donor and acceptor states capable of forming localized molecular ions upon charge transfer. However, the spectroscopic techniques on which their work is based are still controversial (Lowell and Rose-Innes, 1980). More limited attempts to correlate specific chemical structures to charging tendency have led to general guidelines (Cressman et al., 1974; Gibson, 1984). In particular Gibson (1975) quantitatively correlated tribo charging with the Hammett constant, a measure of electron-withdrawing power, for a set of substituents for benzene. As a result of these and other studies, it has been established that highly halogenated polymers, such as polytetrafluoroethylene and polychlorotrifluoroethylene, because of the electron affinity of the halogens, are strongly negative charging. At the opposite end of the triboelectric series, polymers that have nucleophilic sites such as nitrogen or oxygen atoms either within the polymer backbone or as a side group tend to be strongly positive. Examples are polyamides, polyamines, and polyacrylates.

Copolymers have a triboelectric nature dependent on their constituents. A copolymer of styrene, a relatively negative polymer, and *n*-butyl methacrylate, a relatively positive polymer, has a triboelectric nature intermediate between the two, with copolymers containing more methacrylate being more positive than those containing more styrene. Thus any change that modifies the rheological properties of a resin can also modify its charging characteristics.

The polymers most useful for toner because of their rheological characteristics tend not to be highly nitrogenated or halogenated and thus are intermediate in charging characteristics, although they can differ significantly among themselves. Nitrogenous compounds rather than polymers are often added to toner to improve their positive charging, as discussed later, while methacrylates like polymethylmethacrylate are often used as positively charging carrier coatings to drive the corresponding toner more negative. Similarly, the highly halogenated polymers are often used as electronegative carrier coatings to drive toner positive. The rheological properties of a polymer to be used as a carrier coating are not as important as its toughness and resistance to toner filming.

When a pigment is added to the toner polymer, the charging of the toner depends on the pigment also. One of the most significant pigments for xerographic toners is carbon black (Table 5.2). As a result, the charging properties of carbon black in polymers have been extensively studied; this work was recently reviewed by Julien (1993). Carbon blacks without surface functional groups are found to be relatively neutral, lying near the styrene-acrylate resins commonly used in toners. The addition of these blacks to such resins has a relatively small effect on charging properties. On the other hand, there is a large class of acidified carbon blacks that are more electronegative because of the electrophilic nature of the acidic surface groups. Their position in the triboelectric series is close to that of pure polystyrene (Fig. 5.11). As a result, the choice of carbon black can significantly alter toner charging properties.

Carbon blacks can also affect the rate of charging because of their conductivity (Julien et al., 1992). If the charge on a toner particle resides on its carbon black, it is readily available for "charge sharing" when this toner particle collides with a recently added uncharged toner particle. On the other hand, if the charge resides on the insulating polymer, it is not readily available for exchange between toner particles. The location of the charge on a toner particle is determined in part by the difference in energy levels between the charge exchange sites. For negative charging, the carbon blacks lie at the extreme in a triboelectric series of carrier polymer, toner resin, and carbon black; as a

Table 5.2 Typical Carbon Black Properties^a

Type ^b	Surface area (m ² /g)	Volatile content (%)	pH	Contact potential ^c (V)
Regal 330	94	1	8.5	0.00
Raven 1020	82	1	7.0	0.00
Raven 420	28	0.4	9.0	0.00
CSX99	520	5.1	8.3	-0.05
Raven 8000	935	9.6	2.4	-0.25
Black Pearls L	138	5.0	3.4	-0.40
CSX137	290	9.5	3.2	-0.50

^a Except for contact potential, the values are those provided by manufacturer.

^b The Raven blacks are produced by the Columbian Chemical Company. All the others are produced by the Cabot Corporation.

^c Relative to unoxidized (low volatile content) blacks.

(Source: Adapted from Julien, 1982.)

result, they acquire the bulk of the negative charge. This charge is then available for charge exchange. On the other hand, if the same toner is driven positive through the use of a halogenated carrier polymer, the toner resin now is the extreme component, and it gains the bulk of the charge. This is not readily available for charge exchange, and charging processes are slow. Thus the same toner can exhibit very different charging rates depending on the sign of charge it is given.

The charging properties of color pigments are equally important in determining the properties of the associated toners. Macholdt and Sieber (1988) have made toners incorporating pigments in styrene-methacrylate copolymers and charged them against carrier

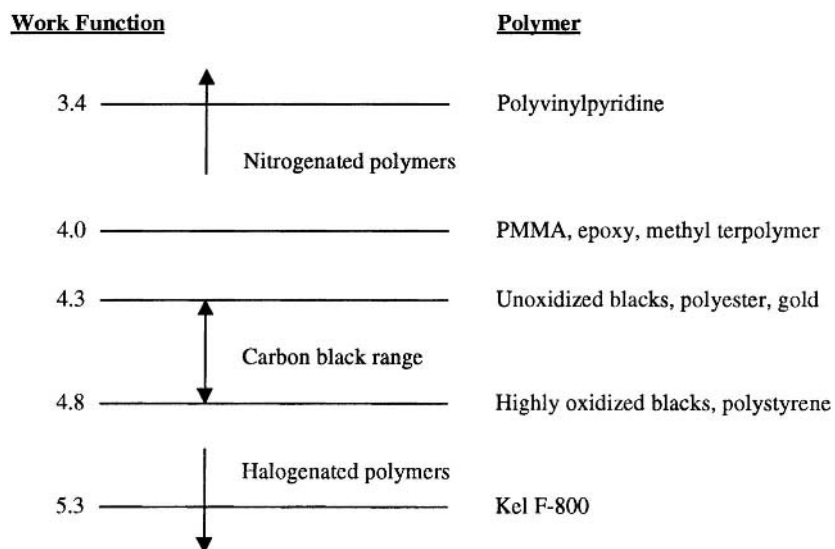


Figure 5.11 Carbon black in a triboelectric series; approximate work function values in volts. (From Julien, 1982.)

coated with the same polymer. They found that the copper phthalocyanines typically used for cyan and blue toner are relatively neutral, while the quinacridones used as magenta pigments are more negative, and the azo pigments used for yellow are more negative still (Fig. 5.12). However, the same authors demonstrate that treatment of the pigment surface can alter charging characteristics dramatically. Treatments include the inclusion of electrophilic or nucleophilic side groups, either deliberately or as a side effect of pigment finishing.

To relate Figs. 5.11 and 5.12, a styrene-methacrylate copolymer would probably lie between polyester and epoxy in work function in Figure 5.11, and the carbon blacks would probably look like the quinacridones in Fig. 5.12.

Of course, a pigment is chosen primarily for its visual characteristics. Since these are often highly critical, it is at times necessary to use pigments whose charging properties in the polymer of choice do not fall within the desired charge range. As a result, certain compounds called charge control agents (CCAs) are often added to toner for the specific purpose of modifying their charge. With black toners it is possible to use colored dyes as CCAs, e.g., nigrosine for positive charging (Guay et al., 1992) and metal complexes for negative charging (Fig. 5.13, Birkett and Gregory, 1984). With the metal complexes the nature of the positive counterion is extremely important and can change the triboelectric character of the material from negative to positive depending on whether the counterion or the metal complex is the more labile (Matsuura et al., 1993).

For general application with color toner, on the other hand, it is necessary for the charge control agent to be essentially colorless. For positive charging there are many nitrogenous compounds that are colorless. The most useful for many applications are the general class of quaternary ammonium salts (Fig. 5.14). Long chain aliphatic groups attached to the quaternary nitrogen tend to make the treated toner less hydroscopic and

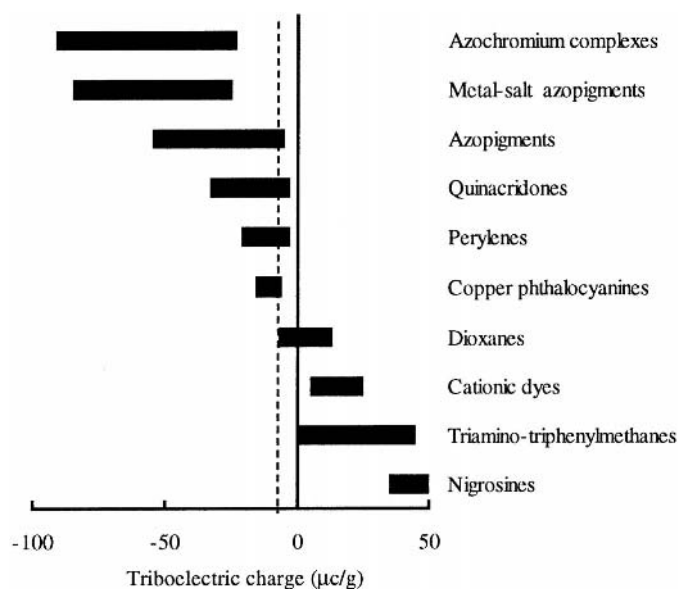


Figure 5.12 Effect of the incorporated pigments on the triboelectric charge of the test toner; broken line indicates the charge of the pure resin. (Adapted from Macholdt and Sieber, 1988a.)

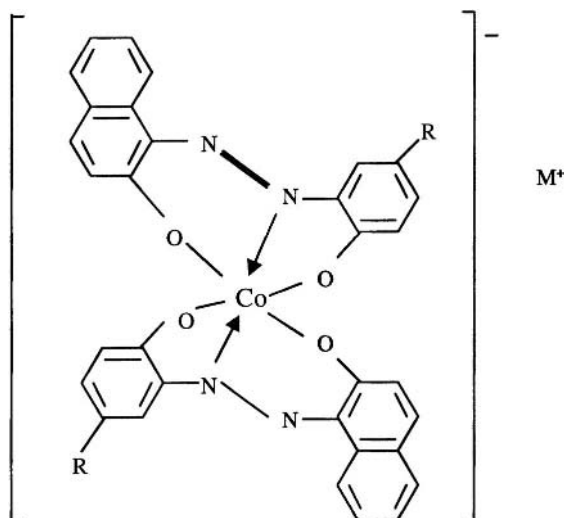


Figure 5.13 Typical metal complex for negative charge control. R can be SO_2 , NH_2 , Cl , etc.; M^+ can be Na^+ , K^+ , NH_4^+ , etc. (From Birkett and Gregory, 1984.)

therefore less likely to experience changes in charge level with changes in humidity. Many variations on the aliphatic chain and counterion are typically examined to find the compound giving the best overall performance in a given formulation.

Compounds related to the quaternary ammonium salts but based on phosphorus or sulfur rather than nitrogen have also been examined for charging performance (Yourd et al., 1985). The concept remains that a large positively charged molecule with at least one aliphatic chain to couple it to the host polymer is combined with a small labile negative ion. One hypothesis for the charging mechanism of these materials is that some of the negative ions migrate away from the toner particle, leaving a net positive charge.

For negative charging black toners, carbon black can often provide all the necessary charging characteristics. On the other hand, color pigments are typically neither conductive nor at the negative extreme in triboelectric nature of the various toner components. Materials intended for use as negative CCAs typically follow the same design concepts as those

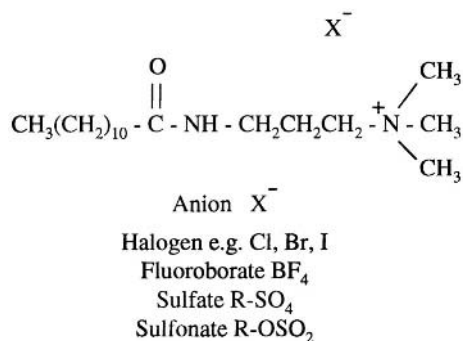


Figure 5.14 Typical example of a quaternary ammonium salt used in positive charging toners. The counter ion, X^- , is commonly chloride, bromide, or sulfate. (From Scharfe et al., 1989.)

for positive charge control agents but with opposite sign. Thus a large immobile molecule carrying a negative charge is paired with a smaller positively charged ion. This positive ion can be as simple as the proton itself. Gruber et al. (1983) found that the charging ability of various acids was directly related to their pKa value (i.e., their tendency to give up a proton).

Metals can also be used as labile positive ions. However, many metal complexes with large organic molecules are colored, hence of limited utility for general application to colored toner.

Surface additives such as fumed silicas used for flow properties can also be effective negative charge control agents (Schein, 1996).

The strong negative charging tendency of fumed silicas becomes a problem if one desires to improve the flow of positive toners. Sufficient silica to improve flow can reduce the positive charge on the toner to an unacceptably low level. Takenouchi (1986) discloses that the treatment of the silica with an aminosilane or other material can give the silica positive charging properties but renders it humidity sensitive. He found that additional treatment with a hydrophobic agent such as hexamethyldisilazane may be necessary. Degussa-Hüls (2000) and Wacker-Chemie (1998) have developed amino-silane treated silicas for positive toner applications.

There are so many requirements on charge control agents in terms of charge level and rate, aging and environmental stability, and interactions with the other systems in a machine that no additive performs ideally in all respects. As a result, there is continual research for better variations.

5.4.3 Special Magnetic Applications

While magnetite in the toner is unnecessary for developer flow when carrier beads are used, it is still useful to have. Inertial forces in the development nip tend to knock the larger toner particles off the carrier beads, generating either background on the copy or dirt in the machine. A small amount of magnetite in the toner generates an additional holding force, holding the particle against the developer roll. By adjusting the electric fields in the nip, one can obtain development as efficient as with nonmagnetic toner but with less toner released into the machine environment. This is especially true if there is a significant amount of low-charge toner in the developer.

An application in which magnetite in the toner is essential is in magnetic ink character recognition printing, abbreviated as MICR (Gruber et al., 1985). Here the characters at the bottom of a check (among other applications) can be read magnetically at very high speed by generating specific waveforms in specialized readers. This is usually done with lithographic inks containing high levels of magnetite. Through the use of special magnetic toners with higher levels of magnetite chosen to retain its magnetization longer than the grades usually used in xerography, printers such as the Xerox 9700 can generate images capable of being read in existing reading devices. A recent discussion of the special requirements of MICR toners has been given by Neilson (1998).

5.5 SINGLE-COMPONENT DEVELOPERS

5.5.1 Advantages and Disadvantages

There are several possible advantages that single-component technology may have over two-component developers.

The first of these concerns the volume occupied by the carrier. There is a constant desire to make things smaller in copiers and printers, to give the customer capabilities that earlier were available only in larger machines. This has put pressure on design engineers to reduce the development subsystem. By eliminating carrier beads, it may be possible to reduce the volume of the housing by an equivalent amount.

At the same time, two-component housings are becoming increasingly smaller. It is quite possible that a two-component housing could be made as small as a single-component housing and still deliver the same performance.

The charge level of the toner on the carrier is dependent on the amount of toner in the developer mix. To keep the toner concentration in a range where development is adequate without background, this concentration is typically continuously monitored and adjusted. This requires additional sensors, logic, and means of controlling toner dispensing. Thus a single-component system could be simpler, which should reduce cost and improve reliability.

Here again two-component technology is continually improving. Sensors and the associated electronics are becoming cheaper and may become an insignificant fraction of the cost of a housing. On the other hand, single-component development typically requires much closer tolerances in the development nip, among other places. A simpler but more precise housing may yet cost more.

Another consideration is development efficiency. Lower toner charge-to-mass ratios deliver more mass and hence density onto the photoreceptor for a given degree of charge neutralization. However, very low charge levels are difficult to work with in two-component xerography because carrier bead collisions can shake the toner off and allow it to fly around the housing, generating dirt and background. Single-component systems do not have to contend with the relatively heavy carrier beads and hence can operate at charge levels below 10 $\mu\text{c/g}$.

Most early single-component development systems relied on high magnetic loadings to control the movement of the toner through the housing. Over the last few years, several companies such as Canon and Lexmark have introduced nonmagnetic single-component systems for full color applications, but there has been little discussion of the toner requirements for these systems in the literature.

5.5.2 Single-Component Charging

The great majority of single-component systems still rely on bringing charged toner into the development nip and using the charge on the toner to control the development process (Fig. 5.4). Without the carrier beads to generate a charge on the toner, other means must be used. Typically the donor roll materials are selected to generate a charge of the right polarity on the toner when the latter is brought in contact with the roll. The toner layer formed on the donor roll either by electrostatic or magnetic forces is then passed through a metering/charging zone before entering the development zone. This zone is formed with either a blade or a pad brought into close proximity with the roll. The pressure or the position of the metering device is controlled to produce a toner layer of the desired thickness on the roll as it enters the development zone. In the case of a metal blade, an applied voltage can be used to modify the charge on the toner.

The design of the donor roll and the metering/charging nip can be at least as challenging as the design of the carrier, and all the questions about the contamination and stability of the carrier surface carry over to the donor roll and metering/charging device surfaces.

If the bulk of single-component charging is done in a small metering/charging zone, there will typically be only a fraction of a second for charging to occur. The result is that toner charging in single-component systems is usually not as complete as is possible for the same toners with appropriate carriers in two-component systems. The charge levels are not as high, leading to more low-charge toner. This low-charge toner can be accommodated by the jumping development process (Takahashi et al., 1982). An AC field is added to the DC development and cleaning fields to agitate the toner in a gap left between the donor roll and the latent image on the photoreceptor. Without the AC agitation, no toner reaches the latent image, and there is no development and no background. The AC field primarily agitates the charged toner; hence only the controlled portion of the distribution actually has a chance to move over to the photoreceptor. Only if the level of low-charge toner is quite large is it pulled along in the toner cloud in numbers sufficient to cause high background.

To satisfy the flow requirements for single-component toner, surface additives are almost always used. These will always have a dramatic effect on charging, because of their location on the surface of each toner particle. Fumed silica is by far the most common surface additive, and it can be treated to modify the charging properties with amines or titanates if positive charging is necessary (Takenouchi, 1986).

5.5.3 Toner Transport and Flow

One of the major challenges of single-component development is to move the toner through the developer housing. The attritted plastic that toner consists of is intrinsically a poor flowing material. In two-component development raw toner is moved from the toner bottle to the developer. This is typically done with foam rolls, brushes against screens, or augers. The last is probably the most practical method when the overall design requires that the toner bottle be well separated from the developer.

In single-component development, the lack of a carrier for transport raises the requirement for good flow characteristics. In practice, essentially all single-component toners have surface additives such as fumed silicas to improve powder flow.

5.5.4 Inductively Charged Toner

For some applications it is possible to charge toner in the development nip itself (Rumsey and Bennewitz, 1986). When toner of an appropriate conductivity is exposed to the development field, charge will flow from the conducting donor roll onto the toner. If the photoreceptor or other device holding the electrostatic image is insulating, the charge remains on the particle as it leaves the development zone. It is thus attached to the latent image by electrostatic attraction and remains on the photoreceptor to form the image.

There are several limitations to this scheme. Magnets are used to move the uncharged conductive toner through the development zone, requiring the toner to be magnetic, hence in almost all cases black. Since there is no intrinsic polarity to the charging/development phenomenon, reversed-bias cleaning fields cannot be used to control background, and only magnetic forces can be used for this control. Electrostatic transfer of conductive toner onto plain paper typically runs into problems because of charge leakage, and either coated paper or an alternative means of transfer such as pressure transfix is often used. However, for applications that fall within the boundaries posed by these limitations, inductive charging can be very effective, since it eliminates many of the problems of charging level, rate, and degradation encountered in triboelectric charging.

Recently, Océ developed a technology enabling bright colors with magnetic conductive color toner (Geraedts and Lenczowski, 1997). The toners are opaque, requiring the use of a seven-color system of cyan, magenta, yellow, red, green, blue, and black to develop a useful color gamut with toner monolayers.

5.6 TONER FABRICATION

5.6.1 Introduction

As stated earlier, dry xerographic toners are pigmented bits of plastic about 10 μm in diameter. Pigment and additive dispersion and particle size and size distribution are parameters that determine the quality of the resultant image; These parameters are in turn influenced by manufacturing techniques. The challenge to manufacturing is to produce the highest quality materials at the lowest possible price.

The great bulk of toner is manufactured by a multistep process consisting of melt mixing pigments and internal additives with the base toner polymer, breaking the pigmented polymer into particles of approximately the desired size, removing unwanted sizes from the size distribution, and blending in any external additives that may be necessary (Figure 5.15). Each of these steps generally requires at least one dedicated piece of equipment, as described in the sections that follow.

At the same time there has been a continuous effort to eliminate many of these steps, and chemical processes for simplified toner fabrication are described in Section 5.6.6.

5.6.2 Melt Mixing

The initial major step in toner manufacture is the blending or kneading of pigments and other internal additives with the polymer binder. The polymer is raised to a temperature at which it flows but with a relatively high viscosity. Higher temperatures at which the

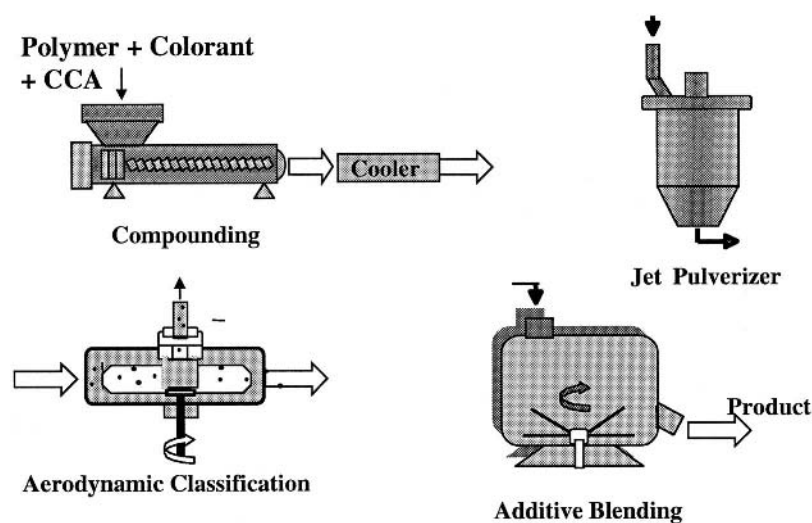


Figure 5.15 Conventional manufacturing process basic steps.

polymer flows more readily will not disperse the pigment as well, while lower temperatures require too much power to knead the pigment–polymer blend. Operating blend temperatures are generally not high compared to polymer processing in general, since the polymers have been designed to melt at as low a temperature as possible to accommodate the fusing of the toner to the paper. Temperatures from 300 to 400°F are typically adequate.

The mixing can be done in either a batch process or a continuous process. One implementation of the batch process uses a mixer such as the Brabender or Banbury. The materials to be melt mixed are premeasured and possibly premixed in a dry powder mixer such as those made by Henschel, Lodge, and others. These are then fed into the preheated melt mixing unit for a given length of time. Generally this is sufficient to form a polymer matrix, but component dispersion may be poor. If necessary, the output of the mixer can be passed repeatedly through a rubber mill until the desired dispersion is obtained.

In general, the intent is to obtain dispersions closely approximating perfectly distributed ingredients; however, it is possible that an ultimate dispersion is not the most useful. A well-documented nonxerographic example of this is the use of chained carbon blacks to give conductivity to a polymer (Sommers, 1984). If the mixing is too vigorous or too long, the chains will be broken, leading to a loss in conductivity. The most effective dispersion of many xerographic additives is not well understood, and often a range of dispersions is produced and evaluated in the course of the engineering studies. It is also true that the best dispersion typically requires the longest blend times and hence the highest processing costs; this also may lead to the use of a less-than-complete dispersion. In these cases it becomes a challenge to manufacturing to maintain the desired dispersion.

The continuous method of melt blending can be done on an extruder. This device allows higher toner production rates and hence lower processing costs than the batch processes. Here a smaller amount of polymer is in the extruder at any time, but the processing time that a given segment of polymer sees is also smaller. As a result, the forces to which a polymer is exposed may be required to be higher in the extrusion methods than in the batch processes.

Extruders offer the option of adding different components at different positions along the mixing barrel and hence at different stages in the melt history of the polymer. This offers more possibilities for process optimization, but also more stringent requirements on reproducibility.

5.6.3 Attrition

The manufacturing scale equipment used for batch melt mixing produces a slab of blended plastic weighing generally in excess of 50 pounds. The output of an extruder is more convenient in size, consisting of pellets roughly an eighth of an inch in diameter. Both these outputs are ground down until particles about 100 μm in size are produced. These are then fed into an air jet mill (jet pulverizer, or micronizer), which entrains the particles in a high velocity airstream in such a way that they collide against one another with sufficient velocity to cause fracture. The geometry of the airstream is designed so that particles below a certain size are carried out of the attrition zone, while larger particles are retained and subjected to further collisions. In this way 100 μm powder is fed in and smaller powder is continuously removed from the apparatus.

As stated in Section 5.2.1, on toner resin, the ability to use this method of toner manufacture is an important attribute of polymer design, independent of the fusing temperature of the resin. For example, a rubbery polymer may have acceptable fusing perfor-

mance but poor jetting performance. Lowering the molecular weight of a polymer will in general lead to faster jetting rates by decreasing the mechanical strength of the material.

5.6.4 Classification

Attrition as it is currently practiced is a violent process. While the average particle size can be closely controlled, many particles are produced that are significantly smaller than desired, and a significant number exit the attrition zone even though they still have a fairly large size. The small particles can have undesirably low charge levels, leading to high background, while the large particles can resist fusing and form spots on the copy. These should be controlled for optimum copy quality.

The small and large particles can be removed by air entrainment technology similar to that in the attrition step. Particles are carried along by an airstream that flows around sharp corners. Inertia tends to carry the larger particles to the outside of the bend, and a knife edge can then separate the large from the small particles. The velocity of the airstream can be changed to adjust the diameter of separation. The cut point between the high and low sizes is generally not very sharp, and often more than one pass through the classifier (or a pass through more than one classifier) is necessary to remove the amount of large or small toner desired without taking away a significant portion of the desired toner size. Material that is rejected by the classifier can often be recycled through the melt mixing stage, but even this represents a loss in throughput capability. The goal is to adjust the attrition parameters so that a minimum amount of material is rejected by classification.

Since toner comes out of the attrition step entrained in an airstream, it is possible to direct it immediately into a classifier, thus producing a continuous process with no loss in productivity. A second stage of classification, if required, would necessitate an additional classifier, trading capital cost for throughput capability.

5.6.5 Finishing

At times an additional step, the addition of external additives, is needed in toner processing. This can be done by injecting the additives into the airstream carrying the toner as it leaves the classifier. Under these conditions, however, it is difficult to obtain good mixing of the often extremely light additives with the toner. More often, the additives are blended in a batch process, using any of a number of dry powder mixers. When extremely small surface additives such as the 10 nm fumed silicas are blended with 10 to 20 μm toner, often highly intensive blending is necessary to break down the additive to the smallest unit and distribute it uniformly over the surface of the toner particle.

The equipment type is typically selected at the time of the design of the plant, but the choice of the best mixing speed and time typically varies with each toner design. With some designs, a plot of the desired property such as flow will reach its final value sooner than others, and unnecessary mixing time can be avoided. Others will actually show a degradation in the desired property with prolonged blending.

5.6.6 Chemical Processes for Toner Fabrication

The polymers that are subjected to all the foregoing processing steps are typically made by suspension or emulsion polymerization processes that produce spherical particles with a fairly uniform size. It would obviously save a great deal of work if the pigment and charge control additives could be incorporated into the polymer during this stage, resulting

in pigmented particles in the proper size range. This would eliminate melt mixing, attrition, and classification.

Polymer beads are typically made to be about a millimeter in size, but they can be produced in sizes down to a fraction of a micrometer. A more fundamental problem is the incorporation of pigment into the polymerization process. The pigment is usually chemically active and can interfere with the delicate reactions that must be repeated hundreds of times without interruption to form a polymer of sufficient molecular weight to be useful. However, several authors have described processes for producing “suspension polymerized” or “dispersion polymerized” toner (Takezawa et al., 1997; Fukuda et al., 1996; Totsuda et al., 1998). Also, Nippon Zeon has been producing commercial chemical black toner based on suspension polymerization for several years (Yanagida, 1998), and Canon and Hewlett Packard introduced products using color chemical toner in 1998.

The problem of polymerization in the presence of pigments can be avoided by starting the toner preparation process with a submicron polymer latex and aggregating it with a pigment dispersion. These “latex aggregation” processes have also been discussed at recent conferences (Edwards et al., 1998; Koyama et al., 1994; Nakamura et al., 1991), and Nippon Carbide has been making black aggregation toner on a commercial basis.

Both processes have the ability to produce small particles with a narrow size distribution. The suspension polymerization techniques form intrinsically spherical particles, although the surface texture can be controlled, while the latex aggregation techniques allow a range of morphologies from “potato” to sphere. The spherical morphology helps transfer (Yanagida, 1998), but it may have more problems with blade cleaning (Koyama et al., 1994). The suspension polymerization technique is well suited to building a layered structure into the toner (Fukuda et al., 1996), while the latex aggregation technique readily allows the blending of different molecular weight latices (Edwards et al., 1998). Many variations within or combining chemical processes are possible, and considerable activity is expected over the next few years.

5.7 CONCLUSIONS

5.7.1 Summary

Dry toner technology is relatively mature, with an enormous base of raw materials, characterization techniques, working knowledge, and processing methods that has been built up over the years. There are an enormous number of options for the toner as part of the overall machine design. Few of the options have been shown to be unworkable or uncompetitive over the years. The sign of the toner charge, the size of the toner particle, and the use of single- or two-component development are matters that have not been decided firmly.

5.7.2 Future Directions

Probably the most obvious future direction in xerography will be the presence of even more color in the marketplace. Personal computers are giving people the ability to command color on their display screen, and color ink-jet personal printers have become the norm rather than the exception. There will then be a need to make copies of these prints. Eventually it will penetrate all volume bands with a mix of color capabilities from single highlight color options to full process color. All copier hardware will require color options. This will put an enormous burden on the toner designer either to deal more effectively

with color in new toner designs or to provide more generic designs that can be used in a variety of hardware.

A multiplicity of color toner designs will also stress the manufacturing capabilities of the various vendors. Individual designs probably will have insufficient volume to justify unique processing equipment, and a sensible manufacturing strategy will be very important. Chemical toner fabrication offers the possibility of efficiently making high quality toner at any scale and should become increasingly important as the technology is mastered.

Lower melting temperatures with adequate blocking characteristics are desirable for improved fuser performance and will become more prevalent as their performance justifies their cost.

ACKNOWLEDGMENT

We acknowledge the contribution of S. K. Ahuja to the discussion on rheology.

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6

Carrier Materials for Imaging

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INTRODUCTION

Since the publication of the first edition of this book there has been considerable activity in the field of xerography, with much attention focused on the carriers used in two-component development. These developments have not revolutionized our understanding of how carriers work or why they are needed. There has been enough activity to tell us that they are still considered important and are necessary, especially in the most rapidly growing sector of the market: digital color imaging. Many attempts have been made to eliminate the need for carriers, an objective that might be achieved sometime in the future, but for the present these unique imaging materials seem firmly entrenched in the world of electrophotography.

During the past 10 years, more than 150 United States patents have been issued in the field of xerographic carriers and carrier manufacturing processes. Of these about 10% have been aimed directly at the color copying or printing portion of the market. Much of the effort in color has been directed at noncontact development, processes in which the carrier approaches, but never touches, the developed image. At least 37 patents have this idea as their subject matter. The details of these and other recent developments in xerographic carrier materials will be covered at the end of this chapter, but for now the previously published information stands with few changes or updates.

6.1 CARRIER DEFINITION AND FUNCTION

Carrier is a general term used in xerography to describe the toner transporting species in a two-component dry developer. In such a mixture, the smaller toner particles are carried

* Retired

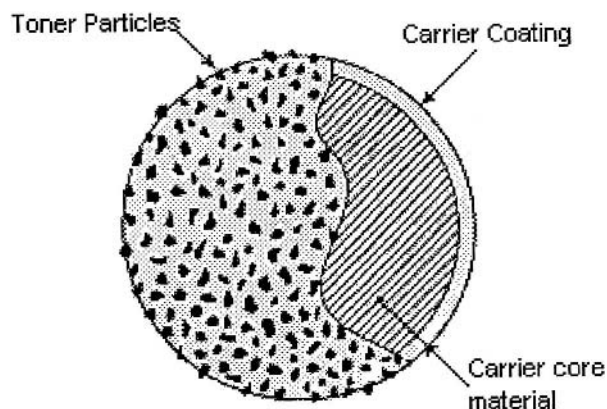


Figure 6.1 Cross section view of a coated spherical developer.

on the surface of the larger carrier granules, as depicted in Fig. 6.1. Here, a coated, spherical carrier is shown in cross section. In practice, however, the carrier may be coated or uncoated, spherical or irregular in shape.

Toner is the “ink” that actually makes the mark on the paper (1). It generally consists of a low melting polymer compounded with approximately 10% carbon black and ground to a particle size ranging from about 12 microns in older products to about 6 microns in the more recent “microfine” toner powders.

The carrier is also a granular material which ranges from 3 to 50 times the average diameter of the toner particle. This component of the developer mix is the subject of the remainder of this chapter.

Xerographic developer mixtures typically contain from 1 to 10% by weight of toner. The toner is transported by the carrier and brought into close proximity with an invisible, electrostatically charged image on a photosensitive surface in a copier, laser printer, fax machine, or multifunctional imaging device. At this point, toner particles abandon the carrier surface and deposit either in charged areas on the latent image, or are repelled into neutral image areas, depending upon the relative charge polarity of image and toner.

One of the most important functions of the carrier is to impart a static charge to the toner particles. This is accomplished by frictional surface contact with the toner during mixing, a phenomenon known as *triboelectrification*. This term comes from a combination of Greek words meaning to charge by rubbing and is likened to the familiar experiment of charging a glass rod by rubbing it with cat’s fur to attract and hold small bits of paper. Another example of tribocharging is the unpleasant experience of walking on a carpet on a dry day and being shocked by touching a doorknob or other grounded element.

In the case of xerographic developers the combination of toner and carrier properties must be chosen to produce the correct level and polarity of electrostatic charge on the toner. This will ensure that the desired amount is attracted to the oppositely charged image area. It is important that the charge on the toner be neither so high that it cannot be stripped from the carrier nor so low that it is not held tightly to the carrier. Loose toner can float around the imaging device, depositing on optical and other machine components, producing dust in the environment, and settling in nonimage areas of the print as unwanted level of background density.

The methods and materials used to accomplish these design tasks are the subject of the remainder of this chapter.

6.2 MATERIALS (HISTORICAL)

6.2.1 Xerox Corporation

Any discussion of carrier materials must start with those substances used initially by the Haloid Corporation, the cradle of the electrophotographic process, which later was renamed the Xerox Corporation. In an early demonstration of xerography by its inventor Chester Carlson in 1938, the carrier used was uncoated iron powder and the image was formed by cascading the developer over the image until enough toner had been deposited to produce a visible mark or readable character (2). In the course of reducing Carlson's imaging method to a commercial process, carriers were chosen from powders available in the market place; most of the design work was empirical because little was known about the triboelectric charging effect.

In 1950 the Haloid Corporation introduced a manually operated offset platemaker called the Model D, in which the carrier was washed and screened sand. This carrier, measuring approximately 600 microns in diameter, bore a lacquer coating to obtain the desired charging effect. From that beginning, many different powdered materials have evolved (see 6.2.2) as the industry expanded to encompass other equipment manufacturers and to suit a wide range of customer requirements. Carrier technology became more sophisticated, enabling output image quality to progress from something barely readable to razor sharp prints with rich black solids and smooth halftones at ever increasing speeds.

Subsystems have progressed from cascade (Fig. 6.2) to magnetic brush development (Fig. 6.3) for delivering the toner to the image. The design of carrier materials has kept pace with these advances, moving much of the early empiricism into the realm of science. As machine performance and copy quality have progressed, so have the developer packages and naturally the carriers. During the early improvements in machine design, there was little carrier development. Design engineers and materials scientists were faced with

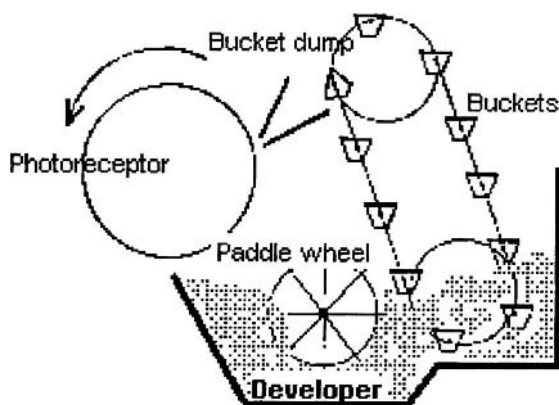


Figure 6.2 Cascade development process.

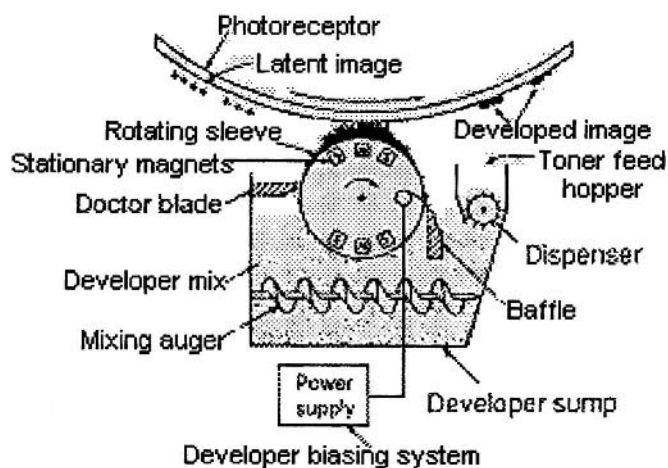


Figure 6.3 Magnetic brush development.

an exploding demand for copiers and duplicators. Further, almost any toner–tribo pair would work as long as the two dissimilar granules rubbed together exchanged charge and could sustain their performance as a developer mix. Toner was consumable and habit forming. The market expansion got somewhat ahead of the technology, a reaffirmation of the dictum, “the art comes before the science.”

Existing powders that were available for other applications were also utilized. Some were specially screened distributions obtained from abrasive powder suppliers. Originally these materials were designed for shot blasting or scarfing applications such as cleaning plastic or metal parts. Others were taken from the powdered metals designed for use in pressing parts by compaction and sintering. Generally copier manufacturers used tailings or fines from these sources rather than develop a process for customized copier powders. As the industry grew, competition and customer awareness of copy quality forced increasingly stringent specifications to be placed on the carriers as well as the toners.

6.2.2 Specific Carriers Used

Table 6.1 is an historical summary of the various powder materials that have been used since the beginning of electrostatic imaging. It can be seen that the industry has progressed from dusting the image with dark powder to delivering the toners with sand, glass, aluminum, iron, steel, nickel, magnetite, and ferrites. All these carrier materials can be used in cascade development. Indeed, the latest magnetic roll systems are based mainly on the last five materials. Starting in the early 1960s, development programs were launched to design xerographic carriers. To date, there have been a few basic carriers generated that were designed directly for specific machines. Some of these are:

1. Spherical iron powders processed by the rotating electrode process by Nuclear Metals Inc. (see Fig. 6.4)
2. Spherical ferrite (magnetic ceramic) powders produced by spray drying and high-temperature sintering (see Fig. 6.5)
3. Magnetite spheroidized by plasma energy
4. Irregular iron powder produced by the reduction of screened magnetite ore

Table 6.1 History of Electrostatic Copier Powders

Year	Event	Copier powder
1777	Lichtenberg demonstrates electrostatic image development	Lycopodium powder
1920	Selenyi develops a facsimile recording process using an electrified stylus, writing on an insulating surface, and powder development	Lycopodium powder
1938	Chester Carlson invents xerography, an electrostatic imaging process for plain paper copying	Uncoated iron carrier and toner
1950	Haloid introduces manually operated xerographic equipment for offset platemaking: the Model D	600 μm lacquered sand carrier and toner
1954	RCA researchers Grieg, Giaimo, and Young invent Electrofax, an electrostatic imaging process for coated paper copying using a magnetic brush	Uncoated irregular iron carrier and toner
1959	Haloid-Xerox introduces the first automated plain paper copier to use Carlson's xerographic technology: the Xerox 914, a 7 page/min (ppm) machine	600 μm lacquered sand carrier and toner
1961	American Photocopy Equipment Co. markets the first plain paper copier to use RCA's Electrofax technology: the Dristat	Uncoated irregular iron carrier and toner
1964	Xerox announces the first copier-duplicator to operate at 40 ppm: the Xerox 2400	600 μm lacquered sand carrier and toner
1969	Xerox demonstrates a major advance in xerographic copier quality using a conductive steel bead carrier and cascade development: the Xerox 3600-III, a 61 ppm machine	450 μm lacquered spherical steel carrier and toner
1970	Xerox unveils a compact high-speed plain paper copier: the Xerox 4000, a 43 ppm machine	250 μm lacquered spherical steel carrier and toner
1971	IBM enters the office copying field with a 10 copy/min machine: the Copier I	170 μm teflon coated spherical steel carrier and toner
1972	Xerox markets a plain paper copier based on the finest spherical steel carrier ever used for xerography: the Xerox 3100, a 12 ppm machine	100 μm lacquered spherical steel carrier and toner
1972	3M Company revolutionizes electrostatic image development with the VQC series of copiers, the first to use single-component magnetic toner	Magnetic toner, 20 μm carrier
1973	Xerox introduces the first nonimpact computer printer based on xerography: the Xerox 1200	450 μm lacquered spherical steel carrier and toner

Table 6.1 (Continued)

Year	Event	Copier powder
1973	Xerox rolls out the first xerographic color copier: the Xerox 6500	2 toner colors with lacquered 100 μm spherical steel carrier and the third color with 100 μm nickel carrier
1975	Xerox demonstrates the fastest xerographic copier-duplicator using mag brush development, operating at 120 ppm: the Xerox 9200	80 μm lacquered spherical ferrite carrier and classified toner
1975	Eastman Kodak enters the office copying field with equipment using nonspherical iron carrier: the Ektaprint 100/150	170 μm laquered irregular iron carrier and toner
1976	IBM commercializes the first laser beam xerographic computer printer: the IBM 3800 operates at more than 150 ppm	170 μm Teflon-coated spherical iron carrier and toner
1979	Minolta markets a copier using “microtoning” technology, the first electrostatic developer to use a fine particle carrier: the EP-310	40 μm magnetic carrier and toner
1979	Canon introduces Ion Projection Development in the first practical plain paper copier to use one: component toner, the Canon NP-200	10–15 μm magnetic carrier and magnetic toner
1980	Xerox offers the first copier in its line to use irregular iron carrier: the Xerox 3300	100 μm lacquered irregular iron carrier and toner
1983	Xerox debuts its first office copier to use an organic photoreceptor: the Xerox 1075	130 μm lacquered irregular iron carrier and toner

There are many variations on these, such as partially reduced magnetite or oxidation of irregular iron for conductivity variation and control. The important powder properties will be discussed later, but it can be noted that the trends are toward smaller size distribution for higher surface area, lower density, lower resistivity, and better flow characteristics.

6.3 MATERIAL PROGRESS

6.3.1 Copier Evolution Effects

Of the two commercially available electrostatic copying methods: Electrofax, the direct, coated paper copier (CPC) process has all but disappeared from the market, while xerography, the transfer, or plain paper copier (PPC) process has flourished. Both methods employ a photoconductive member that can be charged uniformly and discharged in the nonimage areas by reflected light from the original document. In the CPC process, the paper is coated with a photoconductive zinc oxide pigment in a resin binder. This layer is charged and exposed to a light image yielding a latent electrostatic charge pattern corresponding to light and dark areas on the original document. In the development step the charged image attracts charged toner particles from the carrier rendering the image visible. The toner deposit is fixed or fused onto the sheet by heat, pressure, or a combination of heat and pressure. Thus the photoconductor is used but one time, becoming the designed copy.

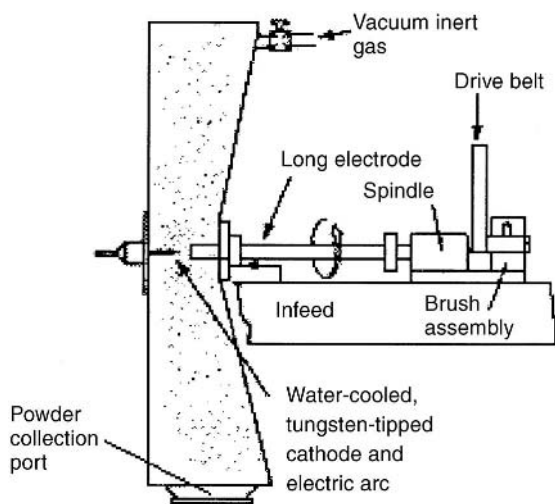


Figure 6.4 The rotating electrode process.

In the transfer process a reusable drum or belt, coated with a photosensitive material such as selenium, is charged and exposed in the same manner as the CPC process, but the toned image is then transferred to a plain paper or film substrate upon which it is permanently adhered by heat or pressure fixing.

Four methods of toner development are known: cascade (Fig. 6.2), magnetic brush (Fig. 6.3), powder cloud, and touchdown. Since cascade and magnetic brush are the most widely used, and the only ones of importance in two-component development, they will be discussed in detail here. Powder cloud is used in xeroradiography, while touchdown development remains experimental and has not found commercial applications.

Cascade development generally uses more spherically shaped beads to obtain better flow characteristics. The machines that use cascade development resemble a Ferris wheel with buckets on a chain drive to pick up the developer from a sump or reservoir. The developer mix is dumped into a trough which allows the material to cascade down over the exposed photoreceptor and the return to the sump.

Toner particles leave the carrier surface upon being attracted to highly charged image areas as the beads roll and bounce over the photoreceptor. In many cases the impact dislodges poorly charged toner particles causing them to become airborne and to deposit in nonimage (background) areas. The result is dust and dirt in and around the machine and a reduction in the quality of the final print. This drawback of the cascade process is one of the reasons that the magnetic brush system is preferred in most of the copiers, duplicators, and printers being manufactured today. This may not be a completely fair statement, because the cascade systems of the past would probably deliver better performance if they were to take advantage of today's developer technology.

Another limitation of the old cascade process is the poor development of solid areas on the copy. This is particularly bad when insulating materials such as sand and glass are used. Again, today's materials would likely improve solid area fill, but magnetic brush development has become the accepted technique over the last 15 years.

Magnetic brush development was invented by Giaimo and Young (3–5). This process uses a mixture of magnetic carrier beads with the toner to make up the developer. The size of the carrier ranges from 30 to 450 microns. Van Engeland gives an excellent

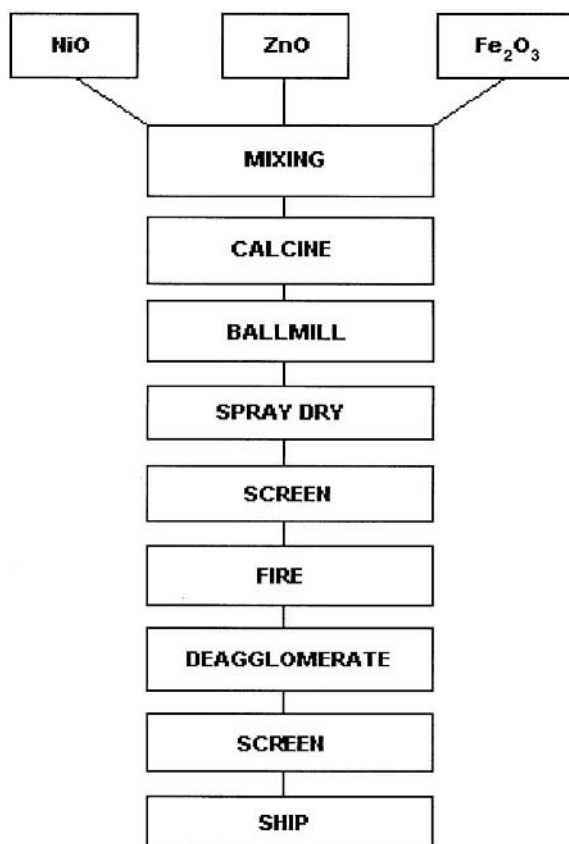


Figure 6.5 Ferrite process flowsheet.

review of this process (6). The physics of cascade and magnetic brush development are treated by L. B. Schein along with other dry and liquid toner development processes (58).

Figure 6.3 illustrates a schematic of a magnetic brush development subsystem. The magnetic developer is attracted to the surface of a nonmagnetic rotating roller by stationary magnets positioned inside the roller. The quantity of material transported is metered by a trimmer bar or doctor blade, which controls the pile height of the brush bristles. The carrier material aligns itself in the field of the magnets and forms a bristle or brush that can make contact with the photoreceptor surface, enabling the toner to develop the charged image.

As the carrier moves past the development zone, the field decreases with distance from the internal magnets. Gravity and centrifugal force return the partially spent developer to the sump. Fresh toner is added automatically to the mixture from the toner hopper to replenish the toner lean developer mix. A mixing auger stirs the material to assure that the fresh toner is charged and uniformly distributed in the developer mix.

The toner concentration of the developer can be monitored in several ways. Most machines have sensors that detect changes in resistivity, magnetics, or reflectance as a function of toner concentration. These sensors can determine when the toner concentration

is low and signal the toner hopper to replenish the spent mix by dispensing toner to the developer housing.

The characteristics of the brush in the development zone are important to determine the supply of toner available to the image. In any given housing the magnetic properties of the carrier determine how hard or soft the brush will be. The resistivity of the developer mix is a major factor in the development of solid areas.

Spherical carriers have better flow properties that improve mixing efficiency and reduce the torque required to drive the housing; irregular carriers can be designed to provide controlled resistivity, but this feature comes at the expense of wear to the photoreceptor, somewhat inferior flow properties, and wear on the carrier itself.

6.3.2 Magnetic Materials Required

As stated previously, all the materials mentioned can be adapted to cascade development. What is required is a mechanism that will move and mix the developer. In the last 20 years, magnetic brush development has restricted the choices to “soft” magnetic materials. This term means that the material is magnetically soft or has very low loss and low remanence. Once the material has been in a magnetic field, it retains very little polarization when removed from the field. If the remanence is high, each bead becomes a tiny permanent magnet, and all of the beads attract each other; this severely restricts the flow properties of the carrier returned to the sump for remixing. The “soft” magnetic materials used are iron, low-carbon steels, annealed nickel, magnetite, and ferrites. Recently, Eastman Kodak broke new ground by introducing “hard” ferrite carrier into some of its equipment. This material has some of the problems of flow after magnetization, but Kodak scientists introduced some rather ingenious developer housing designs to solve that problem. The “hard” materials have considerable remanence and are generally used in permanent magnet applications such as the novelty refrigerator magnets.

The need for cleaner, sharper, high-quality copies with rich solid areas for color reproduction and graphics has prompted many improvements in carrier materials. The ultimate goal is to have copies that compare to lithography for resolution, solid fill, and uniformity. This requires a controlled and consistent resistivity of the developer, generally lower than the insulating sand or glass yet higher than bare iron or steel core materials. Therefore most of the iron powders are oxidized to control the resistivity and partially coated to control electrostatic charging. Irregular iron powders have been used in the last few years, and the theory is basically that the high points are oxidized (15) and poorly coated to supply the required resistivity while the valleys are better coated to supply the charging effect required.

Many of the Japanese copiers used irregular iron such as flake or filings. In recent years most of the two-component copiers have shifted to ferrites because of the semiconducting properties they possess. These materials have resistivities in the range desired because they are transition metal oxides and magnetic ceramic materials that can in some applications be used without partial coating for toner charging.

6.4 CURRENT CARRIER POWDERS

6.4.1 Steel (Spherical)

One of the first uses of 450 micron spherical steel came in 1969 with the introduction of a 60 ppm machine by Xerox Corporation called the 3600-III. The process for these types

of materials is described in patents by R. Hagenbach and R. Forgens for classifying and manufacturing by a two-wire process (7,8).

In the same time frame, development of a rotating electrode process was going on at Nuclear Metals Inc. This process is depicted schematically in Fig. 6.4 and was one of the first materials designed specifically for carrier powders. Another highly successful machine, the Model 3100 copier, was introduced by Xerox in 1972. This 12 ppm machine utilized 100 micron spherical steel as the carrier in a magnetic brush developer housing. The success of the 3100 led to a series of similar machines all using the same developer, many of them are still in use today.

In 1971 IBM joined the copier field with the introduction of its Copier I which used a 170 micron Teflon coated spherical steel carrier. IBM continued to use this material in most of its subsequent machines. Since all these copiers used coated carrier, the developer was quite insulating, and consequently solid area reproduction was poor. In addition, background toning and machine dirt became problems.

6.4.2 Iron (Irregular)

Irregular iron was first demonstrated by Greig, Giaimo, and Young with the invention of Electrofax at RCA for a coated paper copier. This became a commercial reality in 1961 when it was marketed by the American Photocopy Equipment Company as "DriStat." The next important entry of irregular iron came in 1975 when Eastman Kodak entered the copier field with the Ektaprint 100/150 (17). This machine employed a coated 170 micron carrier and made use of resistivity and charge controls by oxidation (15) and by proprietary carrier coating methods as described previously. This material is a reduced, screened magnetite that provides a very rough bead of nearly pure iron.

The same type of material is utilized in the Xerox 1075, which came on the market in 1983. The carrier size is slightly smaller at 130 microns, but the same resistivity and charge control processes were applied. A different 100 micron irregular iron made by water atomization was introduced in 1980 by Xerox Corporation in a machine called the Model 3300. This carrier is oxidized and coated similarly for the same reasons.

In the late 1980s, a partially reduced magnetite was used in some Japanese copiers as described in a joint patent between Kanto Denka Kogyo in Japan and Hoeganas AB in Sweden (9). All of these machines reproduce solid areas quite well and deliver excellent copy quality.

6.4.3 Soft Ferrites (Spherical)

The simple ferrite process flowsheet of Fig. 6.5 illustrates how the spherical powder is formed in the spray drying step. Many ferrite formulations may be produced by this method, which has been adapted to the manufacture of carriers for xerography. The first mention of ferrites to be used in magnetic brush development was by Joseph Wilson of Haloid Xerox Inc. in 1958 (19). The first commercial use came in 1975. This family of materials has grown steadily in the last 15 years from the first introduction in a high-speed machine, the Xerox 9200 (10–14), operating at 120 ppm. Since that time ferrites have been used in over 20 different Xerox machine models.

The use of ferrite carriers spread rapidly to Japanese original equipment makers (OEMs). In 1986 alone they introduced 38 new copiers and printers of which 34 utilized ferrite carrier. These materials provide several important advantages in magnetic brush

Table 6.2 Comparison of Bare, Uncoated Carrier Core Properties

Property	Iron powders	Magnetite	Ferrite	Hybrids	Composites
Magnetic saturation (emu/g)	160–190	88–98	30–96	50–65	30–65
Resistivity @ 100 volts (ohm-cm)	10^3 – 10^8	10^6 – 10^8	10^3 – 10^8	10^{37} – 10^9	$>10^{12}$
Apparent density (g/cc)	2.4–2.5	2.0–3.0	1.5–3.0	1.5–2.5	1.0–1.5
Susceptibility to oxidation	Moderate	High	Low	Low	None
Cost (1–10) Low–high	1–5	4–8	5–10	5–10	8–10
Use in full color applications	Very difficult	Difficult	Preferred	Difficult	Moderate
Versatility of design in systems	Moderate	Low	High	Moderate	Low

Source: Courtesy of Powdertech Corporation.

development. Primarily, they allow the carrier to be tailored to the development housing design and to the charging specifications required for any given machine.

In addition, the magnetic saturation (magnetic saturation moment) can be varied by formulation and process from about 30 to 96 emu per gram, which relates to the developer pickup on the brush and the stiffness of the brush. Too high a moment will result in a stiff brush that might scratch the image, causing nonuniformities in the solids and ragged edges on the line copy or letters.

A comparison of bare carrier core properties (Table 6.2) for iron powders, magnetite, ferrites, hybrids, and composites was recently presented by W. R. Hutcheson of Powdertech Corporation (104). In the case of iron or steel carriers, magnetic saturation moments range from 160 to 190 emu per gram and cannot be varied much outside these limits.

Ferrites are lower density materials and therefore require lower torque to drive the developer housing; this translates into lower energy consumption and less heat generation. Ferrites are natural semiconductors with an electrical resistivity that can be varied across the useful range of carriers, generally from 10^6 to 10^{12} ohm-centimeters. They have been used in some cases without the requirement of partial coating. The surface microroughness can be controlled so that the material is consistently coatable in any given coating process, should it be required. The size range is variable from 10 to 120 microns for the spherical ferrites and can be extended down to 2 microns for irregular ferrites, a property that has begun to raise some interest in the industry (16).

6.4.4 Hard Ferrites (Spherical)

The use of a hard or permanent magnet type of ferrite entered the marketplace with the introduction by Eastman Kodak of the Coloredge machine in 1988. It uses a smaller carrier of a type described in the patent issued to E. Miskinis and T. Jadwin (18). Coloredge is a 23 ppm full color copier, which can run highlight color at higher speeds and black or monochrome copies at 70 cpm. The machine has multiple developer housings to accommodate the primary colors and black for a full spectrum output.

6.4.5 Hybrids and Composites

The Xerox 6500, introduced in 1973, was another color copier that used multiple developer housings to achieve full color reproduction. Some industry analysts believe it entered the

market before its time, as there were not enough color originals for it to copy. Now that full color printers are flourishing, there is an explosion of interest in this area.

The 6500 is included in the hybrid category because it used two different carriers. One color utilized 100 micron "nickel-berry" beads, electrolytically grown nodules of high-purity nickel. Other colors used coated steel carriers. Because nickel is a costly metal that has undergone wild fluctuations in price, and in view of the military priorities placed on this material, it has not been used in other applications to this writer's knowledge.

Another hybrid ferrite composition was developed in 1986 by Hitachi Metals, Ltd., of Japan. It uses two different ferrite crystalline structures mixed together in the standard ferrite process to make a copier powder (20). The composition, used in some of the Japanese machines, is a mixture of a hexagonal "hard" ferrite and a spinel "soft" ferrite. Although it has not been disclosed, the resultant carrier core probably has a two-phase structure. The hard phase would be little affected in the low magnetic fields experienced in the magnetic roll of the machine and has little magnetization effect. However, even in low-gauss fields, flow characteristics and torque requirements differ from those of soft ferrite carriers.

Still another hybrid is a mixture of two or more of the materials already mentioned. An example of this is a mixture of spherical ferrite and iron flake noted in at least one of the Panasonic copiers. There is also a patent by J. Cooper and A. Goldstein which describes a similar mixture (21).

A "composite carrier" as defined by Hutcheson (104), contains magnetic powder dispersed in a nonmagnetic polymer or resin matrix. Composites were developed for their extremely stable triboelectric properties and low bulk density, but they typically exhibit low magnetic moment and a very high resistivity.

6.5 CARRIER MANUFACTURING PROCESS

This section is included to describe some of the methods used to convert the raw powder into carrier. Many carriers are coated, or more likely partially coated, for two main reasons. The first is to enhance toner charging, because polymer surfaces give better charge exchange and less charge recombination than inorganic surfaces.

The second reason is that adhesive force or tackiness is lower with polymer surfaces; thus less toner is adhered to the carrier surface. Such impacted toner impedes development and shortens the useful life of the carrier. When toner is adhered or too highly charged it uses up carrier area until there is not enough charging surface left to support the toner required to produce the desired level of image density. Any further toner additions result in low or zero charging, increased background deposits, and machine dirt. Generally, this is a criterion for "developer failure," which means a costly maintenance call to replace the developer and service the machine.

There is a triboelectric series that has been generated by several investigators by rubbing dissimilar surfaces together and determining the charge exchange between them. The series is arranged to show that a material will acquire a positive charge from the material just below it in the series and a negative charge from the material just above it. The following short list is an example (22).

Air
Glass
Nylon, wool, and silk

- Aluminum
- Cellulose
- Cellulose acetate
- Polymethylmethacrylate
- Iron
- Polyester
- Polyurethane
- Polystyrene
- Polyethylene
- Polypropylene
- Polytetrafluoroethylene (Teflon®)

Many variables affect the charging properties of a triboelectric pair, including moisture, impurities, and surface irregularities. This may account for differences in the triboelectric series as reported by different sources (22). The list of polymer coatings is too long to include here but most of the carrier patents listed in the references for this chapter provide a short history of this technology and an extensive list of materials that have been used.

The majority of the carriers in production today are coated by one of two methods, which will be discussed next. Another minority group uses uncoated carrier or raw powder. Still another small percentage uses an oxidized iron carrier core material, and this type will also be briefly covered.

6.5.1 Solvent Coating

One of the most common methods of coating carrier employs a resin dissolved in a solvent or solvent blend. As an example, polymethylmethacrylate (PMMA) is commonly applied to carrier core materials from a solution in toluene.

There are several types of carrier coating equipment in use today to perform this operation; they range from the very simple to the highly sophisticated. One method uses a vibratory tub with a cover connected to a suction fan to pull the solvent vapors through a cooling unit that condenses and recovers the toluene. Carrier powders, or beads, are normally preheated before being charged to the unit. Some vibratory coaters are constructed with a steam heated jacket to elevate the carrier core temperature. After the powder is heated to a specific temperature, the solution of PMMA in toluene, generally containing 10 to 15 percent PMMA by weight, is added slowly by spraying onto the powder. The combination of heat and the vacuum created causes rapid solvent evaporation, leaving the dried polymer on the surface of the beads.

Most vibratory tubs have a curved bottom such that the constant vibration keeps the powder flowing in one direction and turning over on itself. Generally a stirring bar is required to break up agglomerates that form when the coating goes through a tacky phase. The resin solution is added until the precalculated coating weight is achieved. Agitation and heating are continued until the bed of powder starts to rise in temperature, indicating that the solvent is gone. The agitation continues until the temperature drops to a level for safe removal of the coated product.

A more sophisticated coater is a twin-cone (or twin-shell) vacuum drier equipped with a heated shell and metered solution input. This unit is connected to a vacuum pump, which pulls the vapors through a condenser for solvent recovery. Many varieties of this apparatus exist, some with feedback controls that vary the vacuum pumpdown and solution feed rates to control the temperature throughout the coating cycle.

With such a double-cone blender/drier, the bare powder is charged to the unit at ambient temperature and heated to the initiation temperature. At this point, addition of the resin solution begins and proceeds at a controlled rate. The rest of the process is similar to the vibratory tub cycle. Programmed twin-shell blenders generally provide a more consistent coating, but it is important to note that most carrier powders require only a partial coating, and different methods will yield different toner charging properties even at the same coat weight. Several other solvent coating devices are in use, but the principles are the same, and the results must be tuned to the ultimate application of the carrier in a specific imaging system.

6.5.2 Powder Coating

A second extensively utilized coating method is powder coating. Here, the resin coating is applied as a fine powder that is fused to the carrier bead by heat. Polyvinylidene fluoride (PVF) resin is often used in carrier coating applications. The particle size of the coating powder is less than 5 microns. PVF is added to the core at the desired coating weight and tumbled in a twin-shell or double-cone blender until it has coated the core either by adhesive or electrostatic forces. The material is then subjected to a temperature high enough to melt the polymer and spread it over the core surface.

This operation is generally performed in a rotary tube furnace so that the powder rolls over itself and progresses down the inclined tube. While the output is a coated carrier, it should be noted that the process parameters must be tuned to yield the desired toner charging results for the specific application. This type of coating is mainly used for irregular carrier powders and is effective in controlling resistivity and charging response.

6.5.3 Oxidation

Surface oxidation applies mainly to iron and steel powders, as the ferrites are already oxidized. The process forms a ferritelike oxide surface and raises the resistivity of the base material. Oxidation also prepares the carrier surface for coating, providing better adhesion just as most metal surfaces are primed for painting or coating.

One method of oxidation is described in the patent noted in Ref. 15. In this case the powder is fluidized in a cylindrical vessel. The fluidizing air is heated to a specific temperature for a controlled length of time and then cooled in a controlled atmosphere to produce the fine-grained type of surface oxide required. Often this process is controlled to give a specific color, because the various oxides of iron range from red to yellow to dark blue depending on the time and temperature of the treatment. Of course, the qualifying parameter is ultimately the resistivity of the powder. It may or may not be necessary to coat this product afterwards, depending upon the application.

The fluidized bed operation just described is a batch process. Many carrier makers prefer to use a continuous process, such as a rotary tube furnace, to oxidize their powder. This can be tricky, because the temperature required is generally just below one of the phase transition temperatures of iron oxide, a phase change that is exothermic. If exceeded, there can be a runaway reaction with localized melting. At best, this stops the process; at worst, it can cause damage to the furnace.

6.6 CARRIER PROPERTIES

6.6.1 Magnetic Properties and Testing

The magnetic characterization of carrier powders is important, as are the physical, chemical and electrical properties, in order to obtain a controlled product that will deliver consis-

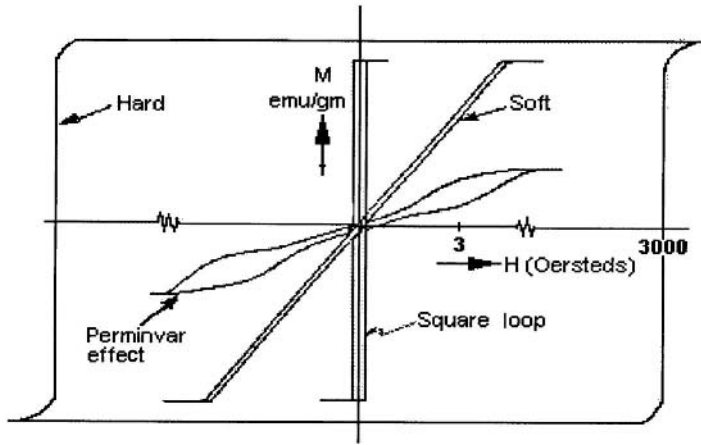


Figure 6.6 Generic hysteresis loops for hard and soft magnetic materials.

tent performance. Most developer manufacturers require two and sometimes three points on the direct current “hysteresis loop” curve to ensure that the carrier meets the specifications set for this product.

The hysteresis loop is plotted by a powder magnetometer that subjects the carrier beads to a slowly increasing magnetic field and measures the magnetization of the sample in that field. The magnetic field is increased to saturate the material and then reduced to zero and reversed to saturate the sample in the opposite sense; the field is then reduced to zero again. The sample magnetization curve is plotted as a function of the magnetic field applied, generating a hysteresis loop that characterizes the sample. Some stylized loops are illustrated in Fig. 6.6. Note especially the soft and hard type of magnetic materials that have been discussed.

Equipment for obtaining this data is illustrated in Fig. 6.7 and is called a “vibrating sample magnetometer” (VSM). This device was developed by S. Foner in the early 1960s and sold commercially since that time by Princeton Applied Research. The principle of operation is simply that the sample is vibrated in a vertical mode while the magnetic field of the electromagnet is applied orthogonally to that motion. Since the magnetization of the sample is the only parameter varying with time, it is picked up by the sensing coils, integrated electronically, and displayed as a function of the applied field.

The VSM is calibrated using 99.9999% pure nickel, which has a saturation moment of 55.01 emu per gram. This calibrates the y-axis for electromagnetic units (emu), and the sample value is divided by its weight, resulting in a traceable, precise, and accurate measurement. The voltage on the coils is

$$E = N \frac{d\Phi}{dt} \quad (1)$$

where N = the number of turns, Φ = the flux from the sample, and t = the time. Integration with respect to time gives

$$E(\Phi) = \frac{Et}{N} \quad (\text{V} \cdot \text{s}) \quad (2)$$

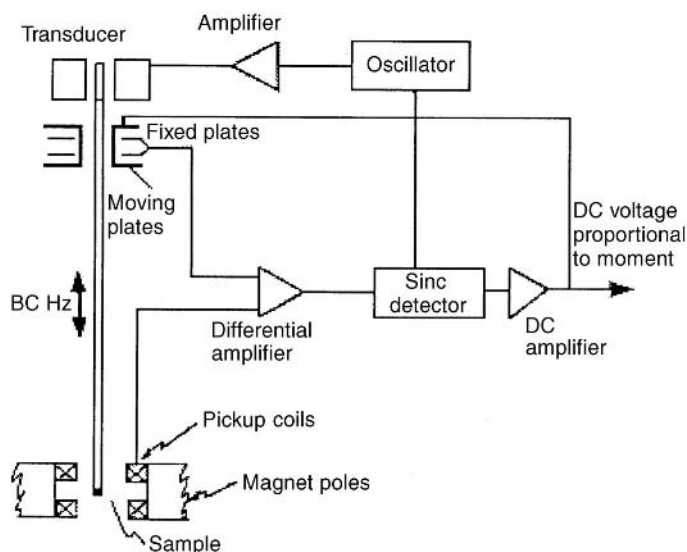


Figure 6.7 Vibrating sample magnetometer schematic.

but this output voltage is calibrated with the standard in emu so that the sample can be read directly in those units. A complete hysteresis loop can be displayed on an x-y plotter giving the type of curve shown in Fig. 6.6.

Recently a more compact and less expensive unit that performs the same task has been offered by Princeton Measurements Corporation (23). It is called an “alternating-gradient magnetometer” (AGM). In addition, there are single point instruments which measure either the saturation magnetization or the remanence magnetization or both. From the xerographer’s point of view these values are useful. The saturation moment, M_s , can be correlated to the stiffness of the brush in any given machine. The remanence moment, M_r , can be correlated to the flow of material in the sump during mixing. The coercive force, H_c , or the magnetic field required to reduce the remanence field to zero, is a measure of the difficulty in magnetizing the material or the “softness.” The higher the H_c , the harder the material magnetically.

6.6.2 Electrical Properties and Testing

Measuring the electrical properties of a powder is not a simple task, as the material is solid but behaves like a liquid. A myriad of methods have been developed to obtain a number representing the resistivity of these materials. Most xerographic engineers like to measure the powder in a cell that simulates the action of a magnetic brush. Many OEMs have constructed cells that resemble the schematic design in Fig. 6.8. It consists of a miniature magnet roll and power supply and is fitted with the appropriate meters. Some measure electrical properties with the brush moving while others form the brush and make the measurements after it has been stopped. Different voltages are used, and the calculations of resistivity all assume some brush cross-sectional area.

There several problems with this method. First, it is difficult to build two identical cells that would enable operators at different locations to obtain identical results. This is not the best situation for vendor–customer correlation.

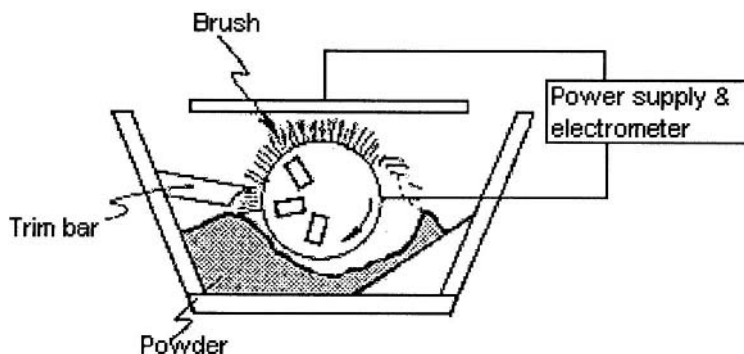


Figure 6.8 Generic dynamic cell.

Second, because there are no standards for powder resistivity, the parties involved must choose variations in the material, establish measurement standards, and negotiate an agreement on the correlation of their measured values. Unfortunately, there is no standard industry cell available; these devices are usually built by the parties engaged in the manufacture and use of the carrier powders.

Although there is no standard material for reference, a more precise resistivity measurement, one that *can* be correlated, is possible with a static cell such as the one illustrated in Fig. 6.9. This guarded electrode cell is normally used to determine the resistivity and dielectric properties of liquids; it is being used, however, to evaluate copier powders, requiring about 1 pound of material for the measurement. The cell is easily cleaned, and the micrometer adjustment gives accurate spacing.

The powder is assumed to be a liquid, and a voltage is applied across the sample while measuring current flow. The area of the inner electrode is used in the resistivity calculation. The measurement is repeatable, and correlation is good between different locations. This cell is an old standard in the industry and is available to everyone. Another

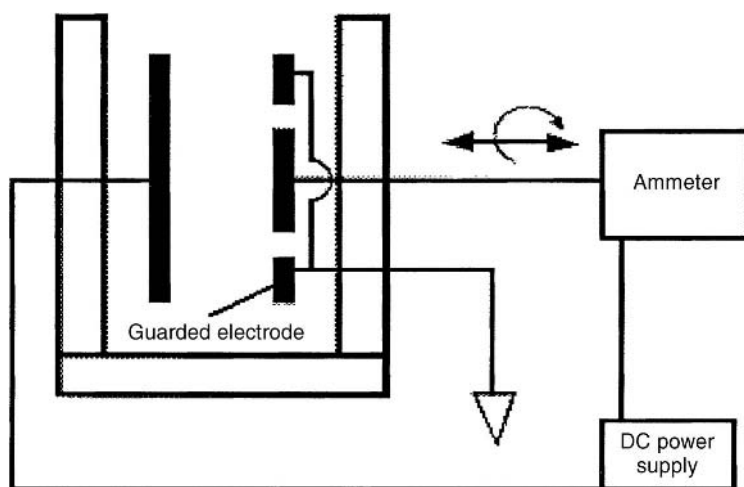
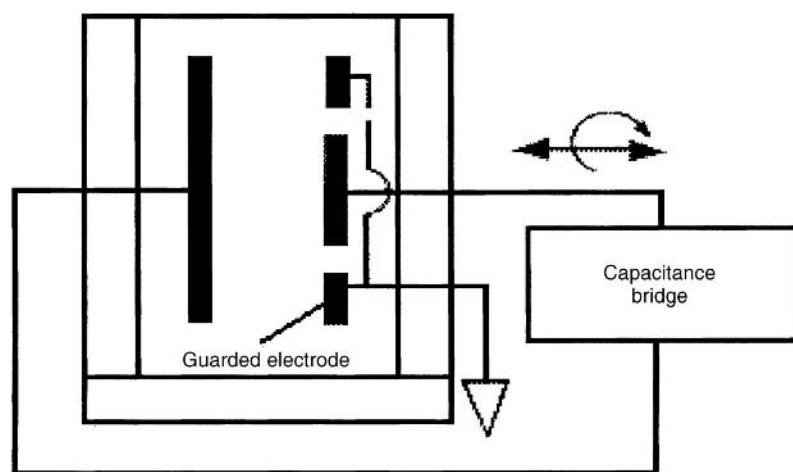


Figure 6.9 Static resistivity cell.



Determine -capacitance & dissipation factor
 Derive - K' & K'' complex permittivity
 -Loss tangent $\tan \delta = K''/K'$

Figure 6.10 Dielectric measurement.

way of applying this cell is actually to measure the dielectric constant and loss factor of the material, especially in the case of ferrites, as shown in Fig. 6.10. Metals are so high in dielectric constant and losses that it would apply to coated materials only. This is done with a capacitance-dissipation factor bridge. Several types are available, some featuring automatic balancing and digital readout.

6.6.3 Physical Properties and Testing

Several physical properties will be discussed in this section, and here is a list for reference:

- Sieve analysis and calculated specific surface area
- BET gas absorption surface area and roughness
- Bulk density and flow properties
- Triboelectric properties (toner charging)

Sieve analysis of carrier materials is generally performed according to ASTM B 214-66 (American Society for Testing and Materials). Often the parties involved agree to a modification of this standard to eliminate screens or use a different weight of sample. The equipment is a Ro-Tap sieve shaker with a timer. The screens used are U.S. Standard testing sieves covering the size distribution required. As an example, for a 90 micron material, the screen mesh sizes would be #120, 140, 170, 200, 230, 270, and 325 with a pan and cover. The Ro-Tap is started and timed for 15 minutes. Then the weight of material is recorded from each screen, and each is calculated as a percentage of the total weight of the sample. Even this procedure is sometimes difficult to correlate between two locations. Matching data to a master screen set by both parties and continual rotation of the screens as they wear are necessary practices to ensure good correlation.

The calculated surface area is just a calculation from the screen analysis that makes the assumption that all the particles are spheres and all particles on any given screen are

exactly the average diameter of the two screen meshes for that fraction. The individual bead density is used to calculate the surface area per gram that a toner particle could see or touch or with which it can exchange charge.

BET surface area is derived by a procedure which uses gas adsorption as a measure of the area that a krypton atom will find by detecting all the crevices, surface porosity, grain boundaries, etc. It is basically the surface that a solvent coating solution could contact. The most common equipment in use is the Quantasorb Surface Area Analyzer from Quanta Chrome Corp. In the unit, Kr is adsorbed on the surface when a Kr/He mixture is passed through the sample at liquid nitrogen temperature. The Kr is desorbed when the sample is removed from the liquid nitrogen, and the amount desorbed is proportional to the surface area of the sample. The amount of Kr is determined by comparison to a known amount of nitrogen that has been correlated to the signal from Kr gas. The BET value divided by the calculated surface area (CSA) results in a quality factor that relates to the coatability of the powder. As an example, a powder with a very high roughness factor requires much more coating weight than a lower roughness material to achieve the same triboelectric charging potential.

Bulk density and powder flow rate are both determined by the ASTM B-212(1) procedure, which establishes a standard funnel arrangement. The rate of flow is timed for a sample of known weight and reported in grams per second. The material from the funnel drops freely into a brass cylinder of known volume (50 cc). The overflow is scraped off and the remaining material is weighed. This weight (in grams) divided by 50 is the bulk density in grams per cubic centimeter. This value depends not only on the true density of each bead but also on the packing factor—a function of the shape of the size distribution. As an example, a very narrow size distribution will result in a lower packing factor and therefore a lower bulk density.

The triboelectric properties of a carrier are best described in terms of a standard toner. This may be the toner to be used in a particular machine that will use this developer, or it may be compared to other carriers by using a common toner for all. In this procedure, the toner is blended with the carrier in the desired ratio (e.g., 1% by weight of toner) in a clean dry container (generally glass) for a predetermined time (typically 30 minutes) on a roll mill.

A small sample of this mixed developer (1–2 grams) is then placed in a Faraday cage, a stainless steel cylinder fitted with appropriate screens at each end. The screen mesh is chosen so that the toner can pass through it, but the carrier cannot. The Faraday cage is clipped to a well insulated electrode that is connected to an electrometer. The toner is then blown out of the cage with dry air or nitrogen, taking its charge with it. The carrier is left with an equal and opposite charge, which is read on the electrometer.

Using the tare weight of the cage, the weight of the cage with developer, and the final weight of the cage, the weight of toner actually blown off is determined. The charge reading is divided by the weight of toner and the tribo results reported in microcoulombs per gram. This value is called the “total blow off tribo” of that developer at that toner concentration. Samples of developer taken from operating copiers are also tested to determine the tribo and toner concentration as a function of the age of the developer expressed in number of copies produced.

6.7 TYPICAL CARRIER PROPERTIES

Most of the carrier powders in current use have been discussed in this chapter. Those properties of special interest today and in the near future will likely center on the electrical

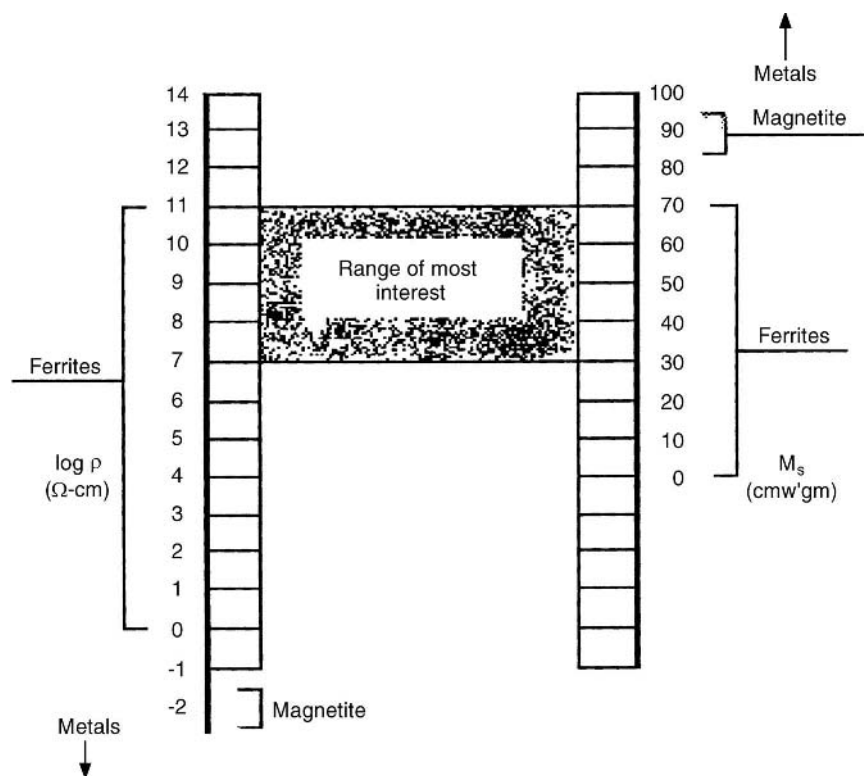


Figure 6.11 Current carrier property targets.

resistivity and magnetics of these unique materials. An illustration of this is shown graphically in Fig. 6.11. Here, two vertical axes represent the logarithm of resistivity, $\log \rho$, and the saturation magnetization, M_s , respectively. The scales are positioned so that the range of current interest matches on each scale. The resistivity is determined by the type of static cell illustrated in Fig. 6.9.

Note that ferrites and oxidized iron both fall nicely within the interest range for resistivity. Unoxidized iron and steel must be partially coated to have these effective resistivities, and they are in many cases successful. Ferrites also fall neatly into the interest range for magnetic properties, but iron powders must be very porous and irregular to bring the magnetization down to these levels. Developer housing design can compensate for these high magnetic moment materials, which are useful in many applications. Spheroidized magnetite has not gained much interest in the imaging industry, but partially reduced, irregular magnetite is gaining ground in Japan.

6.8 NEW PATENT AND LITERATURE ACTIVITY

Now, as mentioned in the first section of this chapter, the carrier activity of the last ten years should be discussed. This section will cover what is relevant in the carrier patent and publication field since the first edition of this book was published. The anticipated

demise of two-component developer systems and the carriers involved is still far in the future. Since 1990 over 230 U.S. patents have been issued which cover four basic categories pertaining to xerographic carrier manufacturing, processing, and end use. These are:

1. Carrier cores and carrier coating processes
2. Color-specific carrier applications
3. Scavengeless image-on-image (IOI) systems, mainly for color reproduction
4. Ferrite-specific based carriers

Note that only U.S. patents that have been issued since 1990 were surveyed for this update.

6.8.1 Carriers and Coating

Nearly 160 patents fall into this category, with most involving additives for improved flow or charge control or methods of mixing coating materials to stabilize charging toner characteristics, or new combinations of coating materials to improve performance. At least 20 assignees (companies) are included in this patent progress. Following is a table illustrating the important features of this progress.

Company	Number	Ref. No.	Comments
Canon KK	15	26	Ten of these describe properties and surface treatments of carriers
Eastman Kodak Co.	22	27	Most of these refer to hard ferrites (Ba or Sr), some mixed with soft ferrite. Five describe two- or three-phase ferrite composites. Coatings of silicone or PVDF are included
Fuji Xerox	21	28	Three of these are variations in ferrite composition. Seven involve coatings of fluoro resins, PVDF, vinyl, or acrylic polymers
Hitachi Metals Ltd.	11	29	Ten cover magnetic carriers of various magnetic and conductivity properties, high surface area for long life; and the most recent is a Li ferrite
Konica Corporation	13	30	Five discuss powder coating, some with fluoro resins, Si compounds, or polyolefin. Three relate to Mg surface atoms and negatively charging developer. Most concern ferrite carriers
Kyocera Corporation	4	31	All describe two-component developer
Matsushita Electric	1	32	Two-component developer properties
Minolta Camera KK	9	33	Three cover composite magnetic carriers, two involve 1.5 component developer (very small consumable carrier), one covers powder coating and two pertain to size
Mitsubishi KK	1	34	Carrier with vinylidene chloride coating and a charge control agent

Company	Number	Ref. No.	Comments
Mita Industrial Co., Ltd.	12	35	Seven cover various coatings, two involve resistivity and carrier relaxation time
Ricoh Co., Ltd.	10	36	Three refer to forming microfields, one covers size and charge, one covers a Si modified acrylic coating, one has a mixture of charge control agents, and one has 2 carriers with one cleaning the other
Tomoe-gawa Paper Co.	2	37	One covers a ferrite composition and one covers magnetic properties of carrier
Xerox Corporation	22	38	Five involve carrier conductivity, eight cover two-polymer coatings, four cover coating methods, one includes additives, and one refers to fly ash

6.8.2 Color Specific Carrier Patents

Company	Number	Ref. No.	Comments
Canon KK	4	39	All cover ferrite carrier, two for yellow toner, one for four colors, one with 2-resin mix coating
Eastman Kodak Co.	1	40	Refers to charge area or discharged area development
Kao Corporation	1	41	Fluoro resin for positive charge for color
Minolta Camera KK	2	42	One covers coating molecular weights and one involves cross-linked styrene acrylic copolymer and melamine resin
Xerox Corporation	4	43	One covers variations in percentage of bare core in developer, two describe preferred properties, and one has charge control and flow additives

6.8.3 Scavengeless Development

Company	Number	Ref. No.	Comments
Eastman Kodak Co.	2	44	One covers method and one involves spacing to keep the brush from touching the previous image developed
Hitachi Metals Ltd.	1	45	Controls the magnetic brush height to prevent touching
Xerox Corporation	33	46	All involve image-on-image development with various methods of supplying an intermediate step for the two-component developer to charge and transfer toner without touching the previous image developed

6.8.4 Ferrite Core Specific

Company	Number	Ref. No.	Comments
BASF	1	47	Ferrite or oxidized iron with controlled resistivity
Canon KK	4	48	Two refer to yellow toner, one involves 4-color development, and one coating of two resins
Eastman Kodak Co.	9	49	Three involve 2- or 3-phase ferrite compositions, one refers to a mix of hard and soft ferrite, one gives a method of producing a ferrite, one covers silicone resin coating, and one provides lower dusting
Fuji Xerox	3	50	All refer to ferrite compositions
Hitachi Metals Ltd.	1	51	Lithium ferrite composition
Konica Corporation	2	52	One refers to a ferrite composition and one covers coating by impacting powder
Minolta Camera KK	1	53	Refers to composite ferrite/polymer carrier
Mita Industrial Co., Ltd.	1	54	Coating ferrite with acrylates to specific electrical and magnetic properties
Powdertech Co., Ltd.	7	55	Three provides lithium ferrites, one offers a mixed hard and soft ferrite, one refers to a small iron carrier (25–40 microns), and one covers coating by microwave heating
Steward Manufacturing	1	56	Liquid phase sintering to make ferrite with no nickel, zinc, or copper
Xerox Corporation	2	57	One coating to specific resistivity and one refers to 2-polymer coating for tribo control

6.8.5 Literature Survey

Over 60 articles have been published on this subject during the 1990s. They can be divided among eight basic categories:

1. General theory
2. Contact charging
3. Two-component developer
4. Coating methods and materials
5. Conductivity (electrical)
6. Triboelectric properties
7. Adhesion
8. Future

No attempt has been made to elaborate on or judge the relative merits of these papers; they were chosen as they represent the most informed workers in this field. The reader interested in pursuing is referred to these references for more in-depth study.

General Theory

This group includes L. B. Schein's book on electrophotography (58) as well as his toner charging theory (59). Surface state models of tribocharging (60) and comparison to experi-

mental data for two-component developer (61) are presented by J. H. Anderson. Vereshchagin and Krivov offer an analysis of the behavior of material particles in an electric field (62), while Jeyadev and Stark (63) describe a transfer function for development to complete field neutralization.

Contact Charging

Castle and Schein (64) present a model for sphere–sphere insulator contact electrification. Impact charging of insulators is also the subject discussed by Masui and Murata (72). A. Diaz et al. discuss an ion transfer model for contact charging and the effects of ionomer ions or dissociated ions (65–67). L. H. Lee presents a dual mechanism for contact electrification by metal–polymer contact (68). Veregin et al. discuss the relation of Kelvin potential to charging (69) and effects of relative humidity on charging for metal oxides (70). Itakura et al. relate tribocharge to contact potential differences of the surfaces (71). J. Q. Feng et al. present arguments concerning electric field effects on nonuniformly charged spheres on dielectric surfaces (73). The contact charging of polymers and the penetration depth of the charge are presented by Watson and Zhao-Zhi (74).

Two-Component Developers

Anzai et al. offer some considerations on development efficiency for two component developers in a magnetic brush system (75). The correlation of low-charge toner to background development, mentioned previously in this chapter, was justified in a paper by Gutman and Hollenbaugh in 1997 (76). P. C. Julien related the relationship of size and charge in developers (77) and the effect of toner clouding from two-component developer in a magnetic brush system (78). Aging of two-component developers as related to toner concentration and how conductive developer aging affects the xerographic response are subjects of papers by R. J. Nash et al. (79,80). Nash et al. also have a paper describing toner charge instability (81), and Nash and Muller offer a paper about the effect of toner and carrier composition on tribocharge and toner concentration (82).

Coating Methods

In 1997 K. Adamiak published a numerical modeling scheme of tribocharging for powder coating systems (83). Muzumder et al. studied the influence of powder properties on the electrostatic coating process (84), and Stotzel et al. described adhesion measurements for this process (85).

Carrier Conductivity Considerations

E. Gutman and G. Hartmann presented in 1996 a study of the conductive properties of two-component developer materials (93). The effect of toner impaction on conductivity aging of a developer was reported in 1992 by R. Nash and J. Bickmore (94), and in 1996 Nash et al. describe how conductivity aging relates to xerographic response (95). N. Felici discusses interfacial effects and offers a criticism of the conduction model (96).

Triboelectric Properties

E. Gutman and G. Hartmann collaborated on two papers that discuss the triboelectric properties of two-component developers (86) and describe the role of an electric field in tribocharging two-component systems (87). P. Julien et al. (88) in 1993, Takezawa et al. (89) in 1997, and Nakamura et al. (90) in 1997 discuss the effect of particle size and size distribution on the charging of toners. K.Y. Law et al. offer a tribocharging mechanism

in a model toner (91), while Shijo et al. (92) report general charging characteristics in two-component developers. In 1997, Lee and Takahashi described the dependence of triboelectric charging on external additives in two-component developers (101).

Adhesion Properties

In 1994, J. C. Maher (97) offered a phenomenological model for describing toner adhesion to carrier and D. Hays (98) gave a general discussion of toner adhesion. In the same year, E. Eklund et al. also presented a paper (99) on toner adhesion physics and measurements of the contact area of toner to substrate surfaces, while M. Ott (100) described the effect of relative humidity on toner adhesion in the presence of surface additives.

6.9 FUTURE TRENDS

Indications are that the future will see carrier design moving further in the directions already implied in this chapter. More irregular powders will likely be seen, probably in smaller size distributions. Indeed, W. R. Hutcheson's study of trends in carrier particle size over the past 30 years, shown graphically in Figure 6.12 (104), supports this direction. The shift toward smaller carrier beads has several advantages: it offers more surface area for transporting toner, it generally results in longer developer life, and for a given toner concentration, the resulting developer mix is lower in resistivity as it offers more core-to-core contact. The latest machines incorporate designs that are better able to contain these fine materials in the developer housing. In addition, with finer carrier materials it is possible to raise the level of copy quality. From a statistical standpoint, more toned carrier surface is offered to the photoreceptor in the development zone.

The industry also continues to move to lower density powders (1) to minimize the torque required to transport the carrier material, (2) to reduce the weight of any individual machine developer charge, and (3) to form a softer brush in the development zone.

All carrier materials are purchased by the pound and used by the cubic inch. As an example, a small copier that might require 2.5 pounds of steel would only require 1.6 pounds of ferrite to achieve the same total carrier surface area for the toner.

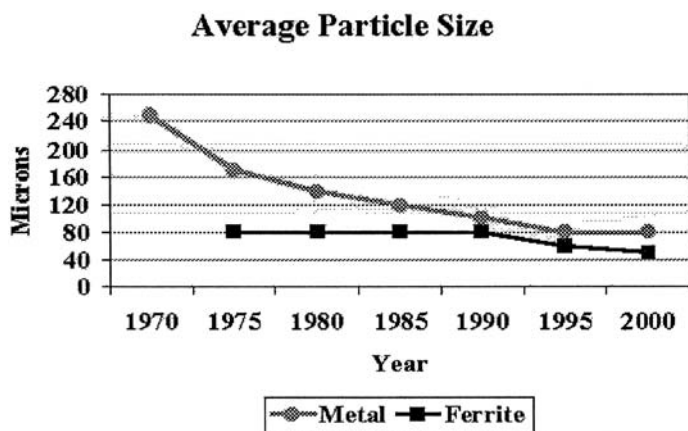


Figure 6.12 Trends in carrier size. (Courtesy of Powdertech Corporation.)

Greater interest is being shown in the various ferrites for most of the reasons given above as the manufacturers move to reduce cost by using less expensive raw materials and more efficient quality and process control. Fine particle ferrites are already in use or on the drawing board with 50, 30, 12, and 5 micron materials now in the field.

The aim has always been to emulate lithographic resolution, density uniformity, and zero background especially in the high volume printers and copiers. A continued increase is expected in color copier and printer applications as the generation of color originals expands from ink-jet, thermal, and toner-based printers. Emphasis will undoubtedly be placed on faster, lower cost color applications using two-component development. Of course, many other reproduction methods are increasing and will continue to increase in importance.

Trends in carrier consumption are illustrated in Table 6.3 for the U.S. imaging industry (in tons). Spherical ferrites exhibited the largest increase, about 8.5% compound annual growth rate (CAGR) over the past five years (1995–2000), with spherical carriers advancing at about 3.9% CAGR. The use of spherical steel powders in xerographic imaging systems has declined at an average annual rate of about 10%, while irregular iron and steel powders demonstrated about 6.0% CAGR. Spherical nickel and irregular sand and glass carriers have all but disappeared from use in U.S. office copiers and duplicators.

Liquid toner development has great capabilities but presents an environmental problem associated with the volatile organic compounds (VOCs) employed. Two-component developers in magnetic brush systems should hold steady for some time to come because the toner charge distribution required for optimum marking can be designed into the system. Monocomponent toner applications have problems in this charge distribution requirement as currently practiced, but the future holds the possibility of a corona charged fluidized bed recharge-expose-and-develop (REaD) as a very strong contender. Recent patent activity indicates research in this area at Xerox Corporation and Moore Business Forms (103).

L. B. Schein provides an excellent review of recent advances in this technology (102), giving the reader an expert's perspective on future trends. For more information about the xerographic process, the reader is referred to books by Schaffert (2) and Dessauer and Clark (24).

Table 6.3 Estimated U.S. Consumption of Carrier Materials (1985 to 2000) (Tons)

	1985 ^a	1990 ^a	1995 ^a	2000	CAGR, %
<i>Spherical Carriers</i>					
Steel	4,430	4,311	4,069	2,400	−10.0
Ferrite	3,415	5,838	8,546	12,850	+8.5
Magnetite	235	348	544	650	+3.6
Nickel	68	23	0	0	—
Subtotal	8,147	10,520	13,159	15,900	+3.9
<i>Irregular Carriers</i>					
Iron and steel	3,252	5,039	8,142	10,900	+6.0
Sand and glass	250	85	16	0	—
Subtotal	3,502	5,124	8,158	10,900	+6.0
TOTAL	11,648	15,644	21,317	26,800	+4.7

^a Source: Ref. 25, p. 582.

ACKNOWLEDGMENTS

I would like to express my appreciation to Arthur S. Diamond for many hours of information exchange and efforts in generating this and previous publications (25). Also, many thanks to Robert J. Hagenbach for his help in many ways along these same lines.

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7

Liquid Toner Materials

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7.1 INTRODUCTION

Liquid toners are charged, colored particles suspended in a nonconductive liquid, used to develop electrostatic images. Liquid toner based imaging systems incorporate features of electrostatic imaging similar to those of dry toner based systems. However, liquid toner particles are significantly smaller than dry toner particles. Because of their small particle size, ranging from 3 microns to submicron, liquid toners are capable of producing very-high-resolution toned images. This high-resolution capability, and the capability of liquid toners to produce pure, transparent color, has led to their use of liquid toners in high-quality color printing and related applications.

7.2 LIQUID TONER ELECTROGRAPHIC AND ELECTROPHOTOGRAPHIC PROCESSES

Liquid development of electrostatic images was first demonstrated independently by Metcalfe (1955) and by Mayer (1957). Since then a large number of liquid toner based electrostatic processes have been developed and turned into products. The electrographic and electrophotographic processes and their individual steps have been well described in several books, including those of Schaffert (1975), Williams (1984), and Schein (1988).

Self Fixing Processes

Printers, platemakers for short-run offset presses, radiographic systems, and copiers were all made exploiting this basic process, and a number of such systems are still commercially

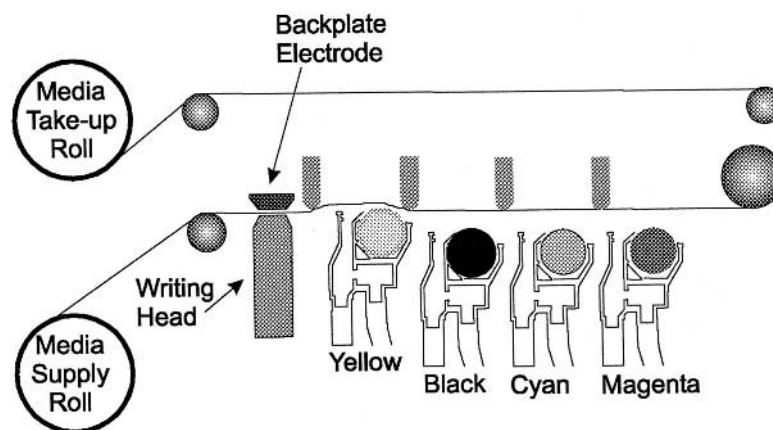


Figure 7.1 Electrographic process. A schematic diagram of the Xerox ColorgrafX Systems 8900 family of wide-format graphics printers. This system is exemplary of a product using the self fixing type of liquid toner process. An electrostatic image is applied to a dielectric medium, which may be paper or film, by means of metal styli addressed with high voltage.

important. These systems are called self fixing because they require no additional heat to fuse the image to its final receiver. For the most part they employ engineered substrates as both the latent image bearing member and as the image receiving substrate. The most common copier embodiment involves a ZnO dispersion coated paper which serves as both the photoreceptor and the final substrate. This substrate is corona (or similarly) charged, and the latent image is generated by standard reflective optics. Development could be quite crude with immersion in the liquid toner and (by today's standards) crude development electrodes. Air knives or rollers are generally used to remove excess toner, and the image is fixed by evaporation of the volatile liquid dispersant. This process is capable of generating quite high-resolution images, although the solid areas are often poor.

Another version of this process uses a conductive paper covered with a dielectric coating. The latent electrostatic image is generated by a direct writing stylus array. Figure 7.1 presents a schematic of the Xerox ColorgrafX Systems 8900 Digital Color Printer, a family of wide-format graphics printers that employ this variation. An electrostatic image corresponding to one separation of the CMYK image is written on the paper by the styli array. This image is developed by flooding the paper with the toner and metering the excess off with a counter-rotating development electrode. The developed image is then dried by passing it through an airstream. The paper is then rewound, and the other separations are produced in turn. Because of the image-on-image nature of this architecture, the toner is required not only to develop sufficient mass (per unit area) to give appropriate color but also to develop sufficiently close to charge neutrality that the preceding image will not be color shifted after passing through the next developer. Simplicity is the primary strength of this family of techniques. Applications where environmental constraints do not dominate and those where the properties (and cost) of an engineered substrate are not barriers will be most suitable for such processes.

Liquid Toner Transfer (LTT) Processes

The requirement for copiers to use plain paper led to the creation of the LTT process and its derivatives. Developed by Savin Corporation and a large number of collaborators

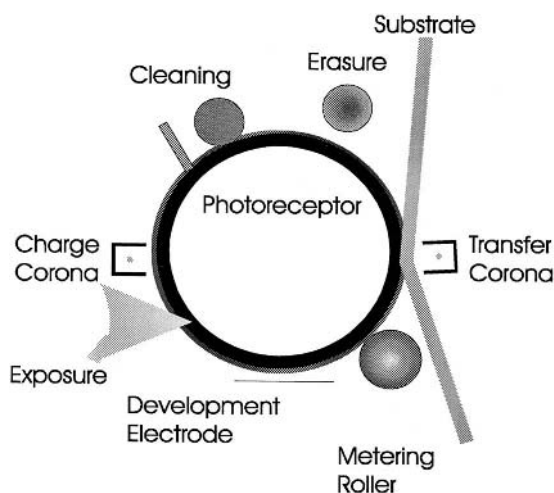


Figure 7.2 Electrophotographic process. A schematic diagram of the liquid toner transfer (LTT) process used in a number of Savin Corporation copiers.

(Jacobson and Hillkirk, 1986) this process enables liquid toner to mark uncoated papers. Figure 7.2 presents the schematic of such a system based on the Savin 870 copier. Conceptually centered around a photoreceptor, the process begins with corona charging followed by exposure, development, metering, transfer, erasure, and cleaning. The imaged paper is then fused by the application of heat (with or without pressure).

A variety of photoreceptors have been used for liquid toner based devices including ZnO, CdS, Se, As₂Se₃, and, most recently, organics. The combination of the optimum charging polarity of the photoreceptors with the ability to practice either charged area development (CAD) or discharged area development (DAD) allows the system designer to make the choice of toner charge sign on system level considerations (environmental issues, exposure source issues, etc.).

The latent electrostatic image is generated by photodischarge of the uniformly charged photoreceptor. In the copier embodiments this is accomplished with reflective scanning optics. However, in later printer embodiments like the AM Graphics Electropress®, diode arrays are also used. In principle, any analog or digital source whose wavelength and intensity are suitable for the particular photoreceptor and speed can be used.

In some embodiments (Riesenfeld et al., 1988; Tam et al., 1988) the photoreceptive element is permanently imaged to form areas of differential conductivity. Uniform electrostatic charging followed by differential discharge of the imaged element creates a latent electrostatic image. These elements are called electrographic or xeroprinting masters, as they can be repeatedly charged and developed after a single imaging exposure.

For development with liquid toners, the liquid developer is brought into direct contact with the electrostatic image. Usually a flowing liquid is employed, to ensure that sufficient toner particles are available for development. The field created by the electrostatic image causes the charged particles, suspended in a nonconductive liquid, to move by electrophoresis. The charge of the latent electrostatic image is thus partially neutralized by the oppositely charged particles. The theory and physics of electrophoretic development with liquid toners are well described by Schaffert (1975), Schein (1988), Chen (1988, 1995), and Chen et al. (1996a, b).

If a reimageable photoreceptor or an electrographic master is used, the toned image is transferred to paper (or other substrate). Most generally, the back side of the substrate to be imaged is charged by a corona, having a polarity opposite to that of the toner particles. This causes the developed image to transfer to the substrate.

Finally, the toned image is fixed to the paper. Heat is applied by the use of plates, rollers, or ovens, wholly analogous to a graphic arts drier. For heat-fusible toners, thermoplastic polymers are used as part of the particle. Heating both removes residual liquid and fixes the toner to the paper. Interaction of the carrier liquid with the toner resin allows the temperature at which fusing occurs to be relatively low compared to that required for dry toners.

Most emissions from the liquid dispersant generated by the process occur during fusing. Remediation techniques include simple venting, incineration, and recovery. The technique selected is application dependent and is responsive to the particular environment (industrial or office, for example).

Completing the cycle, the residual electrostatic charge is erased from the photoreceptor by either blanket exposure or the use of an AC corotron, and any residual toner is removed.

A limitation of the LTT process is its narrow substrate range. If the paper is smooth and the developed image is relatively thick, then the paper can actually cause material flow in a direction opposite to the process direction. This causes image smear, which can be alleviated by decreasing the thickness of the developed image. For smooth papers, this is an acceptable solution. When rough papers are used, however, the thin image does not contain enough toner to cover the paper irregularities, and low-density images are produced. A recent report discusses liquid toner image transfer and paper properties (Simms et al., 1992).

In an effort to address this limitation, Landa developed toners that contained a population of rigid particles such as microspheres, that are larger than the developed image thickness. The paper is uniformly gapped by these separate particles. Toner transfer was purported to occur by the formation of pseudopodia, which carry toner to the paper (Landa, 1983, 1984).

Landa later described a liquid toner called ElectroInk® (Landa, 1986; Landa et al., 1988) designed to give higher resolution and higher density images across a wider range of substrates than were achievable with previous toners. ElectroInk is designed to afford a rigid, cohesive mass upon development, a mass that resists the aforementioned deformation or squashing under pressure of transfer of relatively thick images. Landa's mechanistic model is based on a morphological structure in which particles have tentacles that interlock when brought together, forming the rigid mass. ElectroInk is used in the Indigo E-Print 1000, a digital offset color press. (Niv, 1994).

7.3 LIQUID TONER COMPOSITION

Liquid electrostatic toners are composed of a colloidal dispersion of pigmented or dyed resin particles suspended in an insulating liquid dispersant with added charge control agents that impart an electrostatic charge on the particles. This section describes typical materials that are useful for the preparation of liquid toners.

7.3.1 Dispersants

A liquid used as a toner dispersant must meet a number of demanding requirements. First, the liquid must be essentially nonconductive, to avoid discharging the latent electrostatic

Table 7.1 Isoparaffinic Hydrocarbons Used as Liquid Toner Dispersants

Material	Producer	Predominant carbon structure	Boiling range (°C)	Flash point (°C)
Isopar G	Exxon	C10–C11	155–176	40
Isopar H	Exxon	C11–C12	169–193	49
Isopar L	Exxon	C11–C13	185–206	60
Soltrol 100	Phillips Petroleum	C9–C11	157–173	41
Soltrol 130	Phillips Petroleum	C10–C13	176–208	56
Shell-Sol 71	Shell	C9–C12	179–202	52

Source: Mullin et al. (1990).

image. Resistivities of dispersants are typically greater than 10^{10} ohm cm. The liquid must be chemically inert with respect to other materials or equipment used in the electrographic or electrophotographic processes, including photoreceptors. Low-viscosity liquids are preferred, to allow rapid movement of the charged particles during development. The liquid must be volatile enough to allow its removal from the final imaged substrate, but volatility also should be low enough to minimize evaporation from the developer. Finally, the dispersant must be safe, in terms of physical properties, including those relating to flammability, toxicology, and human health. Moreover, the dispersant must be environmentally acceptable to manufacturers, regulators, government authorities, end-users, and the public at large.

A number of classes of organic liquids meet some or many of the requirements outlined. A variety of aliphatic and aromatic hydrocarbons, certain chlorofluorocarbons, and siloxanes have all been used. With increasingly demanding requirements for safety and environmental suitability, a class of aliphatic hydrocarbons, the isoparaffins, emerged as preferred materials. The isoparaffinic hydrocarbons are highly branched alkanes; those employed as dispersants have carbon skeletons ranging from C10 to C15. They are available from Exxon, Shell Oil, and Phillips Petroleum under the trade names Isopar®, Shell-Sol®, and Soltrol®, respectively. They are offered with various boiling ranges and volatilities (Table 7.1). The Isopars®, in particular, have enjoyed widespread use. Details of environmental aspects of liquid toners and isoparaffinic hydrocarbons are described in Section 7.7.

7.3.2 Resins

Liquid toner resins serve as the vehicle for the dispersed pigments or dyes, provide colloidal stability, and aid in fixing of the final image. The resin must also contain charging sites or be able to incorporate materials that have charging sites. Multifunctional resins that serve to impart a number of desired characteristics are often prepared specifically for use as liquid electrostatic toner resins (Santilli, 1977; Myers et al., 1987; Tavernier, 1988; Elmasry and Kidnie, 1990). Some commercially available resins that have been found effective are homopolymers such as polyethylene, polypropylene, polystyrene, polyesters, polyacrylates, polymethacrylates; ethylene vinylacetate copolymers (Elvax® resins, E. I. du Pont de Nemours, Wilmington, DE); ethylene acrylic acid or methacrylic acid copolymers (Nucrel® resins, E. I. du Pont de Nemours, Wilmington, DE; Primacor® resins, Dow Chemical Company, Midland, MI); ionomers of ethylene acrylic acid or methacrylic acid (Suryln® ionomer resin available from E. I. du Pont de Nemours, Wilmington, DE);

acrylic copolymers and terpolymers (Elvacite® resins, E. I. du Pont de Nemours, Wilmington, DE); styrene or vinyltoluene copolymers with butadiene or alkylacrylate (Pliotone® Resins, Goodyear Tire and Rubber Company, Akron, OH).

It has been recently reported that liquid toners were prepared as dispersions of colored pigments in hydrocarbon solvent using novel polymeric dispersants containing reactive functional groups such as thermally cross-linkable peroxy groups. The overprinted toner film layers could be thermally cross-linked at 140°C to improve mechanical durability (Rao et al., 1996).

7.3.3 Charge Control Agents (Charge Directors)

A charge control agent (CCA) is added to the toner to impart a charge to the toner particles. Ionic surfactants or metal soaps that form inverse micelles in the liquid dispersant are often used as charge control agents. Toner particles can obtain either positive or negative charge depending on the combination of particle material and charge control agent used.

Suitable charge control agents include alkylated aryl sulfonates, which can be obtained with excess calcium or barium carbonate, resulting in basic forms if desired. Typical examples are Basic Barium Petronate®, Neutral Barium Petronate®, Calcium Petronate® from Witco Inc., neutral barium dinonylnaphthalene sulfonate, basic barium dinonylnaphthalene sulfonate, neutral calcium dinonylnaphthalene sulfonate, basic calcium dinonylnaphthalene sulfonate from R. T. Vanderbilt Inc., and dodecylbenzenesulfonic acid sodium salt from Aldrich Inc. Another class of basic charge control agent is the polyisobutylene succinimides such as Chevron's Oloa® 1200 (El-Sayed and Taggi, 1987; Fowkes et al., 1990).

Soy lecithin, mixtures of soy lecithin with *N*-vinyl pyrrolidone polymers, and copolymers of lecithin with ethylenic comonomers have been noted to be particularly effective charge control agents for negative toners (Gibson, 1990; Gibson et al., 1992). Another class of charge control agents are the sodium salts of phosphated mono- and diglycerides with saturated and unsaturated acid substituents such as Witco's Emphos® D70-30-C and Emphos® F27-85. AB diblock copolymers of (1) polymers of 2-(*N,N*) dimethylaminoethylmethacrylate quaternized with methyl-*p*-toluene sulfonate and (2) poly-2-ethylhexylmethacrylate were shown to be excellent charge directors (Page and El-Sayed, 1990). They enable charge director properties to be customized by selecting the molecular weight selection (Chen et al., 1996a,b).

Divalent and trivalent metal carboxylates are excellent charge control agents for positive toners. Examples of these materials are aluminum tristearate, barium stearate, chromium stearate, magnesium octoate, calcium stearate, iron naphthenate, and zinc naphthenate (Croucher et al., 1984b).

7.3.4 Colorants

The pigment or dye used will depend largely on the color of the image required. However, other critical pigment characteristics are particle size, solvent and light fastness, dispersibility, and insolubility in the toner dispersant. The pigment often impacts a number of toner properties including particle charging, so the choice of pigment will also depend on the combination of toner resin and charge director used. Some suitable pigments are listed in Table 7.2. Sublimable dyes are effective colorants for processes involving the transfer of a colored design from a print on paper to a textile or film substrate.

Table 7.2 Typical Pigments for Liquid Electrostatic Toners

Pigment brand name	Registered trade mark	Manufacturer	Pigment Color Index
Permanent Yellow DHG		Hoechst	Yellow 12
Permanent Yellow GR		Hoechst	Yellow 13
Permanent Yellow G		Hoechst	Yellow 14
Permanent Yellow NCG-71		Hoechst	Yellow 16
Permanent Yellow GG		Hoechst	Yellow 17
Hansa Yellow RA		Hoechst	Yellow 73
Hansa Brilliant Yellow 5GX-02		Hoechst	Yellow 74
Dalmar Yellow YT-858-D	✓	Heubach	Yellow 74
Hansa Yellow X		Hoechst	Yellow 75
Novoperm Yellow HR	✓	Hoechst	Yellow 83
Chromophtal Yellow 3G	✓	Ciba-Geigy	Yellow 93
Chromophtal Yellow GR	✓	Ciba-Geigy	Yellow 95
Novoperm Yellow FGL	✓	Hoechst	Yellow 97
Hansa Brilliant Yellow 10GX		Hoechst	Yellow 98
Lumogen Light Yellow	✓	BASF	Yellow 110
Permanent Yellow G3R-01		Hoechst	Yellow 114
Chromophtal Yellow 8G	✓	Ciba-Geigy	Yellow 128
Irgazin Yellow 5GT	✓	Ciba-Geigy	Yellow 129
Hostaperm Yellow H4G	✓	Hoechst	Yellow 151
Hostaperm Yellow H3G	✓	Hoechst	Yellow 154
L74-1357 Yellow		Sun Chemicals	
L75-1331 Yellow		Sun Chemicals	
L75-2377 Yellow		Sun Chemicals	
Hostaperm Orange GR	✓	Hoechst	Orange 43
Paliogen Orange	✓	BASF	Orange 51
Irgalite Rubine 4BL	✓	Ciba-Geigy	Red 57:1
Quindo Magenta	✓	Mobay	Red 122
Indofast Brilliant Scarlet	✓	Mobay	Red 123
Hostaperm Scarlet GO	✓	Hoechst	Red 168
Permanent Rubine F6B		Hoechst	Red 184
Monastral Magenta	✓	Ciba-Geigy	Red 202
Monastral Scarlet	✓	Ciba-Geigy	Red 207
Hehogen Blue D 7072 DD	✓	BASF	Prussian Blue 15:3
Hehogen Blue L 6901F	✓	BASF	Blue 15:2
Hehogen Blue NBD 7010	✓	BASF	
Hehogen Blue K 7090	✓	BASF	Blue 15:3
Hehogen Blue L 7101F	✓	BASF	Blue 15:4
Heucophthal Blue G XBT 583D		Heubach	
Pahogen Blue L 6470	✓	BASF	Blue 60
Hehogen Green K 8683	✓	BASF	Green 7
Hehogen Green L 9140	✓	BASF	Green 36
Eupolen Blue 70-8001	✓	BASF	Prussian Blue 15:3
Monastral Violet R	✓	Ciba-Geigy	Violet 19
Monastral Red B	✓	Ciba-Geigy	Violet 19
Quindo Red R6700	✓	Mobay	
Quindo Red R6713	✓	Mobay	
Indofast Violet	✓		Violet 23
Monastral Violet Maroon B	✓	Ciba-Geigy	Violet 42
Sterling NS Black	✓	Cabot	Black 7
Sterling NSX 76	✓	Cabot	
Tipure R-101	✓	Du Pont	
Mogul L Carbon Black	✓	Cabot	
BK 8200 Black Toner		Paul Uhlich	

7.4 LIQUID TONER PREPARATION

Liquid toners are dispersions of pigments in a resin binder. Because paints and inks are also based on pigment dispersions, it is not surprising that the traditional production equipment used in the manufacture of liquid toners emerged from the paint and ink industries. Batch milling processes are used predominately with equipment such as steel and pebble mills. Milling of pigment with resin and liquid dispersant is typically carried out until a dispersion of a specific particle size has been achieved. Steel mills provide a finer grind (which may or may not be desirable) but also introduce metal contamination, thus requiring the use of a magnetic filter. High shear equipment, such as colloid mills and attritors, are used when the materials comprising the liquid toner formulation are not readily compatible and difficult to disperse. Toners are typically produced in concentrated form and subsequently diluted with additional liquid dispersant to afford a solids concentration of ~ 0.1 to 2% by weight for use in imaging devices. Charge control agents are typically added after completion of milling.

An alternate approach to the preparation of liquid toner particles was developed at Xerox Research Centre of Canada (Croucher, 1987; Croucher et al., 1984a, 1985, 1988; Duff et al., 1987). Particles are made by nonaqueous dispersion polymerization in the hydrocarbon solvent and subsequently colored with pigments or dyes. The attraction of this approach is that particles can be made with well-controlled particle size and size distributions.

To carry out the nonaqueous dispersion polymerization method, a monomer, which is soluble in the hydrocarbon medium, is polymerized in the presence of an amphipathic polymer (a polymer that has two distinct ends, one essentially insoluble in the hydrocarbon medium, the other soluble). When the polymerization has generated a certain chain length, the polymer precipitates from solution, and a core particle is formed. The amphipathic copolymer is adsorbed onto this nucleus, which then grows as a discrete particle. Coloring of the particle can be accomplished by ball-milling pigments into the particles. Alternatively, the particles can be colored by dyeing. Charge control agents may then be added as required.

7.5 MEASUREMENT OF LIQUID TONER CRITICAL PROPERTIES

The characterization of a liquid toner requires the measurement of a number of toner physical properties and image quality testing in an electrostatic imaging device (Novotny, 1981; Schein, 1988). Toner particle size is critical, as it in part determines the ultimate resolution capability of the toner. This capability may or may not be realized in the imaging hardware. Sufficient toner particle charge and electrophoretic mobility are required for development of the latent electrostatic image and if required the electrostatic transfer of the developed image to the final substrate. Other critical properties include but are not limited to conductivity, colloidal stability, viscosity, morphology, surface tension and wetting characteristics, fusing or fixing characteristics, and color and transparency.

7.5.1 Particle Size

No perfect system for sizing liquid toners has yet been demonstrated. Each of the techniques used for the sizing of particles has been applied to liquid toners, and each has its set of advantages. Each, however, also needs to be interpreted in light of the differences between the native state of the liquid toner and the conditions under which the analysis

is performed. In most cases, several techniques are used in a complementary fashion to ensure that a comprehensive picture of the effective size distribution is to be obtained.

A general question that arises in the interpretation of all particle size data concerns choosing the moment of the distribution that is most highly correlated with the functional property of interest. Care must be taken in proper selection of the moments and in investigation of the algorithms used to generate them. It is common in some techniques to make assumptions about the nature of the distribution (e.g., it is monomodal and Gaussian) that do not accurately reflect the sample.

Particle shape can also be an important consideration. In techniques that do not reveal the actual shape of the particles, the equivalent spherical radii that tend to be reported may not correspond to any physical dimension of the particle in question. One of the other common shape-induced pitfalls concerns particles with aspect ratios much different from one. In these cases, care must be taken to understand the effects of the technique selected on the orientation of the particles, and what effect that orientation may have on the analysis. This is demonstrated by the comparison in which a single toner dispersion was measured with three instruments. The results are given in Table 7.3.

Microscopy

Direct measurement of particle size can be obtained by microscopy, but several factors must be weighed in the interpretation of such data. Many liquid toners are of submicron diameter, and ordinary light-microscopic techniques are not applicable for the study of the fundamental particles. Often even liquid toners that have submicron fundamental particles, however, have aggregate structures that are important in their performance that are well within the reach of light microscopy. Liquid toners are also quite optically dense, so often the use of either dilute toner or a thin sample is necessary to obtain sufficient light transmission for analysis. Dilution can alter the charge distribution within the toner, either by changing the charging equilibrium or by effectively changing the “ionic strength” of the medium, thus altering the aggregate stability.

Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used for liquid toner size distribution and morphology determination. Sample preparation artifacts and contrast ratio concerns are important in the interpretation of the results. For SEM, the largest complication is effects induced by removing the carrier liquid. Since many liquid toner resins interact with the carrier liquid, removal of that liquid may be expected to change the size and structure of the particle.

Table 7.3 Particle Size Determination: Comparison of Measurements on a Single Toner by Three Instruments^a

Number	Area	Volume
<i>Brinkman Particle Size Analyzer (median μm)</i>		
1.95 (0.05)	7.00 (0.10)	7.33 (0.40)
<i>Horiba Capa 700 (median μm)</i>		
0.52 (0.07)	2.22 (0.26)	3.15 (0.32)
<i>Malvern Particle Sizer 3600E (median μm—volume)</i>		
10% less than	50% less than	90% less than
3.2 (0.1)	6.7 (0.1)	13.0 (0.7)

^a Standard deviations in parentheses.

In TEM both vacuum and contrast pose problems. The contrast problems can be addressed by the use of contrast agents including many of the heavy metal salts used commonly as liquid toner charge directors.

Light Scattering

These techniques offer many advantages for particle sizing. There is typically little sample preparation required, and the devices are reasonably automated, leading to short analysis times. Most, however, require that the sample be optically dilute to avoid multiple scattering.

There are two types of optical scattering instruments: Fraunhofer diffraction devices and autocorrelation devices. These instruments are used for both dry and wet particle size analysis of powders, suspensions, emulsions, and sprays. The attainment of appropriate resolution and reproducibility is dependent on suitable sample handling. Again, sample preparation is key, and the best results are only achieved when the sample is suitably dispersed before the analysis.

Representative of the commercial equipment is the Coulter® LS Series (Beckman Coulter Corporation, Miami, FL). The LS devices use both Fraunhofer and Mie theories to deduce the particle size distribution from the spatial scattering distribution. The LS 230 uses multiwavelength analysis to give a range from 0.04 μm in a single scan using 116 size channels. The Malvern Particle Sizer 3600E (Malvern Instruments Ltd, Malvern, Worcestershire, UK) uses the principle of laser diffraction to assign particle size. Laser light is scattered and detected over all scattering angles. Large particles scatter light at small angles and small particles scatter light at large angles.

Dynamic light scattering, also called quasi-elastic light scattering or photon-correlation spectroscopy, is applicable to particles suspended in a liquid, which are translating due to Brownian motion (i.e., particles generally of 2–3 μm diameter and smaller). The speed of the translation is inversely proportional to the particle size, and the velocity distribution can be deduced by analyzing the time dependence of the light intensity fluctuations (measurement of the autocorrelation function). Accuracy and information about particle shape and polydispersity of the particle size distribution can be obtained by making scattering measurements at several angles as most commercial instruments do. Some commercial instruments are capable of sizing particle ranges from 0.003 to 3 μm in diameter. The small end of this range is determined by measurement wavelength, incident power, and sample concentration; the high end by gravitational stability.

Representative commercial instruments are the Coulter Nano-Sizer® N4 and N4 Plus. These systems detect particles within the range of 3 μm down to 40 nm analyzing the autocorrelation function by the method of cumulants for determination of polydispersity of an assumed unimodal distribution.

Sedimentation

Based on the Stokes–Einstein equation, the size distribution of a particulate sample can be deduced by the settling velocity (Allen, 1974). The oldest of such techniques uses settling tubes in which the particle suspension was allowed to stand. While this process only worked well for particles relatively large with respect to most liquid toners, it has the advantage of being useful even in quite concentrated suspensions as long as proper account is made for viscosity. A variety of light sources have been employed including x-rays. Modern instruments employ automated observation and data analysis techniques to improve accuracy and productivity.

Representative devices include the Micrometrics SediGraph 5100 Particle Size Analysis System. This instrument is designed for completely automatic operation and employs a moving, temperature-controlled cell and a fixed-position x-ray source/detector. Most commonly used for inorganic powders, the device has a typical range of 300 to 0.1 μm .

Using a centrifuge to increase the settling rate allows faster analysis times and a broader analysis range, especially when the centrifuge is used to change speed during the analysis. Representative equipment of this type includes the Horiba Capa 500–700 (Horiba Instruments Inc., Irving, CA). In this method, the Stokes sedimentation equation is combined with the proportional relationship between absorbency and particle concentration (Bohren and Huffman, 1983).

Volume Determination

Electrical volume determination is another technique that has been developed to determine particle size. The prototype instrument of this class is the Coulter counter (Coulter Corporation, Miami, FL). The Coulter method of sizing and counting particles is based on the changes in electrical resistance produced by nonconductive particles suspended in an electrolyte as they are pumped through a calibrated aperture between electrodes. As particles displace the supporting electrolyte, a voltage pulse is recorded whose height is proportional to the volume of the particle. The manufacturer quotes the measurement range as 0.4–1200 μm .

Particle size can also be determined by optical volume measurement. An example of this type of device is the Brinkman Particle Size Analyzer (Brinkman Instruments, Inc., Westbury, NY). This instrument utilizes a laser based time of transition analysis system that presents statistical information including particle size, area and volume distribution, and sample concentrations. Time of transmission analysis determines particle diameter by sensing the time required for the particle to pass through the laser beam path.

In conclusion, care is necessary in comparing the absolute particle sizes of liquid toners assigned by different instruments. However, a good correlation between particle sizes determined over a broad range by two instruments that utilize very different techniques has been demonstrated. The median particle size of 67 toners was measured with the Horiba and Malvern instruments described above with the correlation shown in Table 7.4. The expected range of Horiba values (median by area) was determined using linear regression at a confidence level of 95% (Trout and Larson, 1988).

Table 7.4 Correlation Between Malvern 3600 E and Horiba Capa 500 Particle Size Instruments

Median particle size (μm) determined by Malvern 3600E Particle Sizer	Expected median particle size (μm) range for Horiba Capa-500
30	9.9 ± 3.4
20	6.4 ± 1.9
15	4.6 ± 1.3
10	2.8 ± 0.8
5	1.0 ± 0.5
3	0.2 ± 0.6

7.5.2 Toner Particle Charge and Electrophoretic Mobility Measurement

Charging of liquid toners is often studied by calculating toner charge-to-mass ratio (Q/M) from the DC current that flows as toner mass deposits onto an electrode in the presence of an applied electric field (Dahlquist and Brodie, 1969; Novotny and Hair, 1979). These measurements are frequently complicated by electrical noise and interference from conductive ingredients in the toner. Electrophoretic mobility measurements provide similar charging information (Schaffert, 1975):

$$\text{Particle mobility} = \frac{6\pi(\text{Particle radius})(\text{Fluid viscosity})}{\text{Particle charge}} \quad (1)$$

Direct measurement of a toner velocity distribution can be made with laser Doppler electrophoresis (LDE). Knowledge of the velocity distribution, electric field, and particle size allows calculation of the zeta potential distribution. These relationships are well known for polar liquids and especially cases where the interparticle separation is larger than the Debye length. However, they have only recently appeared for cases germane to liquid toner (Chen et al., 1996a,b). At the fields and conductivities characteristic of liquid toners, hydrodynamic instabilities can disrupt measurement of mobility (Rhodes et al., 1989), so care must be taken to collect data from within the stationary layer of the electrophoretic cell.

Two commercial instruments are available from Beckman Coulter and Malvern. The Coulter Delsa 440SX uses LDE measured simultaneously at four angles. This zeta potential instrument can determine the relative sizes of particles at different mobilities. The Coulter Delsa contains four 256-channel autocorrelators to discriminate between particles from four optimized angles and detect very small mobility or zeta potential differences. The manufacturer says that this results in an increased accuracy that cannot be achieved by repeating single-angle analyses. The instrument is sensitive over a wide range of particle sizes, from 10 nm to greater than 30 μm .

The Malvern Zetasizer 3 (Malvern Instruments Ltd, Malvern, Worcestershire, UK) uses a patented cell design for measurements in low dielectric dispersants. Intersecting laser beams create an interference pattern at the stationary layer in a flat cell. The beams enter the cell through a transparent electrode. A brief DC electric field (continuously variable up to 0.4 V/ μm) is applied to the cell. Toner particles move through the interference pattern, and the resulting scattered light is collected by a photomultiplier. The mobility of the particles is calculated from the Doppler shift in the frequency spectrum. This is checked by reversing the polarity on the electrodes, sampling the scattered light, and recalculating the mobility (McNeil-Watson and Pedro, 1987; Degiorgio, 1982).

In the past few years, mobility measurements have been developed based on the Debye colloid potential that can measure the zeta potential of particles in concentrated dispersions (Oja et al., 1985; Niv et al., 1986; McNeil-Watson and Pedro, 1987; Larson, 1993). Representative commercial equipment includes the Matec Electrokinetic Sonic Analysis (ESA) (Matec Instruments, Inc., Hopkinton, MA). The ESA applies an oscillating electric field to the sample and measures the sound wave produced by the motion of the double layers around the particles (Oja et al., 1985). The ESA measurement is directly proportional to the AC electrophoretic mobility of the particles and represents the inverse of the Debye colloid potential. The measurement is effective at low fields and has been found useful in diverse systems (Isaacs et al., 1990). Mobilities determined by the Matec

ESA have been demonstrated to correlate with the image quality obtained in an electrostatic imaging device (Larson et al., 1989; Felder et al., 1990).

Direct measurement of the Debye colloid potential can be accomplished by the Pen Kem System 7000 (University of Maine, Orono, ME). This device applies an ultrasonic disturbance to a colloidal sample and measures the electric field produced.

A comparison of mobilities for a series of toners obtained with the Malvern Zetasizer and Matec ESA instruments is shown in Fig. 7.3 (Felder et al., 1990). Similar studies have been reported more recently (Caruthers et al., 1994).

The Indigo Mobility Analyzer (Indigo Ltd, Rehovot, Israel) also measures particle density. This instrument uses a DC field applied across parallel plates to cause toner particles in suspension between the plates to move to one of the electrodes. As the particles deposit onto the electrode, light transmission through the cell increases. The rate of increase of light transmission is related to mobility. This method is useful for determining electrophoretic mobilities at high fields up to $2.0 \text{ V}/\mu\text{m}$ (Niv et al., 1986).

Staples and Koop (1991) describe a technique by which the toner charge and mass are measured simultaneously in a deposition cell. Electrical field flow fractionation is an analytical method based on the differential migration of particles in a flowing stream

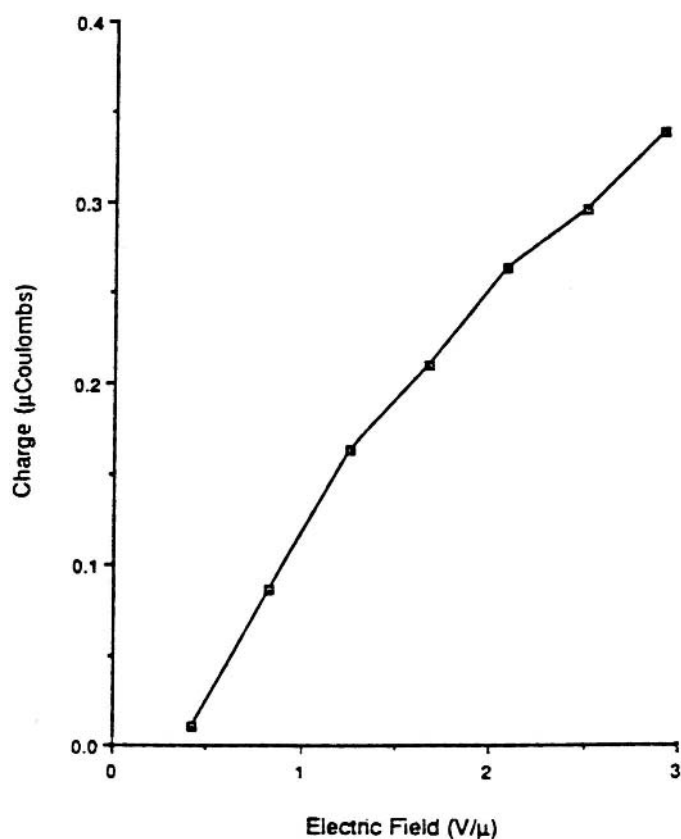


Figure 7.3 Matec ESA vs. Malvern Zetasizer 3 mobility. Correlation coefficient $R^2 = 0.89$. (From Felder et al., 1990.)

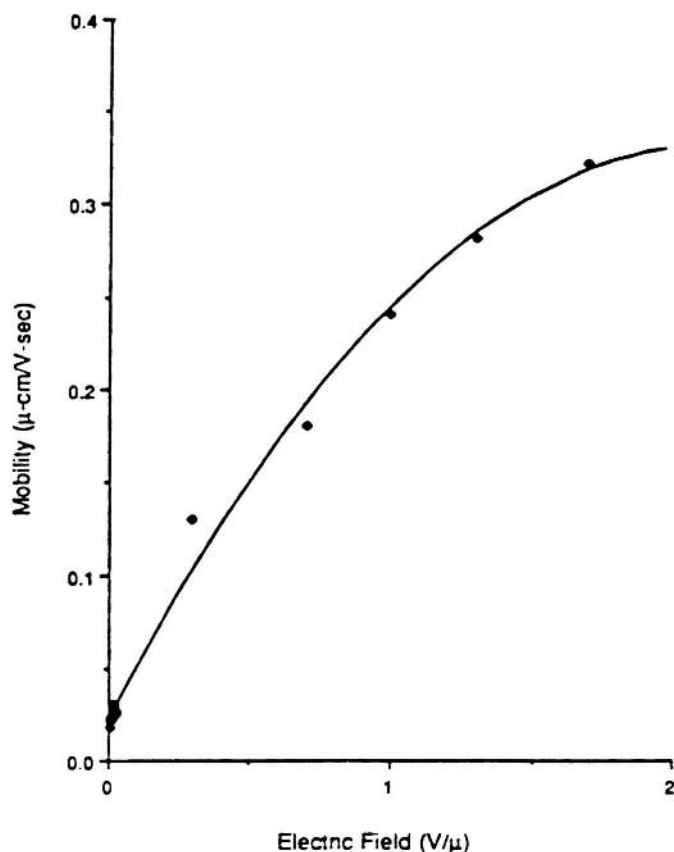


Figure 7.4 Toner charge vs. electric field. Toner charge was calculated from the charge-to-mass ratio, which was determined by placing the toner between two electrodes with a 1 mm separation and applying an electric field until all of the toner was developed. (From Felder et al., 1990.)

that passes through an externally applied electric field. It was reported to be attractive in determining the properties of charged particles in a nonpolar medium. This off-line method has similarities to liquid toner development processes in that charged particles, dispersed in a nonpolar fluid, are passed through an electric field orthogonal to the fluid flow (Russell, 1993).

Characterizing a toner by electrophoretic mobility measurements over a range of electric fields is useful, because as the electric field strength increases, the ionization process required for toner particle charging becomes increasingly favorable. This leads to increased charge on the toner particle and hence increased toner particle mobility (Stotz, 1978; Niv et al., 1986; Felder et al., 1990). This effect is demonstrated in Figs. 7.4 and 7.5. The charge on the toner particles is also impacted by the polarity of the liquid dispersant (Mitchell, 1987).

7.5.3 Conductivity

The deposition behavior of liquid toners makes it difficult to measure the conductivity of such systems. In general, to be effective, liquid toners must have AC conductivities as

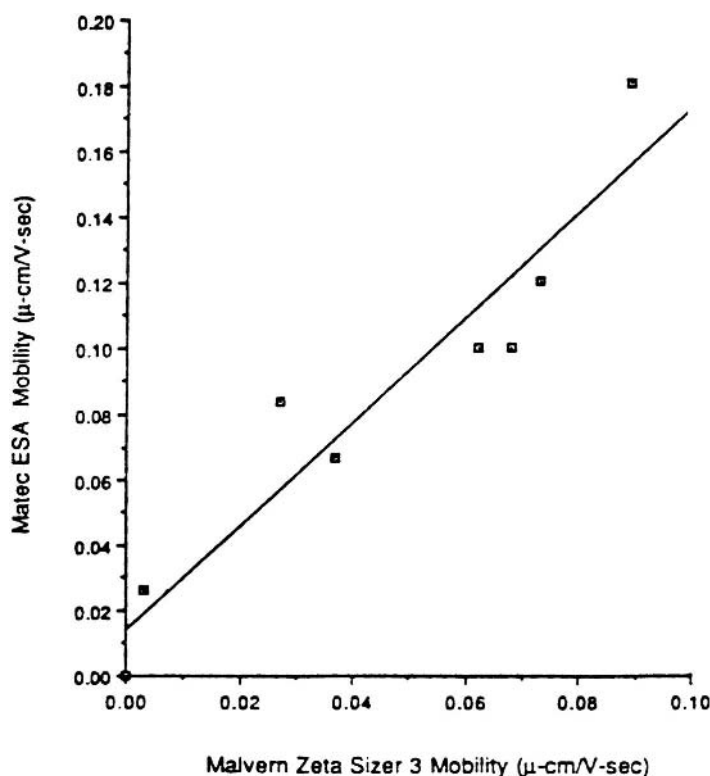


Figure 7.5 Toner particle mobility vs. electric field. Low field values were obtained with the Malvern Zeta Sizer 3, and high field values were obtained with the Indigo Mobility Analyzer. (From Felder et al., 1990.)

much as three orders of magnitude below the sensitivity of most commercial equipment. The device most commonly used for conductivity studies is the Scientifica Model 623 (Scientifica, Princeton, New Jersey) conductivity meter. It is available in both dip and flow-through probe configurations.

7.5.4 Rheology

The rheological behavior of liquid toners varies greatly. While most liquid toners display Newtonian behavior in working developers, there is sometimes a dramatic departure from ideality at concentrations characteristic of developed images. This rheological behavior is shown, in some instances, to map on imaging performance (Gibson et al., 1992). A great variety of commercial instruments exists for viscosity measurement and care must be taken in instrument selection. Measurement geometry and shear rate employed in the measurement should closely correspond to that which the liquid toner experiences in use. Representative commercial equipment includes the SR-2000 and SR-5000 controlled stress rheometers (Rheometric Scientific, Inc. Piscataway, NJ).

7.5.5 Color and Color Strength

The color of a liquid toner can be measured in a number of ways. Most commonly a dried toner film is measured with one of the wide variety of commercially available instruments.

Care must be taken in such measurements to account for the mass per unit area of the toner film and of the optical properties of the substrate upon which the film is deposited. Three types of instruments are generally distinguished: densitometers, colorimeters, and spectrophotometers.

Densitometers measure the transmission or reflection density of a sample viewed through a filter. Differences in filter sets and aperture distinguish among instruments and the various standards. Representative of this type of equipment is the Macbeth 1200 Series densitometers (Macbeth Division of Kollmorgen Instruments Corporation, New Windsor, NY). Such instrumentation is generally rugged and is designed to be used in production environments and for routine quality control.

Colorimeters are typically more sophisticated than densitometers, often acquiring a full reflectance or transmission spectrum of the sample under observation. This data is analyzed and color is reported in one of the common color spaces (L^* , a^* , b^* for example).

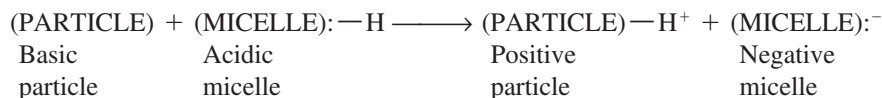
Spectrophotometers like the UltraScan XE, LabScan II, and ColorQUEST from HunterLab (Hunter Associates Laboratory, Reston, VA) offer greater flexibility when measuring a sample's color or color difference as it would appear under different lighting conditions. Flexibility within illuminant, sample form, and data reduction characterize these instruments. While the most flexible and sophisticated of these instruments are best suited to a laboratory environment, several companies offer microspectrophotometers, which combine some of the robustness of the densitometers with some of the sophistication of the spectrophotometers.

7.6 LIQUID TONER CHARGING

Particles dispersed in a hydrocarbon or other nonconductive liquid become charged by the addition of an ionic surfactant (charge control agent or charge director), which forms inverse micelles in low dielectric media. The spontaneous separation of charge between the particle and micelle phases can be accounted for by a number of mechanisms including (1) differences of electron affinity of the micelle and particle; (2) physical trapping of nonmobile charge in one phase; (3) difference of cation or anion affinity of the particle and micelle; and (4) surface group ionization (Hunter, 1981). Although these mechanisms may play a role alone or in combination, mechanisms 3 and 4 are probably predominant. Toner charging can often be accounted for by the acid–base or donor–acceptor properties of the toner materials.

Acid–base chemistry between the particles and the ionic surfactant micelles is believed to result in charging of the particles. According to this model, the formation of a negatively charged particle is enhanced by proton or cation exchange from the particles to the micelles, and formation of positively charged particles is enhanced by proton or cation exchange from the micelles to the particles (Fowkes et al., 1984; Croucher et al., 1984b). This process results in the formation of a diffuse double layer with zeta potentials of over 100 mV in cases of strong acid–base interactions (Ross and Morrison, 1988). A model for liquid toner particle charging and charge director ionization based on a series of reversible equilibria has been proposed and shown to compare well against a limited set of experimental data (Larson et al., 1995).

7.6.1 Acid–Base Chemistry and Positive Particle Charging



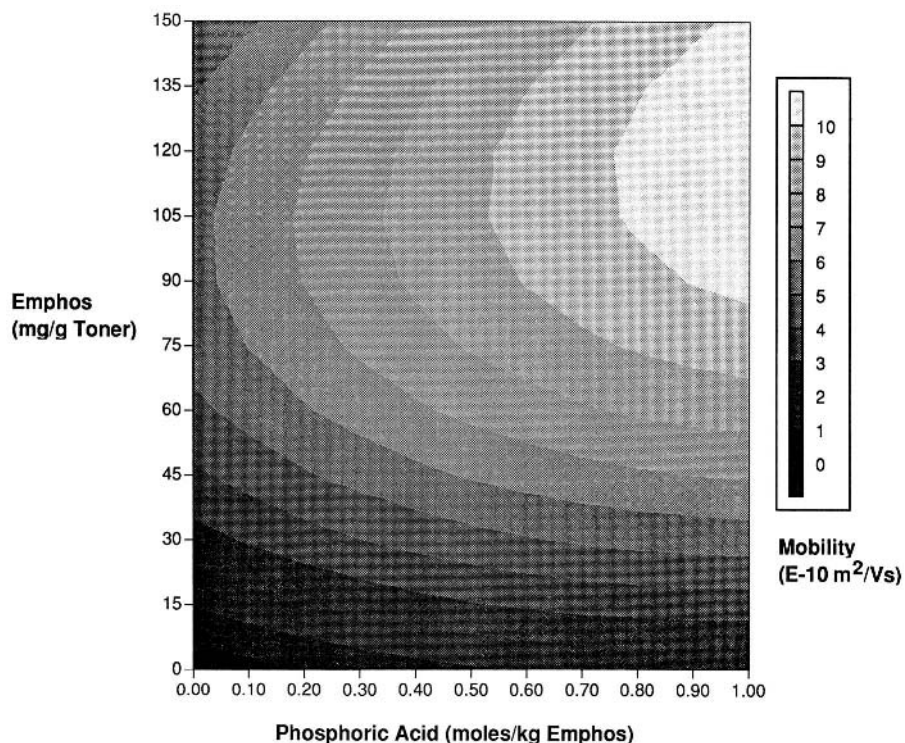
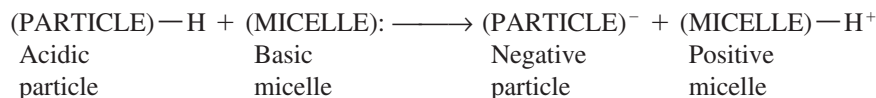


Figure 7.6 Particle mobility vs. Emphos® D70-30C and dichloroacetic acid concentration. Particle mobility determined with Matec ESA.

It has been demonstrated that the addition of micelle soluble acidic materials to the toner dispersion enhances particle positive charging. The acids can be incorporated into the particle initially and then leached into the micelles (El-Sayed and Trout, 1990; Chan and Trout, 1990) or added directly to the micelles (Pearlstone et al., 1990; Pearlstone and Swanson, 1992). Suitable acids include *p*-toluenesulfonic acid, *p*-nitrobenzoic acid, *p*-chlorobenzoic acid, phosphoric acid, dichloroacetic acid, and dodecylphosphonic acid. The impact of acid and micelle forming ionic surfactant concentration on toner charge as indicated by changes in toner particle mobility is shown in Fig. 7.6. The corresponding impact on toner conductivity is shown in Fig. 7.7. Examination of Figs. 7.6 and 7.7 shows that toner particle mobility is primarily a function of acid concentration, while conductivity is primarily a function of ionic surfactant concentration.

Divalent and trivalent metal carboxylates and sulfonates are very effective charge control agents for positive toners (Croucher et al., 1984b). It has been proposed that this is due to the acidity of the micellar cores resulting from the strong acidity of the cations (Fowkes et al., 1990).

7.6.2 Acid-Base Chemistry and Negative Particle Charging



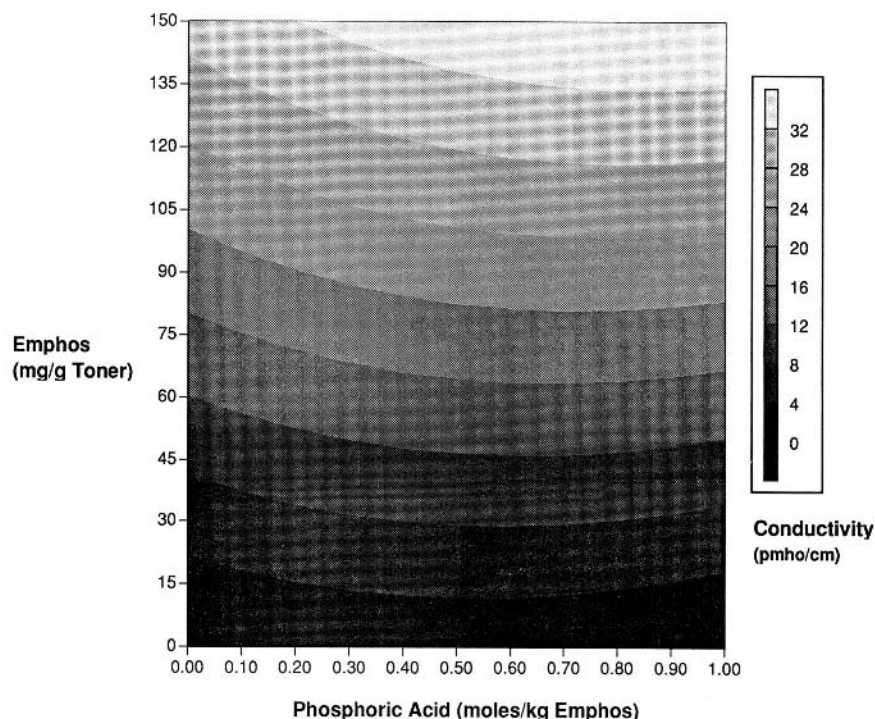


Figure 7.7 Toner conductivity vs. Emphos® D70-30C and dichloroacetic acid concentration. Conductivity determined at 5 Hz and 5 V.

It was demonstrated that copolymers of ethylene or styrene with sulfonic acid containing monomers were better for the preparation of negative liquid toners compared to the homopolymers or copolymers of ethylene with carboxylic acid containing monomers (Larson and Trout, 1987; Larson, 1988a). Suitable sulfonic acid containing monomers include 2-acrylamido-2-methyl-1-propanesulfonic acid and 2-sulfoethylmethacrylate. Similarly, it has been shown that the blending of highly acidic polymers into the toner particle and that the adsorption of acids onto the surface of the toner particle enhance negative charging of the particle (Larson and Trout, 1988, Gibson, 1990).

It has been noted that effective charge control agents for negative toners include basic barium petroleum sulfonates and polyisobutylene succinamides with basic amine groups (Fowkes et al., 1990). The addition of micelle-soluble bases to the toner has also been shown to increase the negative charge on the particles. Effective bases include organic soluble hydroxides like tetrabutylammonium hydroxide and tetraethylammonium hydroxide (El-Sayed and Larson, 1988), aliphatic amines such as tributylamine, 1-hexylamine, dibutylamine, and 1-dodecylamine (El-Sayed et al., 1990), and organic diamines including ethylenediamine, 1,2-diaminobenzene, and 1,2-diaminocyclohexane (Larson, 1988b). Aminoalcohol compounds, including triethanolamine, triisopropanolamine, and ethanolamine, added to a liquid toner, are very effective at enhancing the electrodeposition of negative toner particles (Larson, 1987; Larson et al., 1989).

A number of charge additives are effective even though they do not obviously follow the acid-base charging mechanism as outlined above. It was demonstrated that the amino-

Table 7.5 Effect of Piperidine and Pyridine Derivatives on the Mobility of Cyan Toner Particles

Additive	Mobility ^a ($10^{-10} \text{ m}^2 \text{ V} \cdot \text{s}$)	pK _a ^b
Control	1.6	na
Piperidine	3.5	11.2
2-Piperidinemethanol	5.0	
3-Piperidinemethanol	3.7	
Pyridine	1.7	5.2
2-Pyridinemethanol	4.6	4.9
3-Pyridinemethanol	7.8	4.9
3-Pyridinepropanol	7.0	5.5

^a ESA (1.2 MHz) Mobility for cyan toner 1.5% solids in Isopar L. 50 mg/g toner solids of basic barium petronate. 40 mg/g toner solids of additives.

^b Data from D. D. Perrin. *Dissociation Constants of Organic Bases in Aqueous Solution*. Butterworths. London. 1965. For further experimental details, see Larson et al (1989).

alcohol was much more effective than the corresponding unsubstituted amine, even though their basicities are similar. This effect was assumed to be due to increased particle charging but is not anticipated by the acid–base model because there was no apparent reason for increased proton transfer from the particle to the micelles with aminoalcohols as charge additives relative to the corresponding amines, as shown in Table 7.5. Aminoalcohols and diamines have also been noted to enhance the charge stability of liquid toner compositions (Larson, 1987; Larson, 1988b). Similar charge stabilizing effects have been observed for polyoxyethylene alcohols (Almog and Gutfarb, 1994). Metal salts of beta-diketones such as aluminum acetylacetonate have been found to be very effective negative charging agents and do not follow the pattern expected by an acid–base charging mechanism. It was proposed that the charging in these systems is due to the partitioning of surface ions into charge director micelles (Lane, 1990).

7.7 ENVIRONMENTAL HEALTH AND SAFETY OF LIQUID TONERS

Recent years have brought an increasing awareness of the impact of materials and activities on the environment and on human health and safety. Environmental issues of liquid toners are largely those of the liquid dispersant. The requirements for and selection of liquid toner dispersants have been described above. The widely used isoparaffinic hydrocarbons are synthetic materials, purified by fractional distillation. As high-purity aliphatic hydrocarbons these materials have inherently low odor and low toxicity, which is reflected by their acceptance for other consumer applications. Some of these materials, for example, are used in cosmetics. Also, the isoparaffinic hydrocarbons enjoy U.S. Food and Drug Administration clearances for use in a variety of direct and indirect food applications.

7.7.1 Physical Classifications

The physical classification of liquid toners reflects the physical classification of the dispersant. Flammability is the key parameter. It is normally quantified by flash point, the lowest temperature at which a liquid gives off enough vapor to form an ignitable mixture with

air and produce a flame when an ignition source is present. The isoparaffinic hydrocarbons used in liquid toners have been selected in part because of their relatively high flash points. With flash points above 40°C, all isoparaffinic hydrocarbons of Table 7.1 are classified as combustible materials, rather than flammable, by U.S. Department of Transportation criteria. For air and international shipments, materials are considered combustible if flash points are above 60.5°C. The flash point also bears on classification of liquid toner waste under the U.S. Environmental Protection Agency.

7.7.2 Toxicology

Potential human exposure during manufacture and use of liquid toners exist by inhalation of volatilized dispersant or by skin contact with liquid dispersant. Toxicological considerations thus are focused on the dispersant. The isoparaffinic hydrocarbons used widely as liquid toner dispersants have been studied extensively, and a comprehensive summary of the toxicity studies and human exposure data has been published (Mullin et al., 1990).

The isoparaffinic hydrocarbons are practically nontoxic in acute exposures (single high-level doses) by oral, dermal, and inhalation routes. In numerous long-term exposure studies with animals, no chronic toxicity issues with relevance to humans have been found. In developmental and genetic evaluations the isoparaffins have also been found to be nontoxic.

More specifically, in dermal tests, isoparaffinic hydrocarbons have been found to be nonirritating when evaporation is allowed to occur freely, conditions which realistically simulate human workplace exposure. When evaporation is not allowed to occur, these materials can be slightly irritating, most likely as a result of their ability to solubilize skin oils and defat the skin. Dermal safety of other toner components is considered during formulation of liquid toners, and skin irritation tests are usually performed on the final toner design.

LC₅₀, the conventional measure of acute inhalation toxicity derived from rat testing, could not even be determined for Isopars G and L; this was because the LC₅₀ was higher than concentrations that could be generated for the tests (above 2000 ppm for Isopar G). At least eight other acute and chronic inhalation exposure tests with a variety of animal species have been reported, all supporting the inherent low toxicity of the isoparaffins. Isopar® G has also been tested for respiratory irritation in mice and was found not to be irritating even at ~400 ppm (Mullin et al., 1990).

7.7.3 Occupational Exposure Guidelines

The most widely used guidelines for occupational exposures are the Threshold Limit Values (TLVs) established by the American Conference of Governmental Industrial Hygienists. TLVs apply to time-weighted averages for 8-hour-day, 40-hour-week exposures. However, no TLVs have been set for occupational exposure to isoparaffinic hydrocarbons. Likewise no U.S. OSHA Permissible Exposure Limits, German MAKs, or other governmental limits have been created specifically for the isoparaffinic hydrocarbons (American Conference of Governmental Industrial Hygienists, 1990). However, occupational exposure limits of 100–400 ppm have been established by several manufacturers of isoparaffinic hydrocarbons or of liquid toners (Greenwood, 1990). The isoparaffinic hydrocarbon

occupational exposure levels, based on the toxicology data summarized above, are judged to be those levels to which workers may be repeatedly exposed without adverse health effects. Liquid toner processes and equipment thus are designed to ensure that worker exposures are below these levels.

7.7.4 Indoor Air Quality

Indoor air quality, a growing area of interest, concerns comfort and health issues in homes, schools, public buildings, and offices. Factors beyond the toxicology of dispersants and toners must be considered when using liquid toner processes in such nonoccupational environments.

Scores of volatile organic compounds (VOCs), encompassing a wide range of chemical compositions, are typically present in indoor environments, being emitted from building materials, household and office products, and human activities. Such VOCs, particularly when present as complex mixtures, have been associated even at low-level exposures with a variety of subjective human responses including sensory irritation, the perception of odor, and the perception of poor air quality (Mølhave et al., 1986; Kjaergaard et al., 1989; Hudnell et al., 1990). The nature of these responses and the roles of VOC composition and concentration in those responses are only beginning to be determined. Still, as isoparaffinic hydrocarbons can be considered part of the broad class of VOCs, and have been identified as components of VOCs in indoor air of buildings containing liquid toner process equipment (Tsuchiya et al., 1988), their potential role in such subjective responses needs to be considered.

Several studies have addressed human sensory response to isoparaffinic hydrocarbons and to liquid toner process emissions. In a Danish study, human volunteers, exposed to 100 ppm of an isoparaffinic hydrocarbon for 6 hours, were given a questionnaire to evaluate sensory irritation, fatigue, and other responses. No symptoms associated with solvent exposure were reported (Pederson and Cohr, 1984). In a study reported by Ricoh Corporation, a human panel, exposed to emissions from a liquid process photocopier, ranked odor and discomfort. Odor was almost imperceptible at 22 ppm with slight discomfort noted at 54 ppm (Mullin et al., 1990). Thus, while the nature of human responses to low level VOC exposures continues to be studied, it appears, based on these studies and other workplace experience (Mullin et al., 1990), that acceptability of liquid toner processes in indoor environments, where odor and comfort are considered, is achievable if isoparaffinic hydrocarbon concentrations are kept below ~20–50 ppm.

Standards for human exposures in indoor environments do not exist separate from the occupational exposure guidelines such as threshold limit values (TLVs) previously discussed. However, the suggestion has been made that TLVs are not sufficiently stringent for indoor environments, recognizing that exposures in the indoor environment may be to a complex mixture of materials, for more than a 40-hour week, and may include a broad range of population. It has been noted that it is customary to use as a guideline that a concentration of 0.1 TLV would not produce complaints in a nonindustrial population in an indoor environment (American Society of Heating, Refrigerating and Air-Conditioning Engineers, 1989).

In assuring that airborne concentrations of isoparaffinic hydrocarbons do not exceed recommended guidelines, both process emission and room ventilation rates must be considered. Design of liquid toner imaging equipment and processes will impact source emis-

sion rates, which can be determined through experiments in controlled environments. Required minimum ventilation rates for the field placement can then be used to assure that intended guidelines are achieved.

7.7.5 Total Emissions

Another area of current awareness is the emission of volatile organic compounds (VOCs) to the outside environment. VOCs, including hydrocarbons, have been implicated in complex lower atmosphere chemistry involving nitrogen oxides and sunlight in the production of ozone pollution. U.S. Environmental Protection Agency guidelines require the use of emission control equipment for sources emitting more than 100 tons of VOCs per year, and some regional air authorities have imposed more stringent limits. However, with numerous regions of the United States remaining in noncompliance with federal ozone standards, the EPA and regional air authorities are considering more stringent limits on VOC emissions, and are increasingly turning to so-called small generators in an effort to reduce overall emissions. In particular, the printing industry has received considerable attention from these agencies (Jones, 1990).

Total emission for liquid toner processes is an issue only for high-volume applications, where potential emissions to the outside environment are in the tons of hydrocarbons per year range. Even in these high-volume applications, control of hydrocarbon emissions is achievable.

7.7.6 Containment Concepts

Several approaches to reducing or controlling hydrocarbon emissions from liquid toner processes have been described recently. A solvent recovery system can be used to condense hydrocarbon vapors that are generated in the fusing process (Howe and Hsu, 1988; Szlucha et al., 1988). Alternatively, hydrocarbon vapors generated in fusing can be oxidized catalytically to carbon dioxide and water (Landa and Sagiv, 1985).

In an innovative technique to reduce the overall volume of liquid toner used, liquid dispersant can be recycled for reuse in toning after electrophoretic separation and deposition of solids from excess toner (Day, 1989, 1990).

7.8 RECENT ADVANCES

The main body of this chapter was written in 1996. Here we provide references to more recent work on liquid toner technology.

General: Status of liquid toner technology and problems to be solved have been reviewed by Omodani et al. (1998). The history of liquid toner innovation from 1953–1997 was recently summarized by Case et al. (1998).

Liquid toner materials: Liquid toners were designed using silver flake as a component to enable printing of conducted traces on printed circuit boards and was reported by Kydd et al. (1998). The relationship between paper properties and image defects observed in a liquid toner printing system was reported by Caruthers et al. (1999). Particle mobility in a model liquid toner system and CuPc particles charged with $\text{ZrO}(\text{Oct})_2$ have been measured. These experiments were obtained by a toner charging mechanism based on a site-bonding model as reported by Keir et al. (1999). Performance of liquid carriers for liquid toner systems have been reviewed (Larson, 1999) and a demonstration of optimized

design of liquid toners using perfluorinated solvents as liquid carriers was presented in a recent report by Rao et al. (2000).

Liquid toner process: A liquid toner printing process was modeled as a dynamic analog electronic circuit by A. Kotz (1998), and using a similar technique the impact of “pixel-pixel cross talk” was demonstrated and modeled by A. Kotz (1999). “Reverse charge printing” liquid toner process was demonstrated to give results similar to offset printing (Liu, 1999) and there have been demonstrations of the use of highly concentrated liquid toner to develop high-quality, noise-free images as reported by Mori et al. (1999), Matsumoto et al. (2000), and S. Horii et al. (1997). Fluid removal from liquid toner images by the use of a vacuum-assisted blotter roll was shown to be very effective in a report by Chang et al. (1999). Coordinated theoretical and experimental study of the impact of lateral conduction on liquid toner images was reported (Chen et al., 1996). Optimization of liquid toner composition for use in a process that utilizes an electronic print plate consisting of a two-dimensional array of individually controlled electrodes was presented in a recent report by G. Bartscher et al. (1996). Image on image process using liquid toners was described in a recent report by H. Yagi et al. (1997). Hydrodynamics of reverse roll metering was modeled and demonstrated by Wang et al. (1997).

Liquid toner characterization: The electrophoretic mobility of a model liquid toner system and silica particles in hydrocarbon carrier charged with AOT, was measured using an electrophoretic light-scattering apparatus. The electric field dependence of the mobility was demonstrated (Jin et al., 1998). Measurement of liquid toner layer cohesion was measured using a visualization cell. It was demonstrated that the integrity of liquid toner images are understood through the plastic behavior of granular materials, namely tensile strength and consolidation stress, as reported by Chang et al. (1998). Charging characterization of liquid toner materials using a plate-out cell was described. Charge-transport models were used to rationalize the data in a report by Wang et al. (1999). Charge density in liquid toner images was determined by a series capacitor technique in a report by Chen (1997). Liquid toner electrophoretic mobility was measured with electrokinetic techniques and reported by Russell et al. (1997). Charged-micelle mobilities were determined in a lecithin Isopar system by measuring time-dependent conductivities and reported by Davis (1997).

Liquid toner control processes: Control of liquid toner properties to enable consistent print system output by a replenishment system was modeled and demonstrated by Gibson et al. (1998). Electronic control of the Indigo Electronik® technology was demonstrated to meet the demands of digital production printing in a recent report by Levy et al. (1997).

7.9 OUTLOOK

The best opportunities for liquid toner processes are in areas that take full advantage of the high resolution and high-quality color capabilities inherent in liquid toners. Products based on liquid toners are expanding into application areas that challenge commercial and industrial printing processes, including short-run on-demand printing, variable information printing, and printing on nonpaper substrates.

Recent progress has furthered the mechanistic foundation of liquid toner particle charging. Also, new charge additives continue to be identified. Both areas strengthen the

framework used in predicting and controlling charging properties of new liquid toners being designed and developed.

Much attention has been given to assuring the environmental suitability and acceptability of liquid toner processes. Continued interest in this area will likely prompt more advanced methods of controlling hydrocarbon emissions, work which will only further enhance the future of liquid toner based imaging processes.

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8

Dielectric Papers and Films

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Worldwide Images, Carmel Valley, California

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Specialty Papers & Films, New Hope, Pennsylvania

8.1 INTRODUCTION

The first publication of this chapter in 1991 (1) was based upon material compiled and submitted for publication in 1990, just when many industry observers were confidently predicting the death of the electrostatic plotter market. Right then, the industry was jolted by the introduction of the Scotchprint® Imaging Process from the Commercial Graphics Division of 3M Corporation (St. Paul, Minnesota). At about the same time, Harry Bowers (Bowers Associates, Berkeley, CA), using proprietary algorithms, demonstrated to the world that electrostatic plotters were capable of producing large-format graphics of quality not seen before. This was the beginning of the rebirth of the electrostatic plotter and media markets. What followed was an exciting period.

The growth witnessed during the 1990s would have been difficult, if not impossible, without the close alliances forged between hardware manufacturers, system integrators, and media and toner manufacturers. For instance, the close cooperation between 3M, Synergy Computer Graphics (Sunnyvale, CA), James River Graphics (now Rexam Graphics, South Hadley, MA), and Hilord Chemical Corp. (Hauppauge, NY) led to the success of the Scotchprint graphics fabrication process and its acceptance by the graphic arts and printing industry worldwide.

An alliance between Specialty Toner Corporation (Fairfield, NJ) and Harry Bowers led to the formation of Cactus (Chino, CA), a system integrator and a major supplier of printing systems for the wide format graphics market. Others, such as Onyx (Salt Lake City, UT), Visual Edge (South San Francisco, CA—formed when Bowers Associates restructured), and Colossal Graphics (San Francisco, CA), soon followed, and all set their eyes not just on traditional printing but also on photographic reproduction. At James River Graphics a separate business unit, Display Media, was formed specifically to support these markets.

During the same period there was also a considerable restructuring in the hardware business. Synergy, who manufactured the fast single-pass Color Writer® 410 electrostatic plotter, was acquired by Nippon Steel Co. (Japan) and shortly thereafter closed its doors for good. Precision Image Corp. (Redwood City, CA), a manufacturer of drum electrostatic plotters, saw a similar fate. The company was acquired by Graphtec (Japan) and ceased to exist. Hewlett-Packard Co. (Palo Alto, CA) discontinued the sales and marketing of their line of electrostatic plotters, and CalComp (a subsidiary of Lockheed Corp., Sunnyvale, CA) began a slow retreat from the electrostatic equipment market.

We witnessed the formation of Phoenix Precision Graphics Corp. (Sunnyvale, CA) and the success of Raster Graphics Inc. (San Jose, CA). RGI, having developed novel 22-, 24-, and 36-inch wide plotters, introduced the first 54-inch wide high productivity printer, the Digital Color Station® (DCS) DCS 5400. Xerox (Stamford, CT) restructured the San Jose, California, electrographic arm of Xerox Engineering Systems to form Xerox ColorgrafX Systems and introduced its version of a super-wide multi-pass color electrostatic plotter, the 8954.

Perhaps the most dramatic event during this period was the introduction of the Scotchprint graphic fabrication system by 3M. Initially, this was a turnkey operation, consisting of a Sun computer workstation, proprietary software, a scanner, a Synergy Color Writer 410 color electrostatic printer, and a Pro-Tech® laminator capable of transferring the image from the special dielectric Scotchprint Transfer Media onto self-adhesive vinyl. Later on, the Xerox 8954 and the Raster Graphics DCS 5400 printers were qualified and packaged as Scotchprint systems.

The fact is that Bowers Associates, 3M, Cactus, Onyx, Visual Edge, and the other value-added resellers (VARs) generated a whole new market in the graphics industry, the short-run graphic! In doing so, they created a strong impetus for the media manufacturers to satisfy a growing demand for specialty, high-performance products. Their response to this demand, and their creation of new markets by producing novel papers, forms the basis for the latter part of this chapter.

Today, no one in the industry talks about *plotters*; they are called *printers*. Indeed, the latest generation of these imaging machines has been so productive they may well be referred to as *presses*! This shift in terminology did not occur overnight. It evolved from the gradual penetration of wide format electrostatic devices in the printing industry. It might appear superficial to the casual observer, but the name change has its roots in the primary markets served by these devices. During the 1980s the primary use for them was in the CAD/CAM (computer aided drafting/computer aided manufacturing) market where they produced computer-generated drawings or plots. During the 1990s, on the other hand, they went predominantly into the graphic arts, where they are used to produce computer generated, short-run prints and graphics for advertisements, signage, and display. Thus in this chapter they are printers.

An imaging device, however, would be worthless without the appropriate imaging media. In our opinion, it is the availability of properly designed media for specific markets that facilitates the sales of hardware, not the other way around. Numerous disasters occurred in the early days of electrostatic plotter development, when a manufacturer rushed to introduce a new hardware model to market before the supplies development process was complete. Availability of properly designed supplies for each model of hardware usually trailed after the new model was shipped to the customer. Strict secrecy about any new hardware development would prevent any meaningful cooperation with the suppliers during the design phase. Therefore the advantages of the new hardware would be poorly exploited.

A superb example of how important a joint effort is among the hardware, software, and media and toner suppliers, can be found in the Scotchprint imaging process introduced by 3M in 1991. Its success in the marketplace was assured by a perfect match between hardware design, software design, a specially designed toner transfer dielectric paper (Scotchprint Transfer Media), a variety of self-adhesive vinyls with a toner receptor layer, an assortment of laminating films, and a toner with good ultraviolet (UV) light stability and color saturation. This system of interactive components, known as the 3M Matched Component System or MCS®, played a fundamental role in the highly successful marketing campaign by the manufacturer.

Another fruitful joint effort was the introduction of materials for outdoor advertising, specifically Rexam's Outdoor Poster Grade and Specialty Toner Corp's Weather Durable Toner. These developments were initiated by Cactus, who brought together the technical and marketing groups of these two companies with Gannett Outdoor, a highly respected leader in the outdoor signage (billboard) market.

It is fair to say that the introduction of the Scotchprint graphic fabrication process opened up a whole new market for imaging supplies manufacturers, i.e., the short-run end of the screen printing industry. We have seen the introduction of new and exciting media in the market, such as Rexam's Wear Coat®, a dielectric paper with a special coating which, upon imaging and transfer onto a substrate, produces an image that does not require an overlamination film. The dry transfer image is imbedded in a hard polymeric matrix that protects the toner particles from abrasion, vandalism, and ultraviolet radiation to some extent. Additionally, Wear Coat media can transfer the image under heat and pressure to a large variety of substrates (plastic films and sheets of almost any type, coated canvas, fabric, and many others). Rexam has been hailed as a pioneer for this and other exciting products for the short-run graphic fabricators.

Another similar transfer technique relies on the easy release of the dielectric layer from wet dielectric paper. This so-called *wet transfer* process is a simple, although messy, means to get an image onto a wide range of substrates. The success and phenomenal growth of the short-run graphic market since the introduction of the Scotchprint process provided a strong stimulus to ink jet printer and media manufacturers as well.

Today, the end user will find a wide spectrum of dielectric media that will satisfy almost any commercial application. If one includes transfer media and the associated substrates, as well as the dye sublimation process, the selection of media and the versatility of applications is indeed impressive. During those early days of color electrostatic printing (1980 to 1990), the images, when exposed outdoors, lasted only a few days. Today, outdoor display materials (banners, signs, vehicle graphics) are guaranteed to last up to five years if certain conditions are met.

Shortly after the first edition of this handbook was published, Raster Graphics introduced a novel family of printers for the smaller format market: the printers took sheets cut from a roll and mounted these on a stainless steel belt. The most impressive development from Raster Graphics was full-width writing heads with individually driven writing nibs. The printers had a substantial speed edge and were free of many of the constraints of the prior technology. Raster Graphics demonstrated leadership again in 1993, introducing the 54-inch DCS 5400 printer. It has proven the mainstay of several market segments, especially those, such as the out-of-door industry, where high speed production factors into success. The most recent version, the DCS 5442, can print at 10 inches per second (ips)!

The renaissance in the technology stimulated a newcomer in the hardware area, i.e.,

Phoenix Precision Graphics Corp. (Sunnyvale, CA). A transplant from the now extinct Precision Image Corp., the team at Phoenix Precision Graphics first designed a 36-inch color electrostatic printer that recycles the toner internally, thus minimizing the need for toner waste disposal and making the printer self-sufficient in terms of toner supply. On occasion, the operator need only add dispersant to compensate for evaporation and carry-out by the paper during printer operation. More recently a 60-inch wide version was announced.

The continued growth of the short-run graphic market convinced 3M to develop the most productive yet single-pass, color electrostatic printer, the Scotchprint 2000. At a speed of 2 ips, this monster can produce the graphics for a 40 foot truck trailer in about 18 minutes. No doubt, the 2000 will further erode the low-end runs of the screen printers and convince those who are still hesitating to jump on the digital wide format printing bandwagon.

Color electrostatic printers are still relatively expensive devices. For instance, the 54-inch wide printers sold by Xerox CGS and Raster Graphics cost about \$100,000. That is why we find the greatest population of printers in commercial photographic laboratories, screen printers, service bureaus, and to a lesser extent the in-house printing and CAD/CAM departments of large firms. They are also being adopted by other industries such as the outdoor advertisers. The printers are best suited for businesses where their high production speed and image durability are necessities.

Another recent major business is imaging woven fabric materials (primarily polyester) by dye sublimation (also, *sublimatic*) printing. The key to success was the introduction of special toners containing sublimation dyes. Synergy and Hilord were the pioneers of this technology in this country. In Japan, Nippon Steel Chemical (a subsidiary of Nippon Steel Co.) was the leading force.

One reason the process was not implemented on a large scale until recently was that color consistency was almost impossible to achieve in long production runs, and the process was too slow to be economical. Both problems have now been overcome by the efforts of Cactus, PowerPrint Technologies (Sunnyvale, CA), Paedia Corp. (San Francisco, CA), Hilord, Specialty Toner, and others. Sublimatic printing (see Section 8.6.7) is being adopted for many other materials and being used for snowboards, skis, furniture, and art. Xerox entered the market directly with the 8900 “DS” series, while Raster Graphics had its own variant specifically tailored for this application.

The five toner stations of the latter printer have been used by Specialty Toner Corp. to address one of the undesirable artifacts of sublimatic printing: The dye diffusion transfer process results in high dot gain. Dots can double in size. The few dark pixels needed to produce correct light colors, are often visible to the naked eye. STC’s solution, “V® toners” dramatically reduces this phenomenon and produces graphics that withstand close scrutiny.

Although the rate of development in electrographic technology has slowed recently, new applications are continually being found, and the sales of consumables remains strong—a testament to the power of this versatile technology.

8.2 THE IMAGING PROCESS

8.2.1 Principles of the Electrographic Process

Electrography can be defined as an imaging process in which a latent electrostatic charge image is formed on the surface of a dielectric medium, and made visible by applying

oppositely charged toner particles. The essential process elements of electrostatic writing are as follows:

An electrical potential, typically 400–600 volts (V), is applied across a dielectric layer with a conductive backing, by a writing head and a set of counter electrodes. When the potential across the air gap exceeds the threshold for air breakdown (circa 380 V), a discharge occurs and a net electrostatic charge is deposited on the dielectric layer. By selectively energizing a set of styli in the writing head to levels above the threshold voltage and by moving a charge receptive sheet or web past that head, a latent image is generated. The resulting latent image is then developed by applying toner particles carrying the opposite charge. Electrostatic attractive forces are the primary factor responsible for image development.

To be functional, the dielectric medium used to receive the charge must satisfy certain basic requirements, such as:

The dielectric layer must have high capacitance.

The charge decay rate of the dielectric must be low enough to ensure that the latent image reaches the toning station before any significant charge loss occurs.

The substrate carrying the dielectric must have a short electrical time constant, to ensure that the charge deposition will reach its maximum value during the duration of the writing pulse.

The essential design of the substrate for the process is simple: a dielectric coating on a conductive base (Fig. 8.1). However, the technology in the substrate, required to provide the proper functionality, is complicated and extremely challenging. In particular, electrography is the only commonplace printing process where the substrate is an integral part of the generation of the latent image—in no other is it a major part of the electronic circuitry involved in the placement of colorant! Thus the dielectric imaging element must have, in addition to all the needs for the end use, electrical properties befitting a sophisticated electronic component. That this is a difficult task to accomplish is often reiterated in this chapter.

8.2.2 Evolution of the Electrographic Process

The history of the evolution of experiments and observations with electrostatic charge, from the ancient Greeks through to the early generations of color plotters, is well described in the first edition of this book. The applications covered are now either obsolete or in rapid decline. It is the evolution of color printing that has been the focus of the industry over the last 5 years, and it is that which is addressed here.

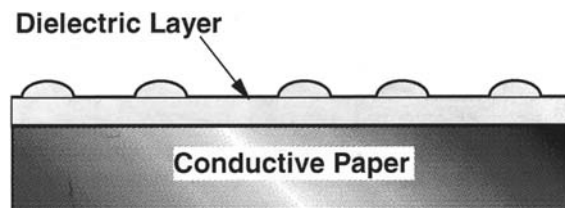


Figure 8.1 Schematic structure of dielectric paper.

Color Electrostatic Printing Technology

In 1983, the first commercial Electrostatic Color Plotter was introduced by Versatec (Xerox). Since then, a succession of companies have entered the market; most have dropped out, but there remains a strong cadre of players that ensures its viability and future.

The Versatec ECP 42 was a multipass 42-inch wide machine. Like all Xerox printers it featured through back-grounding (through grounding) and multiplexed writing. This printer not only revolutionized CAD but also sowed the seeds for the graphic arts industry. It was replaced by the CE 3000 Series, 200 and 400 dots per inch (dpi) machines in 1986, and these in turn were superseded by the 8900 family beginning in 1989. Xerox responded to Raster Graphics superwide printer introduction with the 8954 in 1992. After the ECP 42, the next revolutionary introduction was by Benson in 1987 with a 48-inch wide single-pass printer also using through grounding and multiplexed writing. Only a limited number of Benson printers were produced before the venture halted.

CalComp followed in 1987 with the successful 5700 series, which was a multipass printer with front grounding and multiplexed writing. The subsequent color models were less tolerant and therefore not widely adopted. CalComp departed the market in 1995.

Synergy's single-pass entry, the ColorWriter 400 of 1989, was another strong technological player; its adoption by 3M for the Scotchprint process ensured its place in the market but did not guarantee Synergy's survival. Nippon Steel purchased the company and closed the Sunnyvale offices in 1992.

Precision Image Corporation, founded in 1985, developed and marketed a unique drum plotting method using cut sheet media. The C448 was marketed from 1986 to 1988. It had a ceramic writing head and a unique toning system.

Hewlett Packard filled the gap between pen plotting and inkjet with a robust front-grounded printer, built by Matsushita of Japan, which was sold from 1988 to 1992.

The major contribution Raster Graphics gave the industry was the silicon writing bar, a full-width writing head with individually driven nibs. The first machine, the 22-inch wide Color Station[®] was sold in 1991. A series of 200 and 400 dpi 24- and 36-inch printers followed. This product line was discontinued by 1995 as the company focused on wide format high-speed printers. The first of these was the highly productive DCS 5400, which was followed, in 1996, by the DCS 5442. Oddly, no one else has adopted writing technology similar to the silicon writing bar.

Phoenix Precision Graphics introduced its Model 360, a 36-inch wide multipass printer. Instead of utilizing a 36-inch wide writing head, the PPGC device employs a head several inches wide that shuttles along and across the paper web during writing. This allows significant savings in production cost, and enabled the manufacturer to offer the machine at a lower price than other 36-inch electrostatic printers. In 1999 PPGC unveiled a 60-inch printer, but disappointing sales led the firm to close its doors in the year 2000.

The Scotchprint 2000, from 3M Commercial Graphics, has been the sole important hardware introduction after 1996. A 54-inch wide single-pass machine that runs at 2 ips, it is a veritable media eater. Like all the other new printing systems introduced since 1994, it was designed to satisfy the rigid requirements of the graphic arts market for speed, image quality, and operator control.

8.2.3 Implementation

There are three basic commercial printer configurations: through-grounded multiplexed multipass from Xerox CGS; through-grounded, individually driven multipass from Raster

Graphics and PPGC; and front-grounded, multiplexed, single-pass from 3M. The three configurations are shown in Fig. 8.2. The basic printer components are

- The web handling system, which includes the media supply and take-up spools, the drive roll, and the turning bars or rollers
- The writing system, which consists of the imaging electronics, the printhead, and the electrodes
- The developing system, which includes the toner supplies, the pumps, hoses, fountains, rollers and vacuum bars, as well as the dryer fans
- The printing and control hardware, firmware, and software

All have added features that are intended to satisfy the requirements of the service bureaus producing advertising materials, i.e., they are faster, offer better image quality, and offer more flexibility in setting up printing parameters. The issues of easy maintenance and color consistency have also been addressed.

The 54-inch wide Xerox 8954 printer offers a choice between single-layer and double-layer toning. It incorporates a humidifier and measures the temperature and percentage relative humidity (RH) inside the printer housing. There are many other useful features available from the control panel or via software connections from the operator or designer's computer. For example, the writing voltage of each color can be adjusted

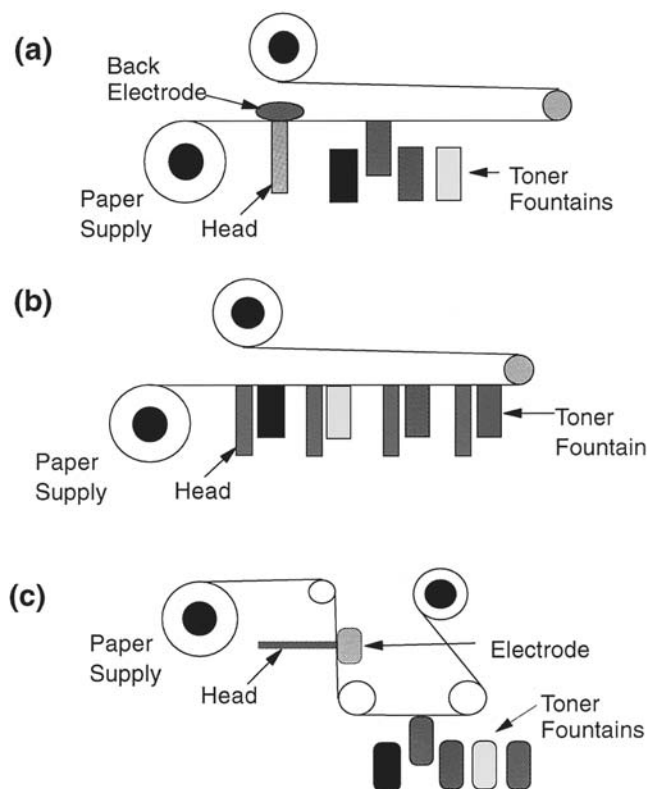


Figure 8.2 Commercial printer configurations: (a) 3M single pass (optional 5th fountain not shown), (b) Raster Graphics multipass, and (c) Xerox multipass.

independently. Further, each color can be written and toned multiple times, or written once and toned twice. Versions with 200, 300 and 400 dpi resolution were offered, with print speeds of 4, 3, and 1.5 ips, respectively.

Xerox also has two models differentiated specifically for sublimatic printing, the 8954 Series III and the 8954DS. The printing process used by Xerox is especially designed for full surface coverage. This, coupled with the 300 and 400 dpi resolution, gave this machine family the edge for photorealistic printing. Xerox also benefited from its world-wide customer and technical support organization.

The Raster Graphics DCS 5442, also a 54-inch wide printer, is a much improved version compared with the earlier 22-, 24- and 36-inch devices. Registration, speed, and paper handling, in addition to other features, have been optimized. The printer has a number of advanced options in addition to the full-width imaging bar with individually driven nibs. These include very high print speeds: 10 ips in draft and 5 ips in premium quality mode. Although the nominal registration is 200 dpi, the length of the dot can be selected as either 200 or 400 dpi for extra fine resolution. There is an optional 5th toner station which can be used for spot colors, or for "Digital Varnish," an overlacquer that improves print appearance and durability. The DCS 5442 comes ready to run standard or sublimatic toners. In the last configuration, it is the basis for the high-resolution V toner system from STC.

The Scotchprint 2000, like the earlier 36-inch 3M 9512 printer, will lay down 4 colors at 400 dpi in a single pass. The big difference is speed—it can output 2,400 sq. ft. of printed media per hour. Some industry observers predict that the 2000 machine will further penetrate the low end of the screen printing business. This rate means producing 400 posters, each 2 ft. $\times$ 3 ft., in one hour, complete vinyl graphics for a 48-ft. semitrailer in 19 minutes, or an 8-ft. $\times$ 10-ft. mural in two minutes. The printer accepts a variety of transfer media, such as Rexam's Wear Coat, standard interior and exterior imaging papers, and the new direct print Scotchprint Vinyl Media. Several options further expand the capability of this device, such as a high-capacity toner module that will allow an 8 hour uninterrupted printing cycle, a fifth toning station that permits the application of accent colors or UV protective dispersions in line with the printing, and a wind/unwind module that facilitates the loading and unloading of the voluminous supply rolls.

The Phoenix Precision Graphics printers have a single head, approximately 2.5 inches wide, containing 1,024 nibs. This head shuttles across the paper (the X direction), then the paper steps forward (the Y direction), in a mode similar to ink jet cartridges in ink jet printers. It offers two print resolutions: 200 dpi (draft mode) and 400 dpi (premium). The print speed varies as a function of the print mode, that is, 1.0 ips for premium, 1.5 ips for standard, and 2.0 ips in draft mode. The printer can accept paper weights from 75 to over 150 grams per square meter (gsm) and film thicknesses up to 5 mils. A remarkable feature of the PPGC printer is the recycling and reuse of the toner. The depleted toner is plated out in a high-voltage cell; the solid residue is then redispersed in Isopar® (Exxon Chemical's isoparaffinic hydrocarbon carrier fluid) and returned to the bottle of working premix. There are several patents covering the recycling operation.

8.2.4 System Interactions

The quality of the printed article, and to some extent the speed at which it is produced, is what the customer sees and pays for. Once the decision has been made to acquire an imaging device, be it an electrostatic printer, an ink jet printer, or a laser printer, the end

user's main concern is print quality and how consistent that quality is over time. Other considerations also come into play, such as hardware reliability, frequency of repairs, maintenance cost, cost of disposal, and availability of local technical support, depending on the application and the production environment.

Service bureaus in the graphic arts market are the most demanding customers from the point of view of quality, consistency, and fast technical support. They operate on tight, rigid schedules and cannot afford to waste time waiting for a service engineer to show up, or to clean the device, or tweak the parameters to get rid of some artifacts.

In comparison with other nonimpact printing technologies, electrostatic printers are highly reliable. There are few moving parts in the system—toner pumps, the differential drive roller, and a few pulleys. It is not uncommon to find printers in the field that have been operating for five or more years without a major failure. Extending the MTBF (mean time between failure) depends largely upon the type of media used in the printing process, the relative humidity in the printer room, and the preventative maintenance performed on the hardware. The writing heads in an electrostatic printer, depending on usage, can last five or more years. In our experience, head damage usually results from metal particles imbedded in dielectric media, although large chunks of conductive agglomerates sticking on the surface of the dielectric papers and films can have the same detrimental effect on the writing head.

Printer design features are only one factor in the image quality equation. The type of media and toner used are equally important. The reason is that the printer, media, and toner form a highly interactive system. Different hardware implementations, and even different models made by the same manufacturer, have their specific requirements with respect to properties and performance. Moreover, each printer manufacturer considers certain system design features to be of a sensitive nature and is unwilling to share this information with the toner and media producers. Only firms that meet certain criteria established by the original equipment manufacturer (OEM) and whose products have been qualified for use in their hardware have access to the inside know-how of system parameters.

If an OEM decides to accept a new supplies vendor, then an extensive qualification process is launched that may require anywhere from 6 to 12 months of product submissions and performance testing. This is a well-justified and necessary ritual. It is a common practice that printer OEMs sell the consumables under their own brand name for two reasons: first, the sale of supplies is a highly profitable business, and second, the end user is assured of high performance and quality, thanks to the OEM's qualification and continuing quality acceptance programs. Today, strong alliances exist between equipment and supplies manufacturers to ensure optimal performance of the printers in the field. The industry has matured.

8.2.5 Strengths and Weaknesses of Electrography

Every printing technology has its limitations. Our perception of the strengths and weaknesses of electrography, as we know it today, depends fundamentally on the applications. As shown in the previous sections, each application has its peculiarities and demands on print quality. The following characterization, therefore, is based on the performance of electrostatic printers in the graphic arts industry, as that is where most of the new printer installations can be found. In the background, we are comparing electrography with ink jet technology.

Strengths

- Speed and productivity
- Reliability
- Resolution (up to 400 dpi)
- Long-term outdoor durability (up to 7 years with overlamine)

Weaknesses

- High equipment cost
- Highly specialized media
- Flammable toner dispersant liquids
- Susceptibility to numerous image defects
- Requirement for highly skilled machine operators

The main reason that electrostatic printers are still popular in the graphics printing industry is their speed, high resolution, and durability of the printed image when certain conditions are met.

8.3 IMAGE GENERATION

There are three distinct phases to the creation of an electrographic image: deposition of charge to form the latent image, image development, and toner fixing. The first step is the most demanding of the substrate, again because it must function dynamically as a component of the electrical circuit that determines image formation. The subsequent demands are comparable to those of other digital imaging media. Understanding the process is aided by considering the electrical circuitry involved within the substrate, and by a separate description of the events. This is the approach adopted in this section.

8.3.1 The Electrical Circuit in the Substrate

The fundamental approach to explaining the development of the voltage gradient, and hence the charging process, is helped by studying the electrical circuits involved. (Fig. 8.3). [A thorough description is also provided by Johnson (2)]. The conductive materials are semiconductors, while other parts are not conductors but function as capacitors. The components of the circuit for a back-grounded printer are the power supplies for the nibs and the electrodes, the nibs (conductors) and electrodes themselves (conductors or semiconductors), the air gap (a capacitor), the dielectric layer (another capacitor), and the conductive substrate (a resistor and capacitor in parallel connecting two resistive layers—the conductive coatings).

The description of the circuit for a front-grounded printer is somewhat different (2) because the back electrode is capacitively coupled to the front side conductive layer. However, the differences mean little for the general discussion of the process that follows. Similarly, nibs energized by either multiplexed drivers or individual drivers respond equivalently.

When a voltage is applied to the electrodes, the potential initially divides between the air gap, the dielectric layer, and the conductive base, so the potential across the air gap is defined by the relationship

$$V_a = V \left(1 + \frac{C_a}{C_b} + \frac{C_a}{C_d} \right) \quad (1)$$

where the terms are as defined in the caption to Fig. 8.3.

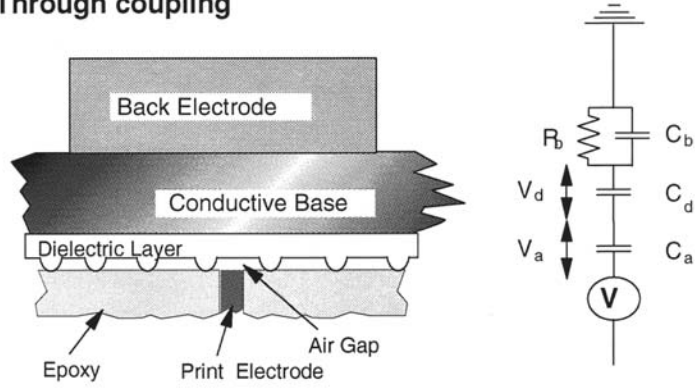
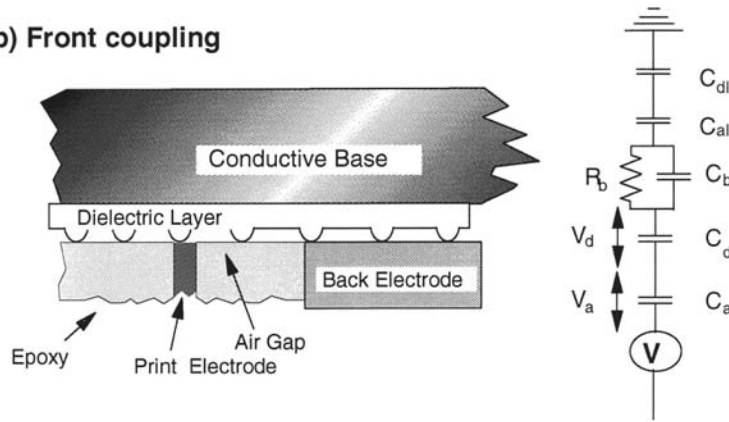
(a) Through coupling**(b) Front coupling**

Figure 8.3 Equivalent electric circuit for (a) through coupling and (b) front coupling electrographic printers. V = potential applied to the nib; V_a = potential across the gap; V_d = potential across the dielectric layer; R_b = lumped resistance of the conductive base; C_a = capacitance of the air gap under the nib; C_d = lumped capacitance of the dielectric under the nib; C_b = lumped capacitance of the base, C_{dl} = capacitance of the dielectric under the electrode; C_{al} = capacitance of the gap between the dielectric and the electrode.

Initially no charge is deposited as the potential is divided among the three capacitors, C_a , C_b , and C_d . The resistance R_b of the conductive base controls the rate of transfer of the mobile charge and hence the redistribution of the voltage. The resistance must be kept low enough so that the relaxation time of the substrate, τ_b , defined by

$$\tau_b = R_b C_b \quad (2)$$

is low enough for the short write pulses to get maximum charging efficiency. Capacity is defined by

$$C = \frac{\xi A}{\ell} \quad (3)$$

where ξ is the permittivity, A is the area of the capacitor, and ℓ is the thickness of the layer. Thus relative values of capacitance per unit area, C' , in the air gap, the dielectric layer, and the base paper, are estimated from

$$C' = \frac{C}{A} = \frac{\xi}{\ell} \quad (4)$$

Some measured capacitances for dielectric papers are $C'_d = 740 \text{ pF/cm}^2$ and $C'_a = 60 \text{ pF/cm}^2$. If the total applied potential is 550 V, the air gap is about 6–15 microns (μm), the surface electrical resistivity (SER) of the base is $10 \text{ M}\Omega/\square$ (megohms per square), and the volume electrical resistivity (VER) is about $50 \text{ M}\Omega \cdot \text{cm}$, an applied surface voltage (ASV) of about 120 V should be obtained.

8.3.2 Latent Image Generation—The Charging Process

In an electrographic printer, a charge is deposited imagewise on the surface of the dielectric paper or film medium by applying a sufficiently high voltage to the nib and across the dielectric layer. The high nib potential causes a spontaneous emission of electrons, and an avalanche of ion flow, as the air in the gap between the nib and the dielectric surface breaks down.

The conditions necessary for the first step in charging, that is, the emission of the electrons from a nib, include a high field gradient and a suitable emissivity of the nib itself. High field strength is found where there is a high potential gradient, expressed in volts per micron ($\text{V}/\mu\text{m}$) and a sharp surface. Thus it is found at the edges of the nibs, and especially when these are freshly polished or abraded. Emission is also easier from clean metals than oxide surfaces and polymers. Again, areas of fresh metal will be better emitters and more likely sites for discharge to begin. Figures 8.4 attempts to illustrate conditions in the gap between the nib and the conductive layer of constant field strength.

The current from electron emission is small—too small to be useful for printing. It must be enhanced somehow. If there is a sufficiently high voltage gradient across an air

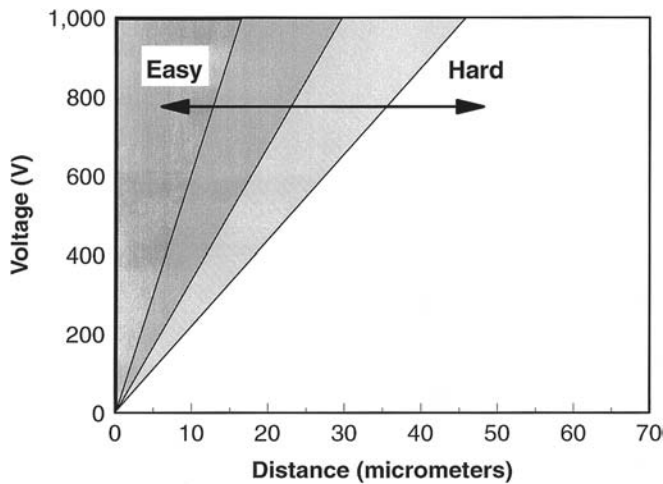


Figure 8.4 Conditions in the gap where nibs of different emissivity will spontaneously emit electrons.

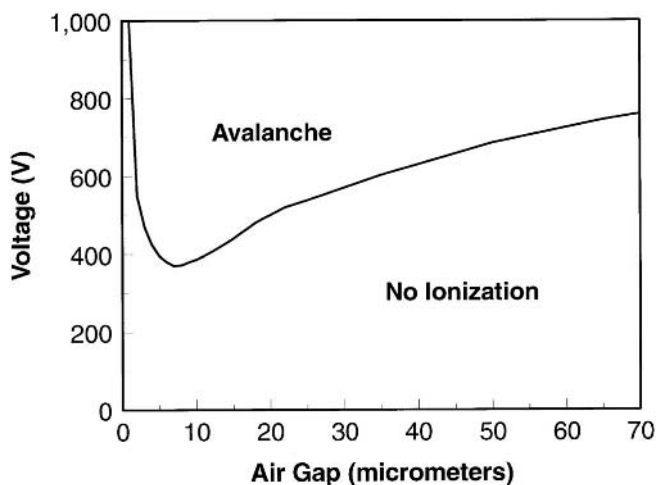


Figure 8.5 The ideal Paschen curve.

gap, electrons in that gap can be accelerated to the velocity that causes them to ionize the nitrogen molecules in the air that they collide with. This phenomenon is described by the Paschen Curve (Fig. 8.5). For a 10 μm gap the potential must be at least 300 V, or 30 V/ μm . Once such ionization occurs, there is a cascade; ions are accelerated to high velocity and stimulate further breakdown in the air gap.

The electrographic printing system requires first, suitable conditions for electron emission, and second, a sufficient gap between the nib and the surface for breakdown to occur (Fig. 8.6). The means to achieve and control this gap and the emissivity of the nib are described below.

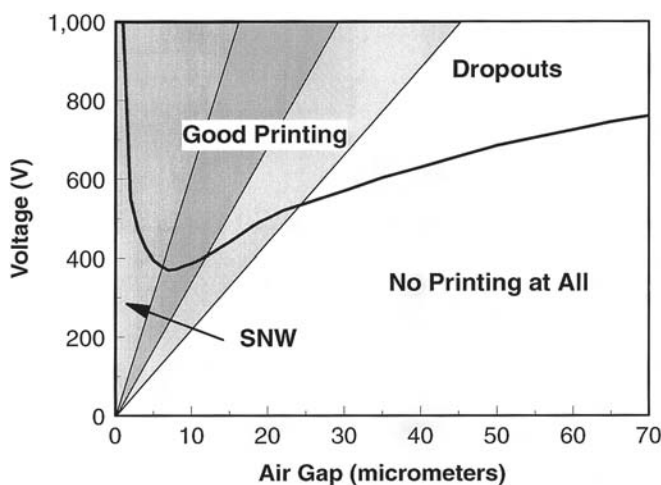


Figure 8.6 Combined Paschen curve and emissivity states showing effect on writing (SNW = spurious nib writing).

The first step in writing is the application of about 400 volts between the back electrode and the nib. This immediately causes a potential gradient between these two elements of about $4 \text{ V}/\mu\text{m}$ with a 100 gsm paper, not sufficient to cause either emission or breakdown. Immediately upon establishment of this field there is a migration of charge, both within the conductive layers and between the front and the back conductive layers, to ground which, if the paper has sufficient Z-directional conductivity, rearranges the field so it is dominantly between the top of the front conductive layer and the nib. Thus across the dielectric layer and the air gap, a combined distance of about $10 \mu\text{m}$, there is now a voltage gradient of about $40 \text{ V}/\mu\text{m}$. This is usually more than sufficient to initiate emission, which leads to avalanche and reproduction of the footprint of the nib as a dot of charge on the dielectric.

The discharge has several effects both on the nib and on the paper. The plasmalike conditions erode the nib surface especially where the field gradient is high. This rounds out sharp edges and oxidizes pure metal. Additionally, there is probably deposition of detritus after the discharge, because of the plasma vaporizing some of the dielectric layer. The nib is therefore in a less active state than before the discharge and so will require a higher voltage to discharge again if the surface is not rejuvenated.

The surface charge on the paper is balanced by a charge separation in the conductive layer as electroneutrality is sought. A surplus of negative charges seek ground. Because these charges are moving under a lower voltage than the applied potential, it will take them longer to be neutralized. If the front conductive layer is not well grounded this charge will accumulate with successive firings, especially if the path to ground has a high resistance. Eventually the accumulated charge will be sufficient to interfere with subsequent printing steps. Examples of the problems caused are described in Section 8.5.3 on image artifacts.

There are two distinctly different nib geometries, which produce dissimilar dot shapes (Fig. 8.7). There are also two different methods of depositing the charge that forms a dot. With solid shape nibs of large two-dimensional footprint, such as wires, the dot is produced by a pulse of short duration—approximately 60 to 120 microseconds (μs). During that time the area under the nib fills in with charge starting with the areas near the

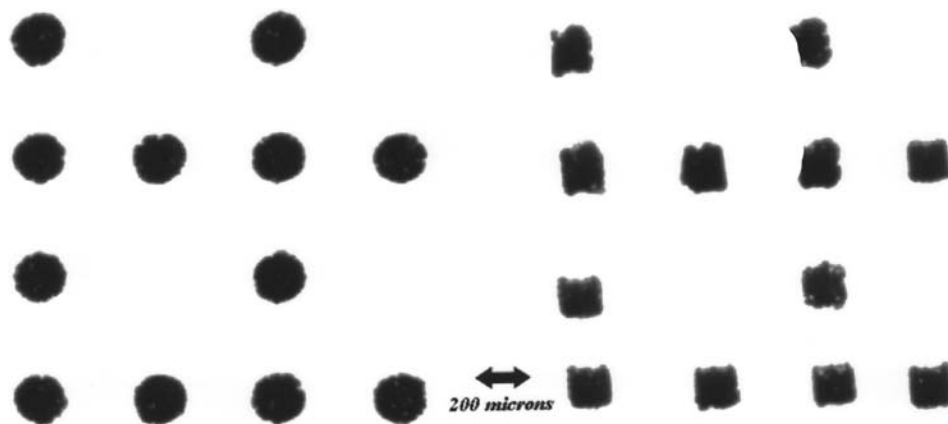


Figure 8.7 Typical high-quality image dots. Left: wire-wound nibs used by Xerox, 3M, and others. Right: ribbon nibs used by Raster Graphics Inc. (Courtesy of T. McBride.)

electrode edge, and then filling in until the voltage gradient in the gap is dropped below the critical value by the buildup of charge on the dielectric. At this point the voltage gradient exists substantially across the dielectric layer. If there is a significant build up of the interlayer voltage from inadequate charge depletion to ground, then the solid area will be incompletely charged. The dot will appear as a donut, or in extreme cases as a crescent (Fig. 8.8).

Printers with individual drivers have narrow, ribbonlike nibs. Dots from these printers are made by a “paintbrush” approach—the nib is energized when the paper at the beginning of the dot passes under the nib, and deenergized when the dot should end. The time for this is about 1 to 5 μ s. The charge is actually deposited in a series of bursts, or flashes not unlike lightning strikes. Such dots appear square (or rectangular when the 200×400 dpi feature is being used.)

Lines from the two writing methods have distinctly different appearances. Wire nibs produce lines that are a series of circles, while the paintbrush heads give lines with greater edge definition (Fig. 8.9). Edge quality is related to the surface structure. The area that gets charged is the area determined by the shadow cast by the nib. When the surface is rough, the nib is further from the surface, and so it subtends a greater area. In the paintbrush mode, the line width clearly follows the topography of the paper surface.

8.3.3 Image Development—The Toning Process

The paper bearing the charge is advanced through a toning station. Here it is brought into contact with the toner, a dispersion of pigment finely ground in a resin binder, and a charge director (or, charge control agent) in an insulating liquid. The ideal carrier for liquid toner is odorless mineral spirits, sold commercially by Exxon under the Isopar® tradename, by Phillips Petroleum as Soltrol®, and by Shell Chemical as ShellSol®. These names represent a series of highly refined petroleum distillates, having different flash points and containing at most trace amounts of water and sulfur compounds.

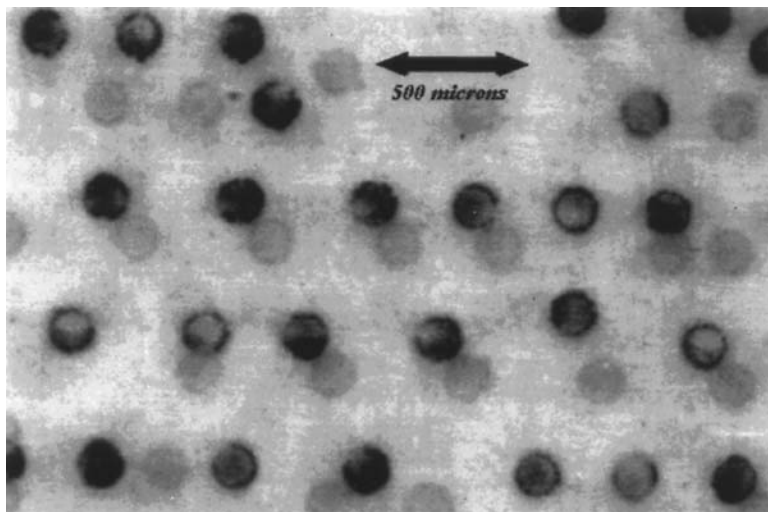


Figure 8.8 Incomplete dots deposited by wire nibs. Note halo/donut structure. (Courtesy of T. McBride.)

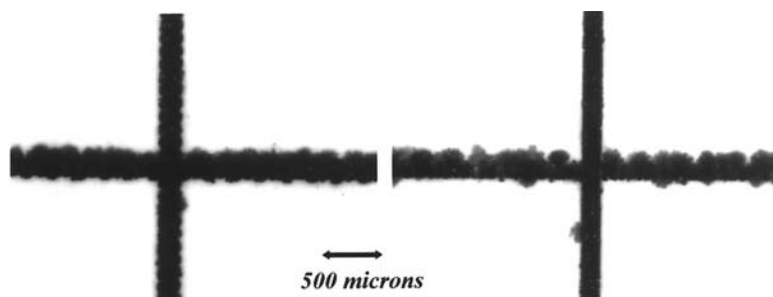


Figure 8.9 Typical electrographic line structure. Left: line from a wire nib with pulse-mode writing. Right: line from a ribbon nib written by paintbrush mode. Note flare on dot leading edge, or nib trailing edge—see Image Artifacts, Section 8.5.3. (Courtesy of T. McBride.)

The toner station is composed of three separate components: an applicator, which ensures that the paper surface is flooded with fresh, active toner; a high-shear mixing zone to impact constantly fresh toner particles with the dielectric in order to neutralize the surface charge completely; and a decoating or doctoring process to remove excess liquid toner. The first station is typically a fountain.

The mixing and liquid removal are both done with a reverse rotation metal roller. On the fountain side this brings about a region of turbulence and mixing as the dielectric is coated with a liquid toner film. On the decoating side, the reverse roller acts as a doctoring member by removing excess liquid from the paper. After this there may be a vacuum channel to complete the removal of the surplus toner and to aid in drying the wet sheet.

There are at least three demands on the dielectric surface: most importantly, it must not dissolve in the mineral spirits dispersant; next, it must protect the weakly bound toner from the agitation of the roller, and finally, it must not be a trap for toner, lest excessive background deposit occur.

8.3.4 Toner Fixing

The toners used in electrography most typically are fixed by drying. These toners are resin-coated particles usually ground in a steel ball mill to a submicron size. Because it is only partially soluble in the dispersant, the polymer is somewhat swollen, or “solvated,” by the carrier fluid giving it a larger volume in suspension than when dry. During the development process the particle is drawn to the surface by electrostatic forces, but it becomes bound thereafter by van der Waals forces. These increase on drying.

The resin is also chosen from a number of polymers for its ability to wet the dielectric—i.e., the dielectric will preferentially adsorb the polymer from the solvent. Thus the soft layer will have conformed to the dielectric surface. On drying this bond is enhanced, increasing the adhesion of the toner to the surface. Cohesion is also critical—it is necessary that not just the first layer be well bound to the surface. Generally, if there is good adhesion to a dielectric there is good cohesion. If not then the choice of that particular resin binder is likely to be the problem. Cohesion between different layers is best if the wettability (surface energy) of the toner polymers for the different toners increases with sequence.

Toner fixing is also aided by heat. However, heat is not designed into any of the current commercial printers; they rely upon room temperature impingement air driven by fans.

8.4 FUNDAMENTAL DESIGN FEATURES

8.4.1 Critical Features

There are three fundamental components of media for electrographic printing, regardless of the printer design, operation, or end use. These are the dielectric layer, the conductive agents, and the substrate. Each must satisfy the functional requirements of the physics of the imaging process, the most critical of which is the deposition of charge on the dielectric surface during, and only during, deliberate writing. The difficulty of design is compounded by the use of liquid toners, printer mechanical design, and especially the end use. It is even further complicated by the contradictory nature of many of the requirements.

The most important requirement for the creation of an individual dot of image density is obtaining a high charge level on the dielectric surface. As will be shown in the following discussion, this is dependent upon the voltage gradient across the gap, the time the voltage is applied, the thickness of the air gap, the composition of the gas in the gap, and the composition of the dielectric layer itself. Each of these is in turn dependent upon a large number of factors including in each case contributions from the paper. All of the following media factors impact charge deposition, and hence image density, in some way: media thickness, uniformity of media thickness, media density, paper porosity, paper surface roughness, conductive material content, conductive material distribution, conductive material chemical composition, dielectric layer chemical composition (dielectric constant), dielectric layer purity (conductivity), dielectric layer distribution (penetration into the base), dielectric layer pigment type, size distribution, and content, dielectric layer roughness, and the content of water in all layers.

Coupled to this are the printer factors which include applied voltage, write time, electrode and nib composition, wrap angle of the media over the writing head, web tension, pressure of any back electrode on the paper, contact area with the back electrode, and speed of movement of the printer. For color printing the dryness of previously applied layers (the quantity of dispersant remaining in the toned layer) is an additional parameter. Another is the nature of the image being printed—there are usually unintended differences in the densities of dots in solid fill areas versus individual dots spaced widely apart.

8.4.2 The Dielectric Layer

The dielectric layer functions, first, as a capacitor and electron acceptor during the generation of the latent image, second, as an abrader of the nibs, to keep them clean and in an electron emitting state, third, as a toner receptive surface during image development, and fourth, as may be required in a particular end use application. The capacitance of the layer is determined by the dielectric constant and its thickness. These in turn are determined by the composition of the materials used, the manner in which they are coated, and the surface of the conductive substrate to which they are applied.

Three different approaches have been employed in applying the dielectric layer to the substrate: aqueous coating, solvent coating, and hot melt extrusion. Solvent coating dominates the industry and has yet to be matched for reliability of performance and for image quality. Therefore it is the main focus of this section.

Aqueous coating formulations have been used (3) but lack the performance of solvent coatings, usually because of difficulty in preserving the dielectric layer as a contiguous insulating film at the surface of the substrate. Aqueous coatings tend to penetrate the base, and the coating methods employed, whether rod, roll, or blade, promote intermixing

of the dielectric composition with the water-soluble conductive layer. Double coating can address this (3) but adds cost and lowers the thickness uniformity of the thin layer.

Hot melt extrusion was investigated thoroughly in the late 1970s at Crown Zellerbach. This is an attractive technology for applying dielectric coatings because the layer is discrete and lies atop the conductive substrate. When properly formulated, it need neither penetrate that base nor have an open structure. The extruded layer had three components as shown in Fig. 8.10. The drawback at the time—difficulty of obtaining a suitably thin coextrudate of the polymers and polymer/pigment mixture—prevented it from being commercialized. Substrate adhesion was achieved by first extruding a thin layer of a copolymer containing carboxylic functional groups. Simple studies in the late 1980s to assess some new materials produced satisfactory imaging on some polymers but were confounded by poor adhesion to the base paper. The result, a clear but weakly supported film with an image on it, was a step towards the development of the image transfer technology described later in this chapter (4).

Solvent coating is used for all but a minor amount of dielectric paper and film products. Toluene with cosolvents such as acetone or ethanol prevails. The three primary components of the dry layer are resin, pigment, and plasticizer. There may be small amounts of other materials such as optical brighteners to whiten the media, viscosity modifiers, or tracers for coat weight measurement and control.

One of the most valuable tools available to the media designer is the microscope. Typical high-performing dielectric surfaces are shown in Fig. 8.11.

Resins

Resins with dielectric constants of about 4 to 5 are most desirable. Typical of these are polyacrylates, most especially Rohm and Haas Desograph® E 342. Polyvinylbutryal (e.g., Monsanto's Butvar® B-76) and polystyrene acrylonitrile are also employed. These are soluble in blends of toluene, ethanol, and acetone for preparation of the coating mixture. The properties endowed by these resins include good film forming (the ability to give an intact, relatively uniform coating layer with limited penetration of the base paper); high dielectric constant, charge acceptance, and charge retention; and surface pH control. The functional groups included in the resin are important for the last factor. The use of amido groups to reduce background has been patented (5).

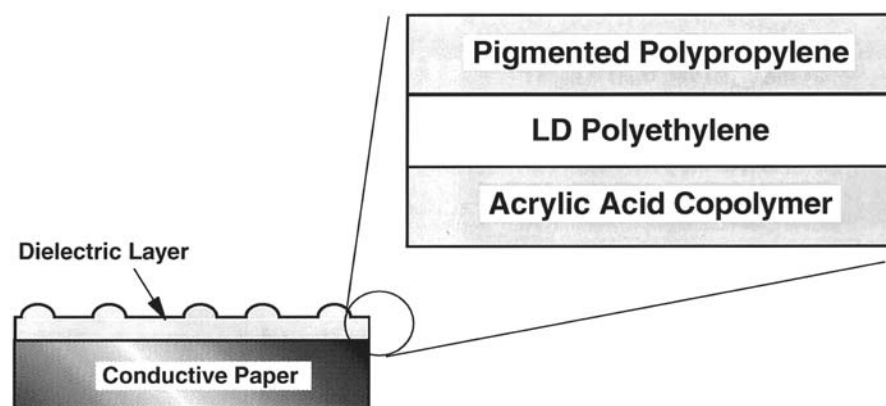
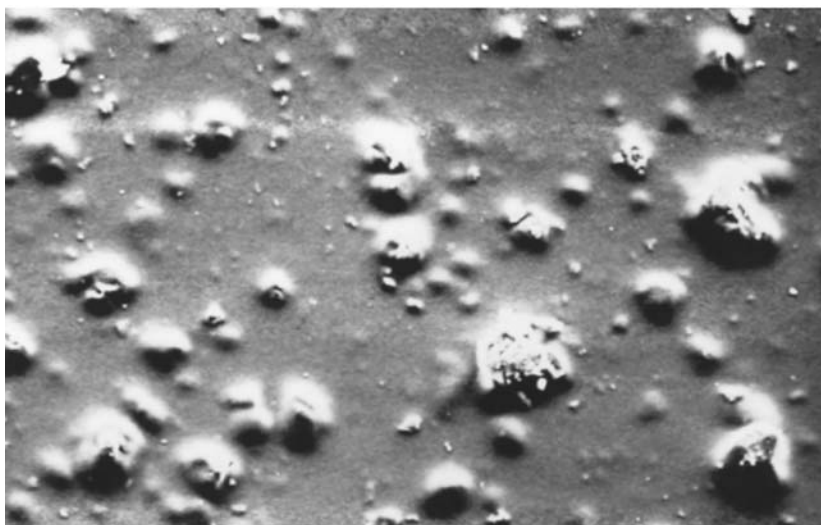


Figure 8.10 Triple-layer structure of hot melt extrusion dielectric coating.



(a)



(b)

Figure 8.11 Scanning electron micrographs at 500 $\times$: (a) dielectric paper; (b) dielectric film. (Courtesy of L. Kondik.)

Resins suitable for aqueous dielectric formulations are largely emulsions of polymers similar to those used in solvent coatings. These include various acrylics, carboxylated polyvinylacetates, and polyvinylbutyral. Cross-linking reduces charge decay in an aqueous system; perhaps the mechanism involves a reduction in the mobility of the conductive agent that inevitably pollutes aqueous dielectrics. The most advanced aqueous coating was developed by du Pont (3).

Plasticizer

Like many resins used in the dielectric formulation, Desograph E 342 is brittle. On drying it will crack unless it is plasticized with, for example, oligomers of polystyrene or other materials. These tend to be more readily extracted into toner than other components, no doubt because of the low molecular weight, but this is not generally a problem with current media nor printers.

Pigments

There are three functions of pigment in the dielectric coating. First, it controls the air gap between the nib and the surface—the so-called *spacing effect* (6,7) for which particles of about 5 to 12 μm diameter are preferred.

Second, it abrades the nibs, keeping them clean and in the proper emitting state. The ideal pigment scrapes the nib to a depth of only a few nanometers, like the finest emery polishing cloths.

Third, it protects the wet toner layer until it dries and becomes affixed to the substrate by the toner resin binder—an effect similar to providing the spacing for the air gap. It is especially critical for the dielectric transfer papers using transfer toners.

Ground calcium carbonate dominates as the pigment of choice for dielectric paper coating. It is low in cost, easily dispersed, readily available in a choice of narrow particle size ranges, and delivers consistent image quality. Additionally, it has an intermediate level of hardness so that under mild conditions it can maintain good, although not ideal, abrasion of the writing nibs.

By comparison, ground silica has a broad particle size distribution. Thus, in a formulation with an appropriate proportion of particles in the 5 to 12 μm range there can be a large number, on an areal basis, of oversize silica particles. Some of the larger ones will move down into the fibrous mat of the sheet, but too many protrude and gouge the soft metal of the nib, leaving it prone to spurious nib writing, or flare.

Precipitated calcium carbonate is available in more discrete particle size ranges and surface treatments. However, it has always been associated with either low image density or high background stain. Further efforts with surface treatments similar to those used for amorphous silica (8) may ultimately resolve this deficiency.

Amorphous silica is also popular because it is a mild abrasive agent, because it is translucent, and because it is available in controlled particle sizes. It is commonly used in this regard as a spacer. When used over highly mobile water-soluble conductive layers, it is necessary to change the surface chemistry from hydrophilic, which promotes wicking of the salts through the particle pores, to hydrophobic (8). However, by itself it has usually not been sufficiently abrasive, and hence it has needed to be blended with a harder material. Silica, unlike ground calcium carbonate, is readily sorted by air classification.

Crystalline silica (9) has been added to dielectric coating formulations to ensure high abrasion and avoid missing dots. Powders having controlled particle size a little smaller than the primary spacer can be included at low concentrations in formulations with amorphous silica to achieve this. The downside is that the abrasions themselves are large and so cause substantial nib writing and flare. A balance can be made by combining soft spacer particles with hard abrasive ones (9), but this is a difficult approach with invariable inconsistencies in performance. Crystalline silica dust is also a health hazard, and so it is unlikely to be incorporated in any new formulations.

Blending both spacer and abrasive particles can be approached also by having a fine abrasive pigment at a relatively high concentration in the coating, mixed with less abrasive spacer particles. The abrasion is then obtained from the small particles in the coating that remain on the spacer after drying.

On the other hand, a particle will protrude from a coating layer at low pigment: binder (P:B) ratios as long as its diameter is greater than the layer thickness. This means that the layer of coating over the spacer particles can have abrasive components, provided these are at a sufficient volume concentration in the formulation. It is necessary to remove the volume of the spacers themselves from the calculation—they effectively act as a discrete phase. Finely ground calcium carbonate and titanium dioxide act in this manner in formulations with spacers. This approach can be used with amorphous silica, starch, and beads of polymers such as polyethylene and polystyrene or polyacrylonitrile.

A substantial effort has gone into establishing the proper concentration of particles in the dielectric layer on film (10–12). These particles are either the abrasive elements themselves or carriers for the abrasive particles. Their surface concentration determines the ratio of nib firing opportunities to nib abrasions or emission regeneration opportunities. If the abrasive event is large, the nib can write multiple times (typically, about 10) without regeneration, although the first firing will undoubtedly have flare. The frequency of particles need only be such as to ensure that contact is most probable in an area covered by the nib during the imaging of multiple (in this case, 10) rows.

On the other hand, if the abrasive event can only sustain one discharge, the nib needs to be given a regeneration event each time the media moves forward one row. The surface concentration of the contacting particles must be high, most especially for a 400 dpi printer. The distribution of the particles on the surface is not regular, so in calculating the preferred concentration a randomness factor is required. A further effect is the size distribution of the spacers. If the abrasiveness is such that a nib needs regeneration after each firing, then the height of the spacers must be similar, otherwise large particles will bear the load for all those around them.

Frequent contact of the abrasive with the nibs is typical for premium monochrome paper grades (13). It is also characteristic of Japanese papers, where high image acuity is essential to reproduce the subtle strokes present in kanji characters. The drawback from having a high frequency is that the capacity of the surface to hold toner is decreased, so densities drop off, marks from the impressions of the drive (pinch) rollers become obvious, and toner is scraped from secondary and tertiary colors.

The search continues for an ideal surface structure, one which has proper spacing, a high frequency of nib regeneration events (all of which are gently abrasive), and the capacity to hold all the toner.

8.4.3 Conductive Materials

The conductive substrate is the embodiment of the active electrical component in the paper. It, too, is critical to the printer's ability to create a complete dot. There are a number of chemical compositions that can give conductivity suitable for electrography. They are of two basic categories, ionic or electronic. Ionic conductors include inorganic salts, organic salts, and conductive clays. As the charge carrier in these materials is an ion, and salts in air are typically hydrated, conductivity is dependent upon the water content of the material (14).

Electronic conductors include semiconductive materials such as polyanilines, tin oxide doped with antimony, indium, or copper, copper iodide, and small concentrations of good conductors such as carbon black, titanate whiskers, or metallic fibers. These materials function independently of water content; they are not affected by the humidity of their environment.

There is a substantial difference in cost among conductive treatments for papers and films. Simple economics have ensured that the dominant conductive materials for electrography are quaternary ammonium polymer salts, often augmented with simple inorganic salts. Unfortunately, as these salts are hygroscopic, the ambient relative humidity determines the moisture content of the substrate, and therefore its conductivity. Although this is a limitation, it has not prevented the universal adoption of ionic conductive technology.

Inorganic Salt Conductors

The simplest ionic conductors are common salts such as sodium chloride (table salt), sodium nitrate, and potassium chloride. Although sodium chloride is the cheapest, sodium nitrate is less corrosive. As stated earlier, because all these salts are hygroscopic, their conductivity depends upon moisture content. This is determined by the amount of moisture in the surrounding air from which an equilibrium moisture content is established.

Simple inorganic salts have a characteristic relative humidity above which they pass from solid to liquid. This property renders them unsuitable as conductors in the form of continuous films. When used with paper, however, they are applied with humectants and become part of the thin film of the water-soluble/water swellable material that coats the fibers. Conductivity (resistivity) changes continuously with relative humidity as shown in Fig. 8.12. Because the response is steep, extremely tight RH control of the printing environment is needed to enable salts to function reliably—too tight, unfortunately, for commercial air handling systems that are normally installed in graphic arts establishments.

Organic Salt Conductors

Three quaternary ammonium polymers have dominated commercial electrographic papers: polyvinyl benzyl trimethyl ammonium chloride (15), polydiallyl dimethyl ammonium chloride, and polymethyl methacrylate trimethyl ammonium chloride. The first, as Dow Chemical's ECR 34, was the most common material in use in the United States until it was withdrawn because one of the precursors is carcinogenic. A family of these organic salts is made in Japan by Sanyo Chemicals and sold worldwide under the tradename Chemistat®. It was used for one of the first-generation electrographic films (8).

Three properties set this family apart from other common polymer quaternary salts: (1) it is a good film former, (2) it is conductive without being sticky at relative humidity levels below 70%, and (3) it shows a lower variation of conductivity with changes in relative humidity.

Among its shortcomings: it is relatively expensive and tends to be used only for high-performance CAD and graphic arts media, and it may have a slightly fishy odor.

Polydiallyl dimethyl ammonium chloride is a common flocculant used in water treatment systems; thus it is readily available in high purity. While being highly conductive and relatively low in cost, it is known to create problems based upon its tackiness at preferred printing room relative humidities. Papers made with this conductive agent are almost invariably high in defects, are prone to blocking, and feel sticky to the touch. In

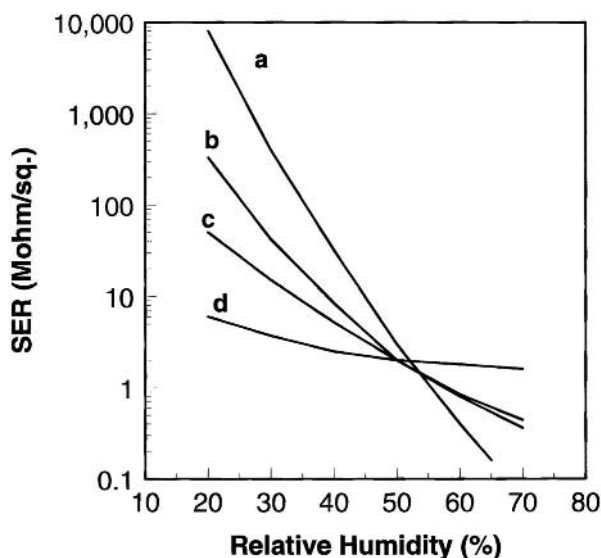


Figure 8.12 Effect of relative humidity on surface electrical resistivity of paper coated with different conductive materials, at equilibrium: (a) simple ionic salts; (b) anionic polymer; (c) cationic polymer; (d) electronic conducting pigment.

spite of these drawbacks, it is used extensively in CAD and low end graphic arts papers. Commercially it is available as Calgon's Conductive Polymer 261® or as Agestat 41T® from CPS Chemical Company.

Polymethyl methacrylate ammonium chloride is intermediate between the other two polymers in all properties: film forming, tackiness, and cost. It is found in papers of all types, especially in Europe, where it is available as Induquat ECR 69L® (formerly Makrovil) from Indulor Chemie. CPS Chemical Company also provides a similar acrylic designated Agestat 1401®. Other quaternary ammonium compounds have been used experimentally but have had limited commercial application (16–18).

Polystyrene sulfonic acid and its sodium and potassium salts (products of National Starch and Chemical) have also been used for dielectric papers and films. Because this acid is highly conductive, only thin coatings are required; but as a strong acid, it is reactive. Additionally, the humidity response of anionic salts is so steep as to make it nearly impossible to maintain adequate control of moisture content.

Because quaternary ammonium polymers are the dominant conductive treatments for dielectric papers and films, ambient relative humidity is an extremely critical aspect of electrographic printing. The equilibrium resistivity of the paper varies exponentially with relative humidity in the 10% to 55% range. This relationship is a strong characteristic, a fingerprint that serves as a means to evaluate different conductive treatments. For commercial papers using polydiallyl dimethyl ammonium chloride, it has been found that surface resistivity, R , and paper moisture content, $[H_2O]$ (in percent by weight), are related by the empirical formula

$$R = [H_2O]^{-4} \quad (5)$$

Thus a 2% decrease in moisture content can raise paper resistivity by a factor of 5!

Interestingly, surface and volume resistivity can have different dependencies upon moisture content. This can be the cause of otherwise unexplainable leading edge fog.

Paper absorbs or loses water rapidly to the surrounding air stream. Figure 8.13 shows the rate of pickup for an oven-dried paper in still air. The rate of change is much faster when the air is blown. Needless to say, in only seconds paper can lose a percent of moisture in a dry room and hence see a substantial change in performance. Given the narrow range for optimum performance for graphic arts printing, it is essential that printer room humidities be controlled tightly. A range of not more than 5% is recommended. For example, presentation media should be printed in rooms at 50% to 55% RH. This is much tighter than the norm for CAD rooms.

The rate at which paper can exchange moisture with the ambient is a function of the driving force, i.e., the difference between ambient moisture content and the equilibrium moisture content of the sheet. High-quality papers are properly and consistently moisturized within a range of no more than +1.0–0.5% upon leaving the paper mill.

There are two well-known approaches to controlling the moisture content of coated papers. First, when water-based coatings are used, the coating and paper are dried to the target. Second, when solvent coatings are used, water is added back to the paper after most of the solvent has been removed.

A device such as a Dahlgren LAS[®] thin film water applicator, or a steam foil, is normally used. Thus a dielectric paper that meets a conductivity specification within 0.5% is possible. Before this refinement was implemented, the surface resistivity of the base paper would fluctuate anywhere in the 20 to 75 M $\Omega/\square$ range, leading to large quantities of out-of-spec product. After the moisturizing step, the resistivity of the final product could be controlled within the 1–10 M $\Omega/\square$ range, a great improvement for CAD materials.

All the ionic conductive agents are water soluble. If the paper or film becomes wet, the dielectric coating will detach from the substrate. There have been many attempts to develop coatings that retain their integrity when wet, especially for use as poster and

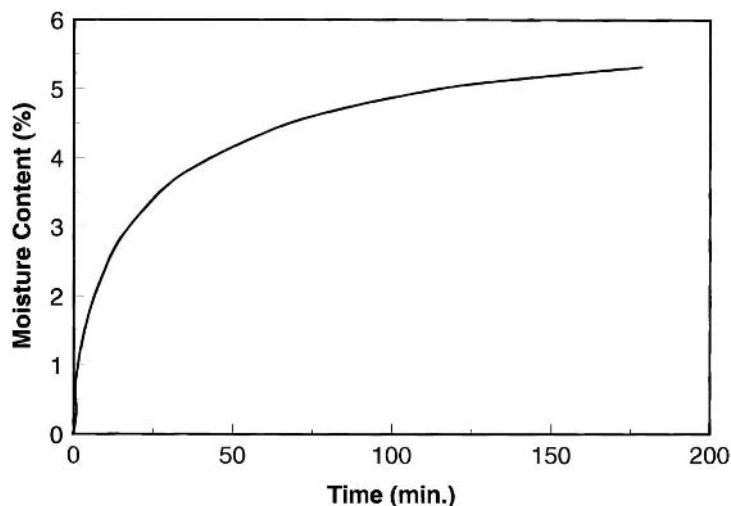


Figure 8.13 Rate of moisture pickup by oven-dried dielectric paper in still air.

billboard papers. Two approaches have been tried in dealing with this issue. The first is to include in the polymer unsaturated groups that can be cross-linked after the coating has been applied to the substrate. This has proven impractical, as it is difficult to drive to completion the necessary chemical reactions given the limitations of the dryer sections of most coating machines. Even when cross-linked, these polymers remain hygroscopic; the bond to the dielectric after wetting becomes very weak.

The second approach has been to form a copolymer of a quaternary monomer with other compounds so that the product is solvent soluble but not water soluble (19).

Conductive paper coating formulations with organic polymer salts generally contain a latex binder and a filler, to ensure that the conductive coating fills the pores between fibers and builds a good platform onto which the dielectric layer can be formed. These coatings give both structural and electrical properties to the paper. The binder selection is difficult, because most latices are anionically stabilized and immediately coagulate when mixed with a cationic quaternary ammonium polymer. Nonionic, or cationic, stabilized latices are more suitable. While most fillers are stabilized anionically, they can be dispersed in a cationic polymer solution if they are “swamped” with the polymer so that there is no chance for them to bridge between the pigment particles. Ground calcium carbonate or kaolin clays can be used.

Better solvent holdout (the ability to keep the dielectric as a discrete layer on the paper surface) can be achieved if hydrophilic polymers such as polyvinyl alcohol, alginates, or starch are added (20,21). Fluorocarbon surfactants can also be used for this purpose (22).

A further factor in applying conductive coatings is the placement of the conductive agent in the paper, and its effect on curl. Using alcohol as a cosolvent can modify the final position of the conductive agent and also allow unbalanced coatings to be applied with minimal curl. This option is becoming more difficult to execute with the rising pressure to reduce emissions of volatile organic compounds (VOCs). Coating monomer blends and curing them by UV radiation is a more environmentally friendly solution. The formulation can be adjusted to optimize penetration, conductivity, and holdout of the dielectric. This approach is now being practiced by Rexam (23,24).

Ionic Conductive Pigments

The montmorillonite clays have expanding lattices in which the hydrated ions that counterbalance the structural charges are able to move. This suggests their use as conductive agents, especially as they are pigments and water insoluble. Various attempts have been made to use natural clays in dielectric papers and films (25,26), but inability to obtain a reliable supply of a consistent product has handicapped most efforts.

Laponite®, a synthetic hectorite clay from Laporte, has good conductivity (27–29) and is available in a variety of forms. One that is best suited for paper coating has a component, neighbourite, which cannot be bound and causes dusting, a problem that has been solved by centrifuging (30,31). Laponite sees use in wet strength papers (32) and premium graphic arts papers. Although it is still affected by ambient moisture, Laponite exhibits the least RH dependence of all the common ionic conductive agents.

Conductive clays must be formulated with binders so that they have physical integrity. Zeolites have pore structures that can also act as channels for hydrated ions but have not found commercial application for dielectric papers (33).

Tin Oxides

Doped tin oxides are electronic semiconductors. They are also water insoluble, making them highly desirable for special dielectric media applications. Invariably, these applications have been with film or filmlike media, as they are too costly for dielectric paper coating. It is interesting to note that those end users who cannot afford to install ambient humidity control are also not prepared to pay the premium price for tin oxide doped media. Ironically, those electrographic printing establishments that produce high-value-added prints and can justify a higher media cost already have the humidity controlled environment that will enable less costly conductive treatments to be used effectively!

Dopants used to enhance the conductivity of tin oxide include indium (34,35), antimony (3,9,10,36), and copper (37). Fluorine is a new dopant for commercial grades.

The dominant application driving the use of doped tin oxide conductive layers was film for CAD. Clarity is necessary because the film is used either as a diazo master or as an overlay. Achieving this high level of transparency with a naturally white or off-white pigment necessitates grinding it until its particle size is too small to cause light diffraction, i.e., until the average particle size is about 50 nanometers (9,10). When combined with antimony doped tin oxide, this approach has been the most successful for electronic ground planes in electrography.

The same pigments can be used with much less grinding for opaque films such as direct write, pressure-sensitive vinyls. This promises to be a major growth area for these materials.

Formulating with these materials is largely a matter of adding the small amount of binder that is needed to give the coated layer physical integrity and flexibility without sacrificing the conductivity. With too little binder, the coating will crack if bent and will show poor adherence to the substrate. On the other hand, with too much binder the coating will lose conductivity because the particles will not be in ohmic contact. A further compounding factor is that solvent dielectric coatings often interfere with the electrical characteristics of this layer.

An alternative approach to obtaining a thin clear film depended upon sputtering a mixture of tin and copper in a controlled atmosphere of oxygen (37). Much of the formulation expertise lies in preparing the metal electrode for sputtering. This technology failed for lack of exploitation during a window of opportunity that closed when pigment doped tin oxides were commercialized.

Polyaniline and Other Electronic Conductors

The first commercial electrographic film, Kodak's product introduced in the early 1980s, was rendered conductive with polyaniline, an electronically conducting organic polymer (38,39). It was humidity independent, water insoluble, and tough. It was, however, colored and expensive, properties that have been the bane of most electronic conductors in this technology.

Potassium titanate whiskers (19,40) and ground copper iodide (41,42) have also been used for conductive media but with little market success.

8.4.4 The Substrate

Commercial electrographic printing substrates fit into two classes, papers and films. As films are usually dimensionally stable, durable insulators, the focus in this section is on the electrical properties of the base sheet and other factors that affect the dielectric layer.

In the imaging process, the properties of the base paper must be such as to allow complete discharge of all the nibs. There are three other important considerations: strength, printability, and esthetic properties.

Base Paper Electrical Properties

A most important electrical property of the paper substrate is the relaxation time between the two sources of the voltage gradient. For a given charging pulse length this time must be significantly shorter to ensure maximum charge deposition. A ratio of about 10:1 to 15:1 is a good guide in developing conductive substrates. For write times as short as 40 μs , the optimum base relaxation time is 4 to 6 μs . The relationship between relaxation time and write pulse length is illustrated in Fig. 8.14, where the total write voltage is plotted against the write time for two values of base relaxation time, 7 and 64 μs . This plot, which was constructed from experimental data, shows that the maximum potential across the dielectric at 40 μs write time can be achieved if the base relaxation time is 7 μs or less, while at 64 μs relaxation time the effective potential is significantly reduced.

The conductivity of the base paper can vary significantly depending on the placement of the conductive material. In general, conductivity is applied by coating processes which tend to leave the bulk of the material near the surface. Even size press applications tend to be surface oriented because the formulations are pigmented and of moderate viscosity. The result is papers that have good surface conductivity but low volume conductivity. Achieving high volume conductivity generally requires large quantities of conductive agent—an expensive addition to the unit manufacturing cost.

Requirements for the earlier CAD multiplexed plotters with back-grounding generally performed well at surface resistivities of 5 to 10 $\text{M}\Omega/\square$ and volume resistivities of about 1 to 50 $\text{M}\Omega \cdot \text{cm}$ at 50% RH. Front grounding CAD printers perform best with a highly conductive layer under the dielectric, usually near 1 $\text{M}\Omega/\square$, while a minimum volume resistivity of about 50 $\text{M}\Omega \cdot \text{cm}$ is sufficient to ensure the countercharge is grounded.

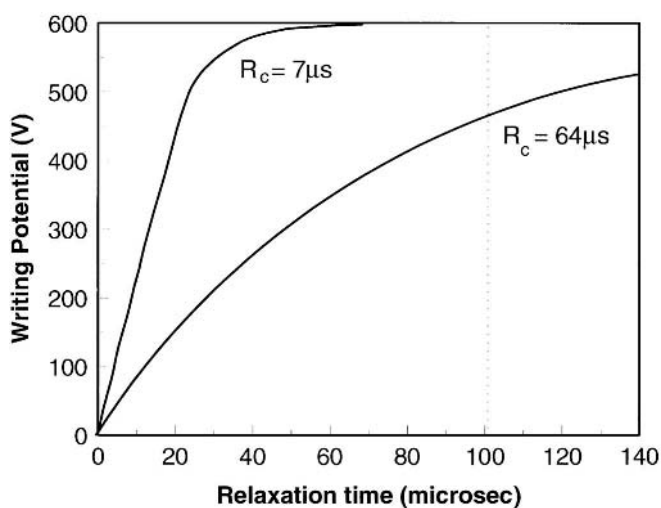


Figure 8.14 Effect of base relaxation time on charging efficiency.

Graphic arts printers now perform at higher speeds and with larger solid fill areas than a decade ago. In all cases these require SERs of 1 to 3 $\text{M}\Omega/\square$ and VERs of less than 1 $\text{M}\Omega \cdot \text{cm}$. There remains with these printers a narrow sweet spot where the complications of multiplexing between the region where conductivity is too low (low image density, many unpleasant artifacts, and low-density striations) and too high (reverse image striations and strong overtoning) do not exist.

Printers with individually driven nibs are much more tolerant, especially when using a paintbrush mode to write dots. Because the write time is long, even poorly conductive papers will write acceptably for line work. But should the paper be used for printing heavy solids, it becomes necessary to provide sufficient volume conductivity to ensure that the countercharge is properly dispersed. Generally speaking, the SER should be lower than 5 $\text{M}\Omega/\square$ and the VER below 0.5 $\text{M}\Omega \cdot \text{cm}$. As described above, control of the amount of conductive agent, its placement, the paper moisture content as packaged, and the relative humidity of the print room are all critical factors in maintaining proper paper electrical characteristics.

Properties that Influence the Dielectric Layer

There are substantial interactions between the base paper and the dielectric coating that can dramatically influence the image. The base properties should be such that the dielectric layer is of uniform thickness (uniform capacitance) and is uniformly distant from the nibs (uniform emission and discharge); and the high points of the layer should be in uniform contact with the nibs (uniform abrasion).

Minimizing grain requires that the penetration of the coating into the base paper must be minimized by uniform solvent holdout. The Kubelka–Munk equation describes the penetration of a fluid into a pore:

$$L^2 = \frac{(R_p \gamma \cos \theta)t}{2\mu} \quad (6)$$

where L is the distance of penetration that occurs in time, t , R_p is the pore radius of the substrate, γ is the surface tension of the fluid, and θ is its contact angle, while μ is the fluid viscosity. Keeping the dielectric out of the paper is then aided by having small holes, high viscosity, low surface tension, poor wettability, and short times. The ideal paper will have not only optimized values of these but also consistent values.

Consistency of pore structure has two components. The first is time dependent. The papermaker must make the same product minute-by-minute, hour-by-hour, day-by-day, and month-by-month. Good process control, consistency of supplies, and regular preventive maintenance are the hallmarks of good practice and will show up in the statistical control charts for air porosity, or solvent holdout using the Hercules Size Tester.

The second pore consistency determinant is spatial. Paper has short-term mass variations from the flocculation that occurs during sheet formation on the wire. The flocs have more matter and are densified to a greater degree during calendering. Pores between the fibers are then much smaller than those in the areas between the flocs—the interflocs. If the formation is poor and holdout is marginal, it is likely that the paper will be grain prone. Poorly made paper has streaks of greater or lesser mass originating from the head box. These too can reflect grain to differing degrees across the image.

Poor formation on a sheet with high solvent holdout will still show poor imaging, but in this case it is more from the dielectric surface being at different distances from the

nibs—it is closer on top of the flocs and further away in the interflocs. The result is mottle—density differences that follow the paper formation. Mottle and grain often go together, although there may be a grainlike deficiency if the paper roughness is the main contributor to the gap. Smooth dielectrics will have low density on the tops of flocs.

The printer design will either exaggerate formation-related artifacts or relieve them. Wrapping the paper around the writing head reduces mottle and grain tendencies (paper will distort so that the inside surface will follow the contour). Longer write times, higher voltages, and good grounding also lower mottle and grain levels.

Paper Strength Properties

Strength properties include tear, tensile, elongation, burst, fold endurance, stiffness, and internal bond, factors that are important for the processing and handling of the material during manufacture, printing, and end use. In general, if the paper has sufficient strength to be coated, it can be printed. Most of the emphasis on these properties is for end use applications.

Paper Printability Properties

Printability refers to those properties needed to ensure that the material can be properly processed in high yield in the printing establishment. Although normal paper strength factors are included, freedom from tears, holes, and wrinkles are more critical. Additionally, flatness and straightness are required. Papers that are not flat, papers with large edge flutes or puckers, may not be held flat going across toner fountains, rollers, or vacuum channels.

There is an interaction between flatness and stiffness in various printers. In those with vacuum channels, nonflat paper that is flaccid will be pulled down so that there is a good vacuum seal. If, however, the paper is stiff, the vacuum seal may be broken and (unless the printer has a low vacuum detector) liquid toner may pass into other parts of the machine. In printers where either the head or elements of the toner system form hard nips with the backing electrode, nonflat flaccid paper will tend to fold and crease, whereas stiffer paper will transport smoothly. The solution to both issues is flat paper.

A related issue is nonstraight paper. If the paper is bowed, unless its elasticity allows the printer to pull out the bow, creases and wrinkles are probable. Roisum (43) has defined both flatness and straightness and given guidelines for good runnability in web handling equipment. Additionally, bow can give registration differences between the two sides for multicolor prints.

A factor that has a much greater influence on registration, though, is dimensional change during printing. Paper shrinks or expands depending upon its water content. Some papers will grow by 1% when equilibrated to a 10% increase in RH. If the paper is not at equilibrium in the environment that it is being printed in, then it will either be absorbing or losing water as the printing proceeds. This can have annoying effects for precisely defined images such as dither patterns and overlaid lines. The effect can readily be visualized by printing four color vertical and horizontal lines spaced by one line. Dimensional changes of as little as a 20 μm will show up as color shifts or color bands. This problem is minimized if paper is provided with a moisture content equivalent to what it would have at 50% RH and 70°F, and the printer is kept in the same environment. This is typical practice for good offset printing houses, whose behavior digital printers need to emulate. The hygroscopic expansivity of a typical dielectric paper is shown in Fig. 8.15.

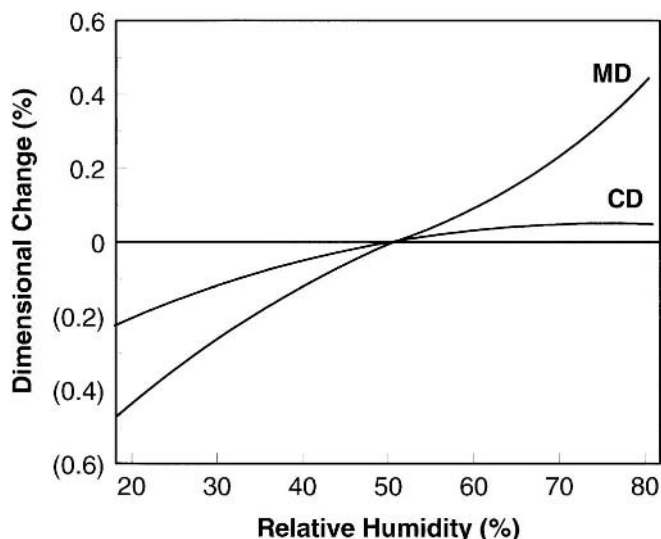


Figure 8.15 Hygroscopic expansivity of dielectric paper initially equilibrated at 50% RH, where MD = machine direction, and CD = cross-direction.

Gross misregistration is generally attributed to a mismatch between the coefficient of friction of the back side of the paper with the rubber tread of the drive roll. Unless there is a good grip, the roll may turn at a speed different from the paper. A consistent level of roughness is recommended. This may come from the paper fiber structure or from the pigmentation and binders in the coatings. In designing these coatings it is critical that they do not come off the paper and accumulate on any part of the printer they might contact. All printers have stationary elements of some type, whether this is a turn bar, a back electrode, or a grounding element. Once material begins to stick there is a snowball effect which continues until the effect is sufficiently gross that the operator stops the printer and cleans up, or the defect eventually tears the web and aborts the run.

Two printer designs that had little issue with registration were the Precision Image Corp. helical scan printer and the Raster Graphics 22-, 24-, and 36-inch printers. All held paper in sheet form firmly onto metal drums or belts. The dot placement was then quite precise (44).

Paper Esthetic Properties

Esthetic properties include color, opacity, whiteness, gloss, brightness, and freedom from dirt, holes, and pinholes. These influence the appearance of direct image prints, especially in background (white or lightly colored) areas. Although whiteness, for example, is generally considered an advantage, overall these properties are most properly defined by the end use.

8.4.5 Overall Design Considerations

The design of a new medium for electrography is nowadays a major task. Development scientists need access not just to good laboratories and pilot equipment but also to a typical end user facility where the vagaries of the printers are understood in a way that focuses

upon application output. Additionally, there are few opportunities to develop a paper for a single printer that functions with only one toner. There are at least two sources of toner and also different variants from the OEM to be considered. Additionally, papers are expected to function in earlier, obsolete, printers, and often, because many printing shops have machines from two OEMs, the expectation crosses platforms.

8.5 IMAGE QUALITY

At first appearance, images produced electrographically by skilled printers can rival those from offset, ink jet, and even photography. Only on close inspection can the limitations be seen. On the other hand, it is a difficult technology to practice, and from the media manufacturer's perspective, it offers endless possibilities to introduce artifacts and imperfections. In this section, the basic nature of the image is described, the causes of artifacts and imperfections are discussed, and comparisons are made to the images available from other technologies.

8.5.1 Image Composition

The most commonly referred to image attributes in the digital printing world relate to printing fine detail, bright colors (solid area), and matching targets (process colors), all without deficiencies.

Resolution

Electrography is a binary process—a dot is either there or it is not. Although there have been attempts to modulate dot size and dot intensity, the complications of the writing process, especially during the generation of the latent image, have thwarted these efforts. This immediately limits resolution, and as the dots are larger than 100 μm the best image appearance requires that it be viewed from at least 4 feet. At this distance, the dots are barely resolved by human eye; they merge, creating the pleasing illusion of a continuous tone image.

The effect of resolution is most obvious with process colors, which are generated, of course, by printing different concentrations of dots of the four primary colors. When light colors are needed, the individual dots are far apart and again quite readily visible, especially if a small amount of black or magenta is being applied to a white or pale yellow background. Intense colors are less affected by dot size.

STC's solution to hiding the visible dots in light colors, most obvious in dye sublimation printing, is its V color process, which uses the three subtractive primaries—cyan, magenta, and yellow—in full strength, along with two additional toners: light cyan and light magenta. Black is generated using three process color. Dark colors are built from the standard-intensity tones, while the lights are made with yellow and the low-intensity cyan and magenta.

Solid Colors

Solid colors have all of the media surface colored with image, often saturated or near saturated with one of the primaries. While this might be seen as relatively straightforward to produce, considering that there are no worries about resolution nor dot drop out, clean, pure, uniform, and consistent solid colors are the most difficult demand for the system to fulfill.

Process Colors

The critical issue in developing a good color palette for a binary process is to obtain the proper concentration of dots of the different colors in a way that is acceptable for the end use. Colors in most CAD software was with pixels, or matrices of dots, often 3×3 or 4×4 . These are prone to patterns from the regular arrangements of the dots, which is actually desired in CAD but unacceptable for most graphic arts. Similarly, except for long distance viewing, multidot pixels, which for a 200 dpi printer could be 50 dpi equivalent, are unwanted in imaging. The coarseness of texture is visually displeasing. A substantial breakthrough for the technology was the generation of software that introduced error diffusion. A recent refinement, well received in graphic arts, is stochastic dot placement. Essentially all graphic arts work is now done with dithering that randomizes dot placement and gives process colors with little organized structure.

8.5.2 Typical Image Properties

Dots and Lines

On good media individual dots made with round wire nibs have a high degree of circularity and uniformity (45). 200 dpi printers have dots about 220 μm in diameter, while 400 dpi printers produce roughly 160 μm diameter dots on the same media. In each case the dot is substantially larger than the nib—the discharge obviously spreads laterally about 45 to 50 μm . The degree of spreading is controlled by the electrical characteristics of the paper, especially those factors that determine the amount of charge that can be deposited, and also by the paper surface roughness. Rougher paper produces larger dots. The resolution of the technology is limited by the amount of dot spreading (dot gain)—the complexity of using closer nib spacing is not repaid with better resolution, as the dots will be at least 100 μm from even the finest nibs. (Spurious nib writing shows that finer resolution would be possible with a process that relies only upon emission without the avalanche.)

Line quality reflects the nature of the nib, whether rectangular or circular, and the charging sequence, whether pulse or duration. Circular nibs give lumpy lines in all directions, while rectangular nibs have high line quality MD and CD but show steps for lines at angles to the paper direction. Paper surface roughness also affects line width uniformity—the line width corresponds to the microroughness.

Solid Areas

Solid areas are more difficult to print than dots or lines because of the interference by residual charges in adjacent areas. With the single pulse printers the dots formed are more likely to be donut shaped and have lesser density in the center—a consequence of the field never reaching its peak. Overall, the density is reduced. The “paintbrush” printers show a different response—they have more difficulty in fully imaging the total surface and tend to leave the higher points without coverage. It is surmised that these printers deposit charge in a multitude of small discharges, confined to small locations rather like lightning strikes. The charge is then highly directed. It is perhaps this factor that distinguishes the two in terms of ultimate quality.

The major media characteristic that influences density is dielectric coating thickness—higher coat weight means less density as predicted from capacitance values. Figure 8.16 is a normalized example. There is a maximum density because at low coat weights the dielectric is too thin to hold the charge—it will pass straight through. Note the steeper

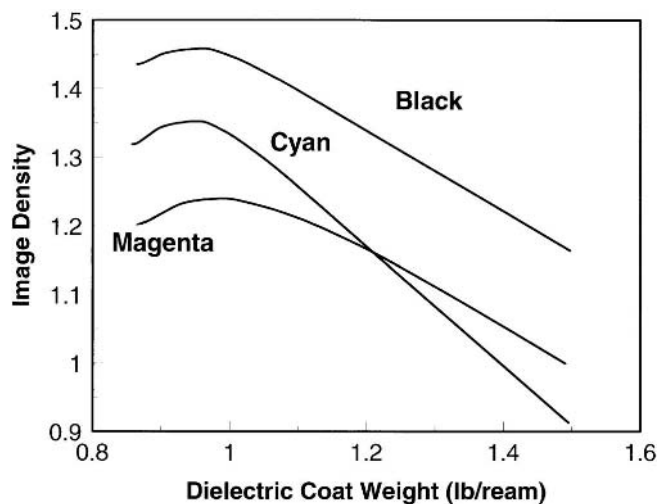


Figure 8.16 Typical relationship between dielectric coat weight and solid area image density.

response of the cyan toner—some cyan toners have distinctly different resins and so behave uniquely. The actual density that is obtained in any system is as much a function of the toner, the printer, and the mode of operation, as it is of the media. The stronger systems tend to give black density of at least 1.50, cyan of 1.45, magenta of 1.35, and yellow of 1.15. This allows large gamuts to be achieved directly, with a substantial further boost from overlamination.

Consistency of density is a major determinant of quality. High quality offset printing maintains image density variations of less than 0.05 units within any sheet and within a run. To maintain that degree of consistency it is essential that variations in the dielectric coat weight are held below 0.06 lbs./ream, or less than about 5%.

The matte nature of the image detracts from its initial visual impact—the apparent image density is low compared to other printing processes especially on glossy material. The porous pigment structure of the toner layer means that light is scattered within the colorant. Intensity can be enhanced when the air is displaced from the toner layer. This can be done by heating the toned image to cause individual particles to coalesce. A hot roll laminator is particularly effective for this purpose. Apparent density can also be enhanced by overlaminating with either hot or cold laminates, or by applying an overlacquer. Image transfer paper takes advantage of this factor too (45).

8.5.3 Image Artifacts

Electrography has its own lexicon describing image artifacts, so many of these are unique. The most common two that interfere with line and dot quality are flare and drop outs (missing dots). Voids, glitches (zippers), striations, reverse striations, overtoning (overplating), mottle, grain, bleeding (tailing), pinch roll marks, and toner scraping all detract from solids. Background areas and light colors can show spurious nib writing, ghosting, and stain. Furthermore, the image can be spoiled by scratches caused by material from the dielectric building up on the writing head, or from the backside accumulating on rolls, electrodes, and stationary elements.

Flare

Flare manifests itself as large “explosions” of charge, occurring somewhat randomly around otherwise well-formed dots (Fig. 8.17). They are typically small, rounded, and on the leading edge of the dot (the trailing edge of the writing nib). They are more problematic with 400 dpi than with lower resolution printers. In severe cases they may double the area of the dot. The flare area, however, is of lower density than the dot proper. In graphic arts, flare is a problem with both light tones and halftones—in the latter case by making the leading edge of a color much more intense than the bulk.

The extent of flare is dependent upon the work function of the nib metal (the ease at which it emits electrons), the roughness of the media, the abrasiveness of the media surface, the relative humidity, and the writing voltage. Electron microscopy has been used to investigate media surfaces directly before large flares. Typically, a substantial abrasive event is found. Metal fragments, like turnings from a lathe, have also been seen nearby on strongly flare-prone media. It is now believed that flares are explosive events that occur during the plasma discharge of conductive shavings abraded from the nib surface. These shavings will accumulate at the trailing edge of the nib. They will not repeat—once burnt off they must be regenerated. They will become visible when nibs have had substantial exposure to abrasion without writing. They can also be seen after cleaning the surface of the writing head by lapping, that is, removal of undesired deposits using abrasive materials.

Although printer manufacturers have developed certain techniques to reduce flare (46,47), it remains as one of the unwanted compromises in electrographic printing technology.

Dropouts

Missing dots are called drop outs whether in a halftone area or in a line. Typically they are measured in line patterns because they are much more visible to the naked eye. The effect in CAD is loss of data, which is unacceptable. In graphic arts, dropout is undesirable but unacceptable only in gross cases.

Dropouts are seen when nibs do not discharge as programmed. The most common cause is insufficient regeneration of frequently firing nibs. After a nib has fired, the field gradient needed to cause spontaneous electron emission is raised. When there are a large number of firings in sequence, eventually the nib will not fire, unless it is regenerated.

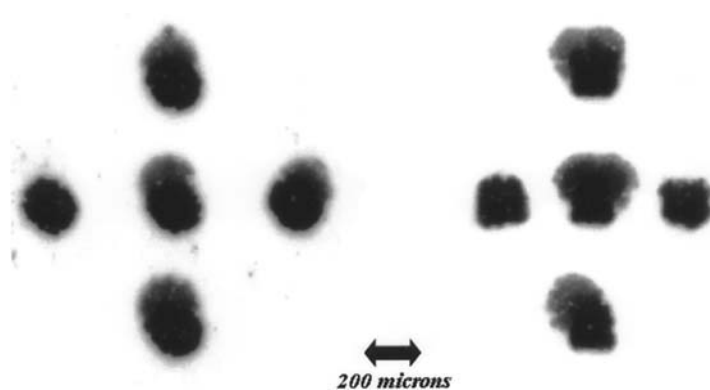


Figure 8.17 Typical examples of flare. Left: wire nib. Right: ribbon nib. (Courtesy of T. McBride.)

These methods are effective: increasing the abrasiveness of the media, increasing the pressure of media onto the nib by raising the force from the back electrode, and raising the applied voltage. Using pigments of greater hardness, of greater size, or of greater frequency in the dielectric is the typical media design response to inadequate abrasion. Alternatives are harder dielectric resins, less residual solvent in the layer, and harder conductive substrates.

Dropouts are seen only when nibs are fired in isolation. When adjacent nibs are fired there is a synergistic effect from charge spreading that ensures the discharge, as one nib triggers the discharge of its neighbors.

Voids and Starvoids

Voids are areas in dense solid colors where the image is missing. They are most commonly caused by lumps of matter that increase the distance between the media surface and the nib beyond that at which discharge can occur. They may also be formed by large holes in the dielectric or by the absence of conductive agent in the substrate.

Starvoids are voids in only one color of a multicolor image—the void-causing event being present for only some, but not all, of the printing passes. Particles as small as 50 μm can cause visible defects. Obviously, coating lumps, dust, dirt, dandruff, and paper fibers can be the problem.

A common cause is pickoff of conductive matter from the web that is transferred to the dielectric surface in the roll. The pickoff may happen in the printer but is more commonly an artifact introduced during the paper manufacturing process. With modern production operations in place, void levels can be directly related to dust levels in printer rooms. In general, printers that produce consistently clean prints have clean rooms with wet-mopped floors, low airborne dust levels, and no trash. Multipass multiplexed printers are the most prone to these problems—single-pass machines offer little opportunity for web contamination.

Glitches

There is an artifact that is unique to solid prints in multiplexed pulsed printers. Glitches, also called “zippers” because of their characteristic appearance (see Fig. 8.18), are formed when a conductive pathway through the dielectric shorts out a nib. This means that the conductive layer near the nib will not hold charge, and the voltage gradient between it and the neighboring nibs will be too low to produce a proper discharge. When the printer moves forward, the short circuit stops and printing resumes. Glitches commonly persist for only one or two line widths.

Commonly glitches come from paper fibers, holes from bubbles in the coating or pinholes in the base, lumps of conductive material, or pickouts of dielectric pigment particles. They also may be formed by conductive polymer wicking through the pores of hydrophilic spacer particles (8). Rashes of glitches are often seen when the dielectric coat weight is too low.

Striations

Multiplexed printers also suffer from striations, or low-density bands associated with the boundaries of the elements of the backplate. They occur when printing solid colors. When groups of nibs fire, there is a residual charge left in the conductive layer under the dielectric. If this charge is not quickly dissipated, the intensity of the adjacent image will be reduced. Xerox introduced ping-pong writing sequences so that the adjacent groups were

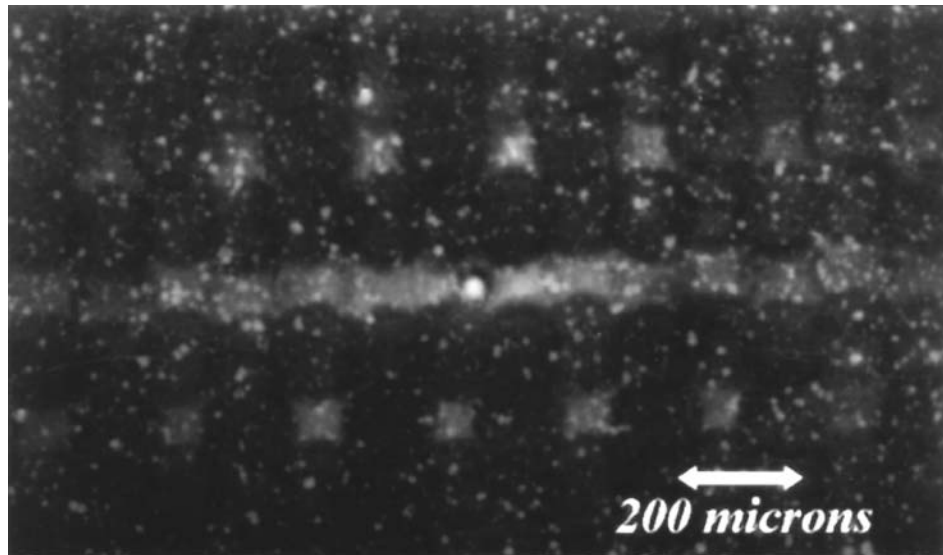


Figure 8.18 Glitches in a solid image. Note the hole in the center. (Courtesy of T. McBride.)

not written sequentially (48). This helped significantly until other speed-limiting factors were overcome and the issue reappeared in less than optimum situations.

Striations are seen when the relaxation time for the media is long compared to the time between adjacent nib groups printing. The characteristic media deficiency is insufficient conductivity in the base and especially to ground. Often it is seen with media that has been allowed to dry out, is being printed at high speed in a room of lower than optimum relative humidity, or was perhaps insufficiently conductive for the application. Ways to reduce the problem include raising printer room humidity, increasing printer writing voltage, and running the printer at a slower speed.

Reverse Striations

Reverse striations—high density bands between the backplate segments—can occur if the media is too conductive. This is often seen with front-grounded printers when media moisture content is relatively high. Paper should be provided with a narrow range of moisture content—it should be within 0.5% of that it will have if equilibrated at 50% RH. The protective packaging used by most manufacturers should keep it at that level for extended periods.

Overtoneing

If the charge deposited on a dielectric sheet is not neutralized by toner it can persist for long periods. On any subsequent pass this charge will attract toner. Thus cyan can become mauve and magenta red. The phenomenon is called *overtoneing* or *overplating*. Likely causes are dielectric coat weights that are too low, writing voltages that are too high, insufficiently charged toner, or a development time that is too short.

Overtoneing can also occur on a small scale and reflect paper base formation or fiber structure. The relationship between coat weight and degree of overtoneing is well known

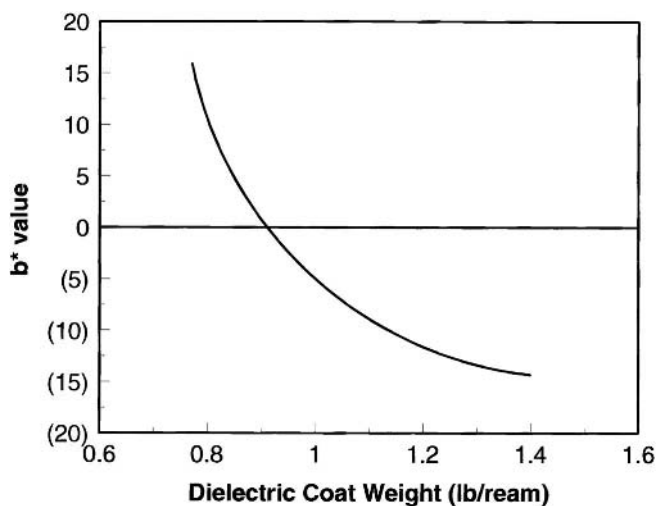


Figure 8.19 Effect of dielectric coat weight on overtoning of magenta with yellow. Yellow shift is shown as b^* .

(Fig. 8.19). Maintaining consistent color with heavy solid areas requires close attention to dielectric coat weight on both a macro (roll-to-roll) and a micro (point-to-point) scale.

Mottle

Cloudy density patterns in the image of the order of several millimeters are described as mottle. Inevitably, they follow the formation of the base paper (see for example Ref. 44). In these areas the paper thickness and density vary so that the conductive coating, dielectric layer, or gap may vary in thickness. The mottle pattern is often visible as either overplating or grain.

Grain

Fine structures that are improperly toned are referred to as grain. Most often they correlate with high paper roughness in which poorly toned areas mirror gaps between fibers. In these areas the dielectric surface is too far from the nib. Poor solvent holdout exacerbates this imperfection.

Topographic analysis is useful for studying grain. The average surface roughness for good paper should be not more than $2\text{ }\mu\text{m}$ (13). The surface itself should be about 5 to $10\text{ }\mu\text{m}$ below the plane of contact of the spacer particles. Pits deeper than $10\text{ }\mu\text{m}$ will not be properly toned.

Mottle and grain can both be measured by image analysis (49).

Pinch Roller Marks

There are several artifacts that arise when media is too smooth. Pinch roller marks appear when these drive elements come in contact with the wet toner and leave an impression. A Sheffield roughness of about 100 mL/min prevents this. The toner layer must itself be thick, thus the problem is associated with solid secondary or tertiary colors where more than one toner is laid down.

Toner Scraping

Toner scraping is also symptomatic of a media surface that is so smooth that it cannot protect the incompletely dried, liquid toner layer. Contact with stationary elements scrapes off the weak toner layer. This is a particular problem in single-pass machines where the dry time is limited, and again is seen in the high-density areas of secondary or tertiary colors. The thickness of a normal single-toned layer, in comparison to the roughness of the dielectric, is shown in Fig. 8.20.

Bleeding

Bleeding and tailing are terms used to describe fuzzy outlines around printed images. The usual cause is under charged toner.

Ticks

Sometimes on low-grade papers at high humidity, little check marks in the machine direction are seen at the leading and trailing edges of features such as lines. These repeat each time a particular nib fires. Ticks (also extradata) arise from conductive material transferring by electrophoresis from the paper surface to the writing head; they extend the region of nib discharge.

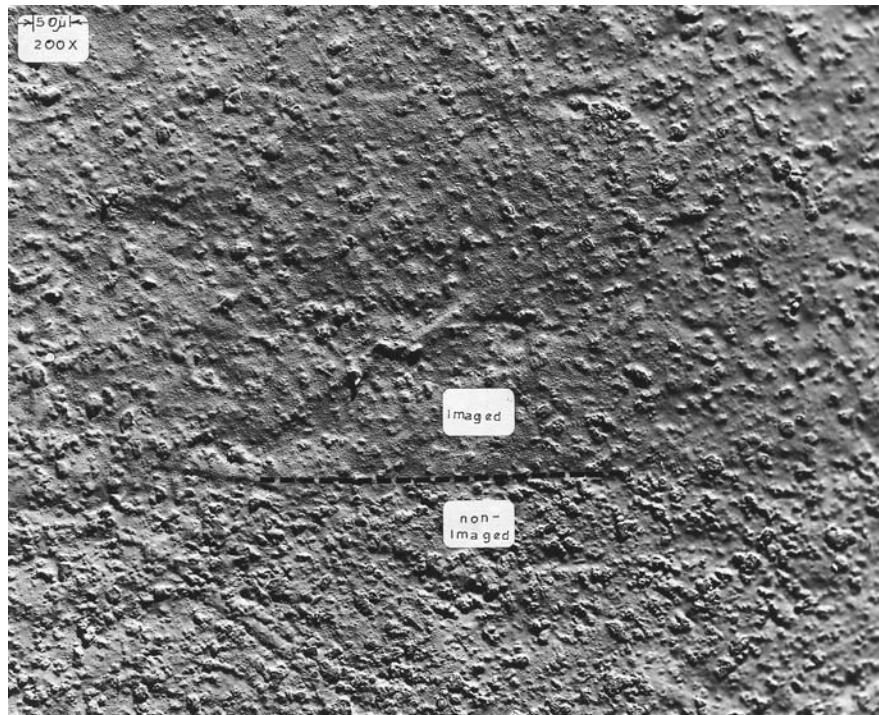


Figure 8.20 Photomicrograph at 200 $\times$ of imaged (top) and nonimaged (bottom) dielectric papers. (Photo courtesy of D. Quackenbush.)

Spurious Nib Writing

Like flare, *spurious nib writing* (the characteristic trail of dots is shown in Fig. 8.21) is another artifact unique to electrography. It has essentially the same origin: excessively large abrasive events that produce metal spurs on the trailing edges of the writing nibs. When pulsing the printhead in the nonwriting mode, the field strength at the spur may be sufficient to cause spontaneous electron emission (see Ref. 50 and Section 8.4.2). Close microscopic inspection generally shows that it starts immediately after a large pigment particle or clump of poorly dispersed particles passes across the printhead.

Ghosting and Leading Edge Fog

Reflection of the image in nonimage areas is called *ghosting*. The most common type is leading edge fog which is seen when the countercharge is unable to move freely to ground, but can ground capacitively through the toner fountain. This charge then attracts toner into unwanted areas.

Stain

Any other accumulation of toner in otherwise unimaged areas is often classified as *stain*. This may be caused by entrainment of toner in the media surface crevices, by stray electrical fields, or by electrochemical attraction between the dielectric surface and the toner particles. Resin choice and pigment treatment have a strong effect on stain.

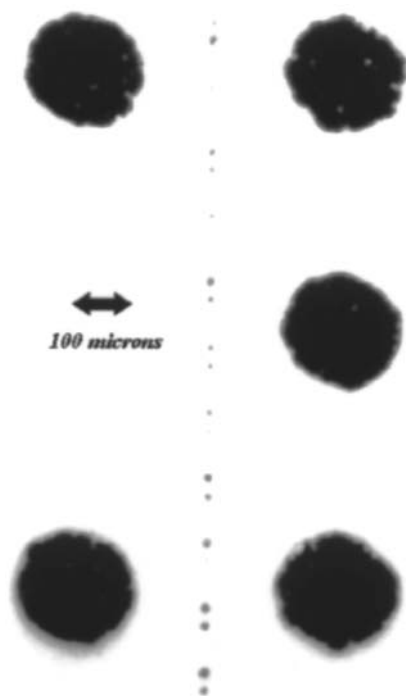


Figure 8.21 Spurious nib writing among regular halftone dots. (Courtesy of T. McBride.)

Other Defects

In addition to the above artifacts, the image can be spoiled by scratches caused by material torn from the dielectric layer that accumulates on the writing head. Similarly, residue from the backside of the dielectric paper or film material can accumulate on rolls, electrodes, and stationary elements causing image defects. There is also a myriad of defects that can be introduced by careless workers responsible for handling the media. Such damage is beyond the scope of this chapter.

Overall Quality

The manufacture of dielectric papers and films involves complicated operations and processes that require absolute attention to detail, rigorous quality systems, and thorough, frequent review of the quality control data, to ensure that good-quality imaging can be obtained reliably. Consistently obtaining high-quality imaging is also the responsibility of the printer operator, who must be well skilled at balancing the various factors under his or her control.

8.5.4 Comparison to Other Wide Format Printing Technologies

The quality of electrographic printing can be quite high when all parts of the system are optimized and the image being printed has been well chosen. With overlaminating it is possible to have images that appear flawless when viewed from a moderate distance. Thus electrographic images find extensive use in point-of-purchase displays, posters, billboards, truck signage, and other wide format reproduction applications. It is when the image is inspected closely or when compromises must be made that the flaws inherent in the technology become apparent. For closely viewed images electrography also lacks the resolution and fine structure of halftone technologies such as offset printing and continuous ink jet. However, it is much better suited to short runs than offset and of course has productivity benefits over this type of ink jet.

Screen printing is well suited for solid designs with extensive use of spot colors and highlights. However, producing process colors with this method requires extensive preparation of the screens and has long lead times. Electrography, while doing an adequate job of solid prints, executes process colors well, making it a strong contender for wide format imagery.

8.6 PRESENT TYPES OF DIELECTRIC PAPERS

Today there exists a broad range of dielectric papers available for the operators of electrostatic printers. This includes products for the conventional electrostatic writing process, as well as a choice of papers for transfer printing. In the former category are distinctions by image quality, basis weight, and transparency to ultraviolet light. Among the latter, we recognize three product types: toner transfer, image transfer, and sublimatic printing. This section deals with the construction and use of the dominant commercially available dielectric papers.

8.6.1 CAD Papers

Although electrography is rapidly losing favor to ink jet technology in the CAD market, it is still the workhorse for large corporate engineering organizations and service bureaus

where high productivity and fast turnaround are essential. Monochrome printers have been extensively replaced by ink jet, direct thermal, and laser printers, especially those in the 22-, 24-, and 36-inch widths. New color electrostatic printers retain an edge for productivity, but the ease of operation and low cost make the transition to color ink jet hard to resist. Even so, substantial quantities of dielectric paper are still being made specifically for this market.

There are four types of dielectric paper for CAD: Report (Opaque), Translucent, Vellum and Semitranslucent. Each is distinct and designed to meet those market demands that evolved during the transition of CAD from pen plotting to electrography.

Report

Report papers are the electrographic equivalent to bond or plain papers. They are the low end opaque grades with typical basis weights of about 65 to 75 gsm (40 to 45 lb./sq.ft.) designed for either monochrome or color printing.

Monochrome papers have the simplest construction and the least sophisticated coating. As the only critical requirement is good contrast between the black lines and the unprinted area, the tolerances for performance fall within a rather broad range. Low-cost components tend to be used, the manufacturing processes are run at relatively high speeds, and only modest levels of production control are needed to make a print of satisfactory quality. Cost considerations dictate a low level of conductive treatment based at least upon some simple salts that deliver poor image quality at low relative humidities (below 40% RH).

Because color report papers are used for color CAD drawings, they must be capable of reproducing not only lines but also solid fill areas. Seismographs and microelectronic circuits (integrated circuit chip design, printed circuit board design, etc.) are usually printed on these grades. To meet the higher image and durability requirements, color papers start from better formed base stocks with greater solvent holdout, tighter porosity, greater smoothness, and more uniform and higher volume and surface conductivity. These parameters are controlled much more tightly than in the case of monochrome grades. Additionally, the dielectric coating is formulated with blends of several polymers and pigments—often with twice the number of ingredients as for monochrome papers. The greater complexity is reflected in the price of these dielectric grades.

Translucent

Translucent electrographic papers are designed for use as masters for diazo reproduction. Therefore, their design and price points are focused on achieving a suitable image quality in the reproduction process while allowing for easy generation of multiple copies. A secondary use is for overlays and tracing, where images must be seen through several—usually four to five—sheets of paper. Accordingly, the critical parameters of translucent papers are optical transmission to UV and visible light, good line quality, and physical strength. They are generally about 80 gsm in weight and have high density but low tear strength.

Because these papers are typically very brittle, their useful life as a diazo master depends upon the care taken in handling. For example, creasing and folding will lead to stress fractures, which propagate tears. Creases also scatter UV light, forming defects in the diazo copy.

Translucent dielectric papers are made in the same manner as tracing papers, i.e., by using highly beaten pulps, large quantities of starch and synthetic polymer, and extensive

calendering to ensure they are free of any opacifying component or artifact. As a consequence, the base sheet is quite sensitive to changes in relative humidity, and can show a dimensional change of up to 3% with ambient changes from 20% to 80% RH. Prone to curl and cockle, they are unsuitable for drawings with precise dimensions.

The dielectric layer for translucent papers must be relatively transparent to UV light and thus is formulated with a low pigment content (P:B ratios of between 0.5:1 to 0.8:1) and without opacifying agents. Calcium carbonate is the primary pigment, but low concentrations of silica and talc are sometimes used. As the primary use is monochrome line printing, image quality expectations are relatively low.

Vellum

Vellums used in reprography are made from cotton (rag or linter) fibers. These are much more durable than wood fibers. Drawings made on vellum can be stored for very long periods, hence it is the preferred substrate for archival keeping. Other unique properties include high folding endurance, excellent tensile strength (a measure of toughness), good dimensional stability, and high resistance against crease formation. With these characteristics it is preferred as a master in the diazo process when many copies are to be produced.

Vellum derives its translucency from a transparentizing process wherein the raw paper is saturated with oils like low molecular weight polystyrene or polyalphanaphthyl styrene. Traditional transparentizing uses solvents (e.g., xylene) to transport the oil into the paper on a squeeze roll coater. A drawback is that oil present in the base sheet raises solvent retention, giving this dielectric grade the tendency to exhibit a stronger solvent odor. One maker uses an aqueous, hence solvent-free, transparentizing treatment that enables the addition of conductive agent early in the process. This gives the product additional volume conductivity.

Dielectric formulations for vellums differ little from those used for translucents. As might be expected, imaging performance is similar, although the slightly higher level of volume conductivity delivers higher image densities.

Semitranslucent Paper

The high cost of vellum and translucent papers created an opportunity in the market for a sheet based on chemical pulp that could be priced closer to opaque papers yet feature only minor compromises in overall performance. These semitranslucent papers are made from moderately beaten wood fiber. The degree of defibrillation is higher than standard opaque papers but much less than for translucents. It is made without any opacifying pigment to keep the UV light opacity at moderate levels yet sufficiently opaque to provide adequate contrast after imaging.

Conductivizing is achieved to a greater degree when performed on the paper machine because the sheet then has a modest level of porosity, reducing the demand for a heavy conductive coating on the surface of the sheet. The dielectric coating composition is similar to that used for translucent paper.

Overall imaging performance of the semiopaque papers is very good for CAD work, but one drawback is slower diazo reproduction speed. Nevertheless, the lower cost of this grade resulted in its widespread adoption.

8.6.2 Lightweight Color Papers

Early developments in electrography focused on lightweight papers for color CAD. At the time, they were called *premium* or *color report* grades, and they functioned as the

preferred material when purity of color, whiteness of background, and opacity sufficient for direct viewing were all called for—a role they still fill for CAD. Color electrography was also adopted quickly by the seismic industry. This use placed two additional requirements on the paper that were instrumental in making it suitable for graphic arts. The first was freedom from defects. Voids and starvoids could lead to misinterpretation of the seismographs alerting plant personnel to surface contaminants and pickouts at all phases of the manufacturing process.

The second was adjusting the paper to the stop–start mode of the printer. In these early days, the computers storing and transmitting the data could not match the speed of the printer. Thus the printer would print in a stop–start mode. While stopped the toner particles on the paper needed to stay in place and not be “washed” away by the continuing flow of toner fluid. Additionally, soluble materials in the dielectric could be extracted into the toner and poison it. A solution for this problem came through dielectric coating formulation and toner modifications.

Color report grades are now the everyday papers of the graphic arts segment of the electrographic industry—the paper used when bond or “plain” paper would be called for in other modes of printing. Dominant uses in this market are volume low end graphics (in-store advertising), and for checking images prior to printing on more expensive grades. They may also be used for the wet transfer process—see Section 8.6.6.

8.6.3 Premium Color (Presentation) Papers

Soon after the first color photographs were reproduced by electrography the deficiencies of the existing dielectric papers were recognized. There arose a demand for high-performance papers comparable to the premium offset printing grades.

Presentation grade papers were specifically developed to meet this need. They were introduced at different basis weights, first 100 gsm, then 80 gsm, later 150 gsm (100 lb), and most recently, 120 gsm. They are characterized by high whiteness, exceptional formation, high consistency, low artifact levels, and premium image quality, properties obtained from their heritage of photographic paper making. Typical properties for these papers are shown in Table 8.1. Presentation papers are the image quality leaders. With them, printing is most consistent, gamuts are broadest, mottle and grain are least observed, and other visual nonuniformities such as striations are minimized.

Table 8.1 Typical Properties of Presentation Grade Papers

Presentation grade	80	100	120	150
Basis weight (gsm)	80	100	120	150
Thickness (μm)	73	88	110	125
Density	1.10	1.15	1.10	1.2
Burst	180	250	300	400
Stiffness				
MD	20	40	90	150
CD	35	80	150	250
Opacity (%)	80	85	87	92
Brightness (%)	92	94	88	94
Moisture content (%) (at 50% RH)	7.0	7.0	6.8	6.8
Suppliers to North American market	Rexam Sihl	Rexam Sihl	Rexam Sihl	Rexam

Overlaminating adds greatly to image intensity and snap—it is normal for photoreproductions. Stiffness is a significant aid to laminating. Yield losses from attempting to laminate lightweight papers can often greatly exceed the anticipated cost savings that might be realized by using the lighter paper. The heaviest grade is preferred for applications where lighter grades must be laminated, not for esthetic reasons, but merely for stiffness and durability. However, this stiffness is also a drawback because it makes runnability more difficult in some printers.

Higher basis weight papers have some water-resistance, retaining sufficient strength to be actually handled when wet, especially if the time of exposure is short. Thus some use of these grades for wallpapers, murals, and even outdoor posters has developed, although extra special care is required for these applications.

A wide range of applications has developed with these papers. Any use requiring true color photoreproduction is best handled with this family. Examples are point-of-purchase advertising, standees, and backlit advertising (with two images mounted together in perfect register to obtain the additional image density).

8.6.4 Wet Strength Papers

There are three basic markets for digital color printing that require wet strength papers: billboards, maps, and wall coverings.

Billboards

Electrography lends itself to billboards and other outdoor advertising applications. It has good resolution, has good color, and can produce customized prints for short runs—even single images or “one offs”—cost effectively. This application was envisioned soon after the first graphic arts capable systems had been assembled. However, the papers and toners available at the time were totally unsuitable. The color report grade papers had no wet strength, and the color toners faded and bled or ran when wet. If the opportunity was to be realized, a paper that, once printed, could be immediately used by the existing installation industry was needed. Simultaneously, toners suitable for the outdoors had to be introduced.

The issues were solved together in a manner characteristic to the industry: Cactus, a VAR, brought together the materials manufacturers (Specialty Toner Corp., Chartham Paper Mill, and James River Graphics) and a potential end-user (Gannett Outdoor). The result was both a paper, namely, Rexam Graphics' Outdoor Poster Grade (27), and a toner (Specialty Toner Corp.'s Weather Durable®) that met the standards of the billboard industry.

The critical properties for a billboard grade include good imaging performance, good wet strength, controlled wet expansion, and some level of paste absorption. Obtaining wet strength in paper is well known—a chemical that will provide covalently cross-linked bridges between the fibers is added at the wet end or size press. Styrene maleic anhydride and Kymene® (a polyamide-polyamine epichlorohydrin adduct wet strength resin offered by Hercules) are two commonly used reagents. These react with the cellulose when heated during drying and so provide strength whenever water loosens the hydrogen bonds that normally give paper its strength. The minimum wet burst of paper that can withstand the common practice of prepasting is around 100 lbs.

Changes in the manufacture of the base paper are needed to obtain paper with such

performance. It is typical to cut refining back, but this can be at the expense of solvent holdout and hence loss of image quality relative to presentation papers. A modest degree of paste absorption ensures that the paper will remain bonded to the surface it is applied to when rained upon. Nonabsorbent papers tend to slide off when put up with the potato starch pastes most commonly used in outdoor advertising. This is actually more important than having wet strength once the board is installed.

Opacity must be high to hide the colored material remaining on the billboard face from prior advertisements, when a new face is being installed. The requirement is not just for dry opacity, which is comparatively easy to obtain, but for wet opacity, which is much more difficult; the opacity should be at least 90%.

Maps

Cartographic applications have somewhat different requirements for a dielectric paper substrate. The attraction of electrography becomes apparent when it is realized that geographical databases are always in a state of flux. Because new information is always being generated, maps can go out of date even before the proofs are prepared. In some instances, such as military events, obsolescence can occur in hours. Additionally, these databases are now digital. Map printing directly from such databases is an ideal that is attainable provided the toner, the paper, and the final image can all stand up to the rigors of the end use.

Traditionally, quality maps are printed on paper with a moderate degree of wet strength so they can be read in the rain. Outdoor poster grade has some suitability for mapping, but the existing 36-inch printers that have been adopted by the cartographic industry do not handle it. Nor does it have the fine surface structure needed to reproduce fine lettering. Some success has been possible with a wet strength 100 gsm presentation grade. However, most electrographic maps are printed on presentation imaging grades and laminated for extreme service. There remains open a good opportunity for a dielectric paper specially designed for map making.

Wallpaper

Wallpapers require wet strength for installation only, unless washability is essential. A grade specifically designed for wallpaper has been marketed. It supplements outdoor poster and heavyweight presentation grades that have been used with moderate success. These papers, protected by a layer of Rexam's Fluorex[®] film (see Section 6.6) have demonstrated high functionality as wall coverings in kitchens and bathrooms.

8.6.5 Toner Transfer Paper

Toner transfer is an operation in which the toned image alone is transported, intact, from one substrate to another. The first electrographic transfer process was the Scotchprint[®] vinyl printing system. It is deceptively simple: an electrographic paper that weakly binds toner and is printed in mirror-image form, mated with a suitable substrate (usually a vinyl), and subjected to heat and pressure enabling the toner to transfer to the substrate. The vinyl print is then overlaminated (Fig. 8.22). The image is thus highly protected, trapped between the substrate and the overlaminate. The process as developed is well-defined in the patent literature (51). It has been extremely successful.

As in many cases, what appears simple in concept has many complications in the

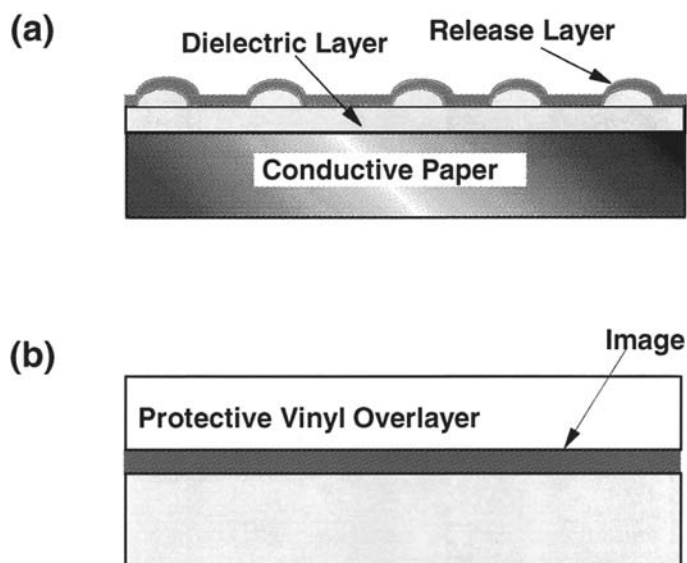


Figure 8.22 Schematic representation of 3M Scotchprint materials: (a) transfer media with toner release coating over dielectric layer; (b) final product with the image encapsulated between the substrate and the overlamine.

details. The critical factors in the toner transfer process are balancing opposing forces at each step. The first of these is to have a surface that will hold toner firmly during the multiple writing and toner steps, yet will release the toner completely in the transfer process. There are two elements to this—chemical and physical. The surface of the dielectric needs to have a low surface energy, but not so low that it has no affinity for the toner. This is achieved by coating a thin layer of a release agent, such as Syl-Off® (51) or silicone urea block copolymers (52,53), over a dielectric paper with good charge retention properties—the surface energy being controlled by the ratio of nonpolar dimethyl siloxane groups to polar urea elements. The toner properties are such that it does not fix upon drying but remains weakly bound. It is the combination of both the surface layer of the dielectric and the properties of the toner that ensures this response.

The release surface must remain with the dielectric coating during both the toning step and the transfer process. Thus it must be insoluble in the toner carrier fluid, and it must be well-fixed or integral to the dielectric layer. The silicone urea block copolymer satisfies these requirements, whereas commercially available release agents, when used in this application, became contaminated with residual silicone, which poisons the toner.

The weak adhesion of the toner to the paper raises the need for physical protection to be provided by the dielectric paper to ensure that the image is not degraded by scraping from machine elements encountered along the paper path. The spacer particles in the dielectric layer serve this purpose. The test is most severe for the thickest toner layers—not just secondary colors but tertiaries bearing the richest hues. Making the particles large enough to ensure that the thickest layers are not in jeopardy, however, makes the surface excessively rough—too rough for the best imaging, and too rough for the total transfer to the substrate.

The ability to print without scratches varies among the different printer designs. The original single-pass machine had this capability with little modification. The Xerox 8900 family has also proven reliable. Both have the paper wrapping the writing head with pressure from a compliant back element. The Raster Graphics printers have been prone to scratches on all materials, but most especially for toner transfer, because there is no compliant element at the writing head—both the head and the back element are comparatively rigid, so that the paper cannot distort when a large particle is to be passed. This has been improved with the DCS 5442, which has the web wrapping the head, while a thin stainless steel back electrode serves as the compliant member.

After printing, the image on the release paper is fragile and must be handled carefully. It is preferred to leave the paper on the wind up core in the printer, although sometimes it may be unwound and reviewed for manual touch-up of imperfections.

Transfer of the toner to the receptor substrate is effected with both heat and pressure. Originally this was done with a flat-bed hot laminator (51), but commercial operations now use a hot roll laminator. The transfer takes place in the nip between two heated rolls. One is covered with silicone rubber, while the other may either be rubber-covered or chrome steel. A relatively high pressure is applied by air cylinders at each end of the roll pair. Electrical elements inside the rollers provide the heat source.

One of the difficulties has been maintaining a comparatively constant temperature across the roll face; it is normal to use a roll at least 8 to 10 inches wider than the material to be transferred to avoid the end zone where the temperature drops off. There are separate supply shafts for the imaged paper and the substrate. Twin take-off shafts wind up the substrate with the image and the used release paper.

The most fundamental requirement of the receptor is that it makes good contact with the toner layer in the laminator. Extremely high pressures must be used to ensure 100% surface contact, even with a compliant layer. This paper is not recommended for toned image transfer onto a rigid substrate such as polycarbonate, but compliant materials, such as polyvinyl chloride, are suggested. A suitable coating on the receptor sheet can also improve transfer efficiency.

The substrate itself requires a receptive surface with both proper surface energy and glass transition temperature to bond the toner firmly. It also must have the ability for at least the surface layer to flow when hot so that the toner layer becomes one with the new substrate. Standard calendered or cast polyvinyl chloride has generally been unsuitable and not given sufficient adhesion. Special thermoplastic receptors have been necessary. Coatings of polymers of ethylene acrylic acid, methylmethacrylate, or butylmethacrylate can give the proper qualities, while vinyls can be modified with acrylics or vinylacetates to do the same. Both approaches have been utilized.

The thickness of this coating is adjusted to compensate for the rigidity of the receptor substrate—pressure-sensitive vinyls have thin layers, while more rigid materials have much thicker layers, sometimes as much as one-third the thickness of the paper itself. A good description is provided in the patent literature (54).

After transfer the image is still susceptible to damage from abrasion, making an overcoat or overlamine essential. Overlamination is the predominant process. Clear vinyl films, with either heat seal or pressure-sensitive adhesives, can be applied by the same laminator used for the transfer step. When pressure-sensitive laminates are selected, the transfer and overlamination can be done simultaneously in one process step. The overlamine is chosen to suit the application.

When the image is to be in a gentle environment, for example in point-of-purchase advertising, a light 3-mil clear vinyl is appropriate. However, for heavy duty work such as fleet or floor graphics, 7- or even 10-mil thick laminates may be taken. The durability of the laminate has been matched by the light fastness of the toner.

Overlaminated prints on self-adhesive vinyl have found numerous applications in the advertising world, such as murals, trade show displays, corporate logos, sporting events, museum exhibits, trucks, vans, trains, airplanes, and many others. A new material has been designed for use on windows whereby the graphic is seen from outside while from inside the view is essentially unrestricted. When applied on transportation vehicles, with proper material selection, the images can last for five years without appreciable fading, cracking, or other deterioration caused by environmental factors. The concept of wrapping buses with printed vinyls, first developed by and commercialized by SuperGraphics, Inc. (Sunnyvale, CA), has been especially successful. By renting the bus space to advertisers, public transit agencies are deriving hefty revenues (up to \$8,000 per month) which help the agencies keep the bus fare low. It is a situation where everyone wins, including the bus passenger.

8.6.6 Image Transfer Papers

Image transfer is the term used to describe methods where both the image and the dielectric coating that supports it are transferred to a new substrate. Two approaches are used—the simple dry transfer process and the more complicated wet method.

Dry Transfer

Dry transfer printing (55,56) is similar to toner transfer in that the image is printed in mirror form on a special paper—3M's Image Transfer or Rexam's Wear Coat. The image is transferred to a substrate with a laminator, but both the dielectric and the image are transferred. The image is then sandwiched between the substrate surface and the dielectric (Fig. 8.23). The product from this one-step process is then ready for use in environments where the dielectric layer provides sufficient protection for the image.

Dry transfer paper has the same basic structure of dielectric media—a conductive substrate carrying an insulating coating—but there is a release layer under the dielectric.

The release layer is a critical element of the structure. Its surface energy has been carefully matched with the dielectric so that the bond is weak. It has the integrity to hold the dielectric in place during manufacturing and printing operations, but it will separate if the dielectric is bound to another surface. There have been two variants of the release layer. The first generation of image transfer used a thin, high surface energy, silicone release coating. While this was highly functional, it also acted as a dielectric material and therefore reduced the image density achievable with useful thicknesses of the dielectric layer.

The second generation of dry transfer paper uses a proprietary combined conductive release coating that greatly increases the apparent density of the imaged product. Resolution is not changed—the transferred dot remains essentially the same size on transfer (45). Grain and other microscale nonuniformities can be reduced.

Further, the conductive release layer can be applied at much higher coat weights; it can be laid down with many different textures, which are then reproduced in the surface of the wear coat on transfer. Glossy, sheen, and flat surfaces can be produced (23,24).

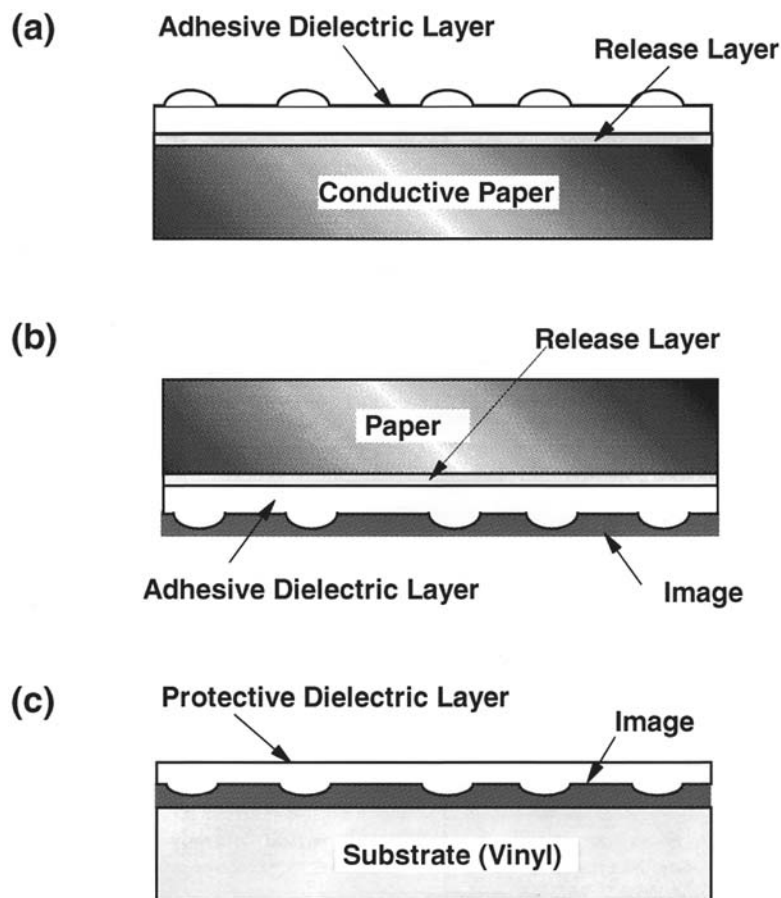


Figure 8.23 Schematic representation of the Rexam Dry Transfer dielectric paper, showing (a) the special adhesive dielectric and release layer, (b) imaged paper ready for transfer, and (c) the final product after the carrier sheet is removed. The image is encapsulated between the substrate and the thin transparent dielectric coating.

The transferred dielectric layer functions to protect the image for short periods, of approximately 30 days duration. Image durability is good and particularly useful for promotional applications, such as banners, signs, and advertising. When protected from intense sunlight and harsh abrasion, it has shown little loss of integrity even after outdoor exposure for more than two years.

Nevertheless, regular dielectric coatings, especially if formulated to act as hot-melt adhesives, are not very durable. They degrade under UV light, can harbor mildew in damp environments, and are prone to scratching from even mild abrasion. They also tend to offset if folded or rolled—a fact that induced most banner producers to overlamine dry transfer prints.

A solution to this was introduced by Rexam (57). In the new product, a thin layer of Rexam's Fluorex, a durable polymer alloy, is applied on the release coating, and this in turn is coated over with a thin dielectric layer. The combined layer has the thickness

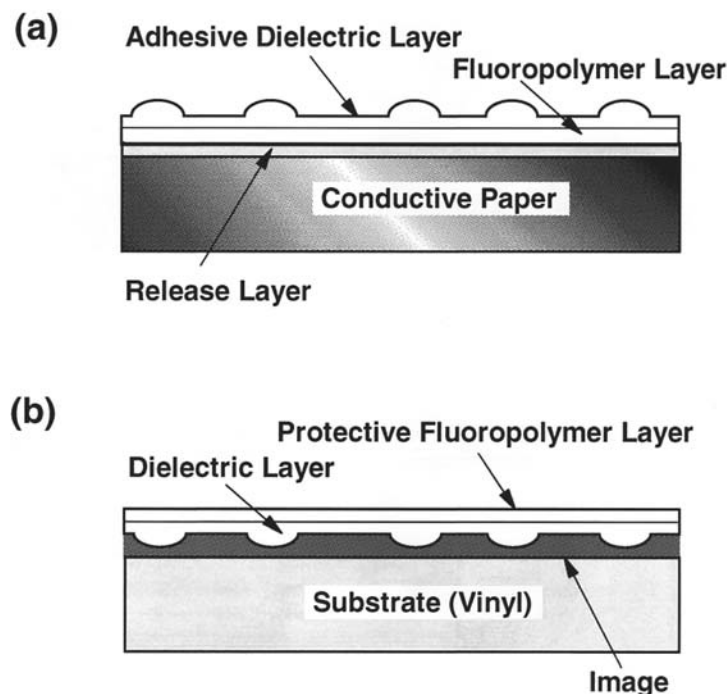


Figure 8.24 Schematic representation of the Rexam Dry Transfer Paper (a) with Fluorex layer on top of the conductive layer, and (b) with the protective Fluorex layer exposed.

of a standard dielectric. When transferred, it is now the Fluorex layer that is exposed to the elements (Fig. 8.24). This layer raises the durability of the coating dramatically—abrasion resistance increases tenfold, UV degradation is cut to less than 1/10th, chemical resistance is greatly improved, nonsolvent graffiti removers can be used to remove paint and other materials, and the coating is mildew resistant.

Wet Transfer

Wet transfer takes advantage of the fact that the common quaternary ammonium polymers used to conductivize most dielectric papers are water soluble. When wet, these cause failure of the adhesive bond between the dielectric layer and the base paper. The typical process starts with direct imaging onto the substrate. An overlaminating film is then applied to the image surface in one pass through a laminator. This may be either a hot or a cold laminating film. The paper is then passed through a water saturating station, such as a bath, which weakens the dielectric bond. The paper can then be stripped off and wound up on a separate core. The overlaminate/image/dielectric sandwich is wound up separately. Usually, there is residue from the paper on the back side of the dielectric that must be wiped off continually. In a second step, the dielectric is bonded to a substrate. The whole process is shown in Fig. 8.25.

Wet transfer has the advantage of using off-the-shelf direct imaging papers, producing the same image as the direct write paper and less expensive imaging paper. On the other hand, in the most common approach it is two step process, requires an overlaminate, and is typically messy.

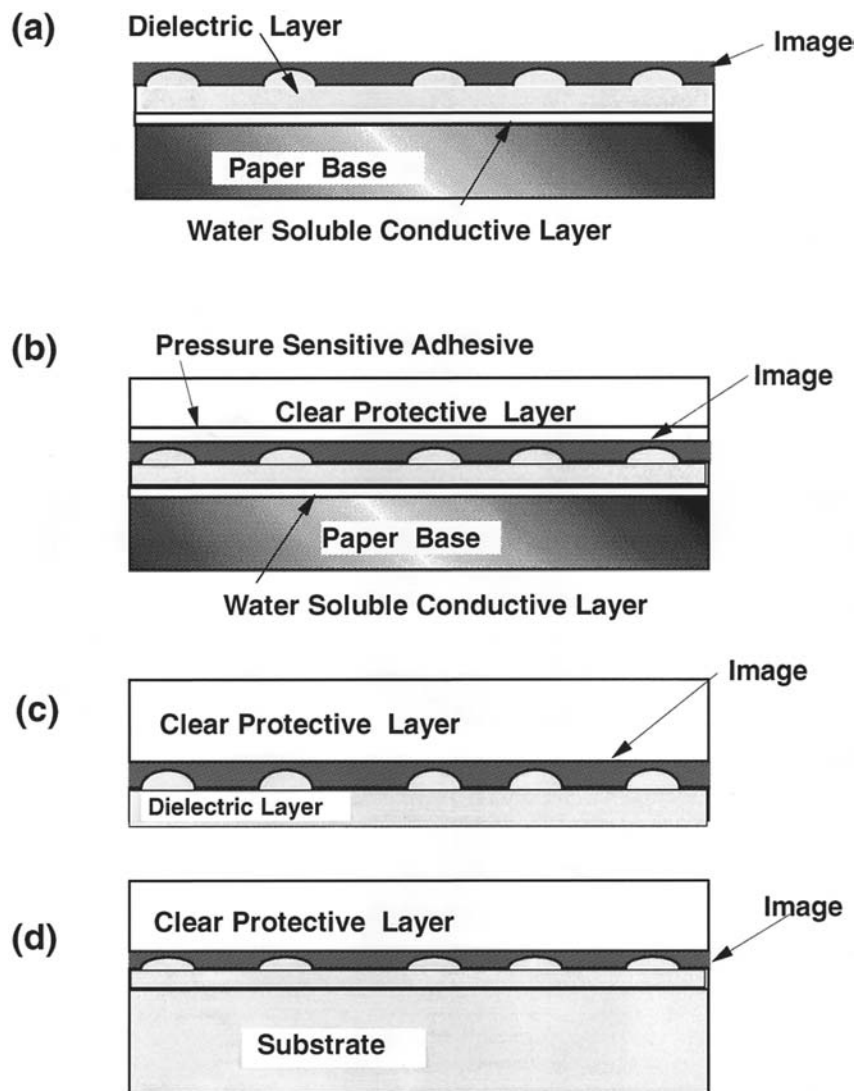


Figure 8.25 Schematic representation of the steps of the wet image transfer process, showing (a) imaged dielectric paper, (b) imaged dielectric paper overlaminated with protective film, (c) image and protective laminate remaining after wetted paper is stripped off, and (d) final product mounted on substrate. Note that the image is encapsulated between substrate and overlamine.

8.6.7 Sublimation Transfer Printing Papers

Printing fabrics by dye sublimation transfer is a traditional process for fine silks, limited edition blouses, white goods, and other items. Dyes that will sublime or diffuse at high temperature are printed onto paper by either offset or serigraphy (silk screen) as a mirror image. The paper and fabric are mated and exposed to about 350° to 400°F for about 30 seconds in a transfer press. The paper is peeled off and the fabric is thereby imaged. The technology is, of course, limited to combinations of fabrics and dyes that will function

this way. Polyester is the staple of the industry. This plastic softens at a suitably low temperature and can absorb the dyes that are mobile, again at that temperature. The dye, in vapor form, penetrates, or becomes dissolved in the polyester fiber in a process called imbibition printing. Once trapped inside the PET strand, the dye cannot be attacked, making it highly resistant to laundering and dry-cleaning.

This is another market area that is fertile ground for on-demand, digital color printing—the textile industry. In this highly fashion-oriented market, styles and colors change rapidly. The long lead times required for prepress or makeready operations and the extended run lengths needed for these methods to be economically feasible make electrography an attractive alternative.

The appeal of a fully digital process is obvious. Electrography has been adopted readily because it has appropriate image quality for many applications and good productivity; and the dyes can be incorporated into liquid toners. There have been a number of systems in Japan, and a handful in the U.S., supported first by Synergy and then by Nippon Steel (58), printing this way since the early 1990s. Recently, the technology has been picked up by value-added resellers, and about 30 systems have been placed with either Xerox or Raster Graphics printers. They have been concentrating on flags, banners, proofing, and uniforms, and other applications where polyester textiles are functional or already in use.

It is not textiles alone that can receive the dye. Certain polyester-based coatings are available, such as STC's Soltex™, that enable the transfer of images by dye sublimation onto everything from wood, vinyl, and wallpaper to ceramics, textiles, and metals.

Electrographic sublimatic technology is just what is expected by printing with electrography and transferring traditionally. A summary of the process is outlined here.

Printing

Software used for apparel design and fabric prints has been adapted to electrography. The patterns are printed in a regular manner although the optimum printer operation can be quite different from processes using pigment toners—the image as produced is muddy-looking, and true colors are not apparent until the transfer is made. Color matching has a distinct art component, although advances in software are simplifying this step.

Printers

Resolution is important to most fabric printers, as fabric is usually seen at close proximity. Therefore 400 dpi has become the norm, although 200 dpi is entirely satisfactory for banners, flags and furniture.

Toners

The toners are similar in structure to other electrographic toners, i.e., dispersions of pigments with polymers and charge directors in odorless mineral spirits. The pigments, of course, are the same as or similar to those dyes used for traditional sublimatic printing.

Transfer Presses

The two types of transfer press are roll fed and sheet fed. The sheet-fed units have a stationary hot press and a fabric carrier on which the imaged paper and the fabric are placed. The carrier is pushed into the press, which closes automatically for the preset time. It is then pulled out, the treated sample is removed, and a fresh combination is put down. The primary problems with this type of press are paper curl before the press closes, and

image blurring when the image shifts across the fabric surface just when the press is opened, but before the temperature has dropped sufficiently to condense the gaseous dye.

Roll-fed presses are normal for large runs of printed material. Curl is not an issue. However, this process rapidly raises the paper temperature so that there will be a propensity for blistering with heavier paper, especially if it has a modest water content. Hence, lighter weight papers have not only a cost advantage, but also a performance advantage for roll-to-roll transferring. However, superior imaging on the fabric has given a preference for 100 gsm presentation grade. The blistering problem can be overcome with a simple radiant heater in the web path between the printed paper unwind and the hot roll. This can bring the paper moisture content down to from 4 to 5%.

The two process steps that especially stress the imaging paper are image generation and hot transfer. The transfer process requires that the paper not curl uncontrollably on entering the press nor blister in it. It should not shrink independently of the fabric, as the image will appear diffuse. Excessive adhesion of the dielectric coating to the fabric must be avoided for obvious reasons, and finally the paper should not transfer objectionable odors or chemicals in the press. In fabric printing, background from any cause is problematic: “White must be white.” Thus low stain is a requirement, and a total absence of nib writing is an ideal. Both of these are functions of the dielectric coating, the toner, and the printer writing voltage. Low dot gain is desired also—it is achieved by avoiding conditions that promote flare and by keeping writing voltage low.

The ideal paper is one with low moisture content, to avoid blistering and shrinkage; low refining, to give good dimensional stability; good conductivity, both surface and volume; a thin dielectric layer having a uniform roughness level; and a low-temperature adhesive. This ideal leads to many conflicts and compromises: dimensional stability, for example, is better for coarser fiber papers that are weakly refined, but such papers have poor coating holdout and uneven surfaces, so that they produce images with poor small-scale uniformity.

8.6.8 Self-Adhesive Papers

Direct imaging, self-adhesive papers have utility for posters and advertisements. They are simple in construction (Fig. 8.26) with a direct imaging paper laminated to a pressure-

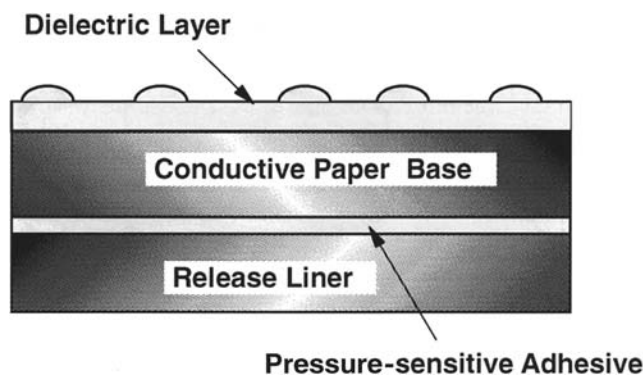


Figure 8.26 Schematic diagram of self-adhesive dielectric paper. Removing the release liner exposes the adhesive on the paper.

sensitive adhesive coated onto a release liner. After printing, the image is trimmed to size, the release liner removed, and the print installed. Repositionable adhesives are preferred, as the paper must be applied dry and will tear if the bond is too tight. The compromise in printing has been leading edge fog, as release liners and pressure-sensitive adhesives are not good conductors. This is solved by separating the writing and toning passes.

The size of the market has yet to be determined. The competitive methods include laminating liner and adhesive to imaged stock after printing—most of the laminate manufacturers offer such goods.

8.7 PRESENT TYPES OF DIELECTRIC FILMS AND FABRICS

The dielectric paper substrates described thus far have a conductive agent dispersed or diffused completely through it, so that the conductive layer under the dielectric coating is in electrical contact with electrodes on the back side. This section describes the structures of dielectric films and fabrics and the challenges that have been met in adapting them to electrographic imaging. The main focus is on polyester film, because that technology has been fully described in the patent literature.

8.7.1 Polyester Films

Historical Overview and Markets

Polyester films (polyester terephthalate, or PET), when compared to paper, offer clarity, dimensional stability, and durability. Additionally, they have sufficient tensile strength to be transported through the printer without distortion—a limitation for many otherwise useful plastics. These are properties desired by the seismic industry, where huge amounts of data are obtained and which were being analyzed by visual comparison of massive seismographs, laid one atop another. This market sector provided a major impetus for the development of an electrographic film product. Development began seriously in 1979, with most of the work in the United States occurring at GAF (59,60) and Eastman Kodak (38). At the same time, a plotter modification was necessary to handle and print film successfully. Versatec succeeded with the introduction of a suitable printer-plotter in 1980.

The major printing obstacle was the large electrical barrier of the film in the back-grounding configured printers—there can be no electrical path through the film because it is an insulator. There have been efforts to make a film with suitable volume conductivity, but these have failed because the full range of properties has not been obtained, while the compromises have been unacceptable.

However, modeling studies showed that fast capacitive coupling could be effected if the footprint of the back electrode was much larger, and higher write voltages were used. Once the relative ratios of the electrodes was determined and the higher write voltages needed were established, the program moved from “bootleg” to “sanctioned,” and a working electrostatic film plotter appeared shortly thereafter. It had an enlarged, flexible backplate electrode, high writing potential (up to 750 V), and new electronic architecture (write time and pulse amplitude), features that have not only permitted the use of electrographic film but also given printers the capability to image nonstandard paper grades. Today, a separate “film” mode is a standard option on electrographic printers.

Front-grounded plotters were able to accommodate film more readily because they relied upon capacitive coupling through the dielectric. However, the interaction of the dielectric pigment with the electrodes was an issue demanding careful design.

In addition to the seismic market, electrographic film found wide usage in the reprographic industry where high speed led to substantial displacement of pen plotters as CAD placements grew. Both clear and matte films were provided—the matte type was preferred because it could be altered or overdrawn by hand, but both could serve as diazo masters.

The bulk of the film used for CAD was made with water-soluble conductive polymers. Unfortunately, there were a few incidents in which film plots—thought to be archival—were destroyed by water from floods, pipe breaks, or sprinkler accidents. The media manufacturers then invested in electronic conductor layers, so that the current films are all archival.

A special application for film arose in the aerospace industry, where film templates are used as masters to control large cutting tools. High precision drawings are made on polyester film. The traditional process with pen plotters was very slow—electrographic plotters offered a massive time saving, but with two important criteria: media that is flat and straight so that highly accurate drawings could be made on it; and plotters that would guide the film and image on it with the desired accuracy. Both requirements taxed the plotter manufacturer, the media suppliers, and the polyester film manufacturers. Nevertheless, a moderate degree of success was obtained, and the approach was implemented.

The final area that film attempted to enter was full-color printing for graphic arts applications. Some spectacular prints were produced on film made with white opaque base.

Polyester Film Structure

Polyester electrographic films share the same five structural elements (Fig. 8.27):

1. A PET substrate
2. A conductive layer with surface electrical resistivity from 1 to 5 $M\Omega/\square$
3. A dielectric layer over the conductive layer
4. Conductive grounding stripes at each edge
5. An antistatic backcoat

Substrate

The polyester is typically 3 to 4 mils thick, although 7 mil film is used for precision plotting. It provides the high-temperature stability, low moisture absorption, durability, high tensile strength, resistance to tear, and dimensional stability required for film applica-

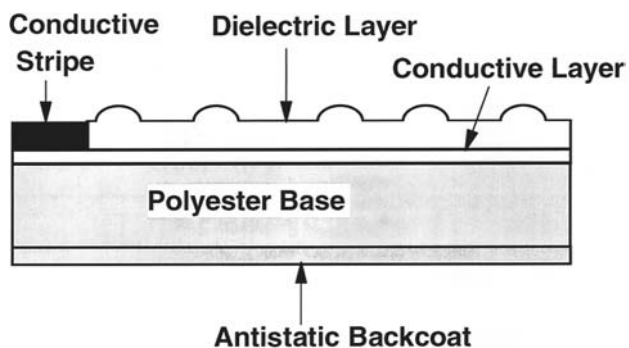


Figure 8.27 Schematic diagram showing a dielectric film structure.

tions. Optical clarity is a requirement for clear films but not for matte. Adhesion promoting bond coats are provided on each side to ensure the coatings are properly bound. Suitable films are offered by DuPont Teijin Films, Kimoto, Mitsubishi, and Toray.

Conductive Layer

The surface resistivity of the conductive layer typically falls into a $3 \text{ M}\Omega/\square$ wide band somewhere in the region of 1 to $10 \text{ M}\Omega/\square$. It must be situated under the dielectric layer for the process to function. However, because it is there it must have other properties as well: it should be colorless, essentially transparent for clear film, ensure the dielectric layer remains firmly in place (good adhesion with the base and the dielectric), and it must not detract from the other performance attributes of the medium. Of these, surface resistivity has been the most difficult property to control.

Six chemical families have been used to lend conductivity to dielectric films: quaternary ammonium polymers, polystyrene sulfonic acid or its salts, polyanilines, indium doped tin oxide (ITO), copper doped tin oxide, and antimony doped tin oxide (ATO).

Early on in dielectric film development, quaternary ammonium polymers were already in use with conductive papers. Polystyrenesulfonic acid and its sodium salt were likewise in use by the film coating industry for antistatic purposes. Thus the extension of both to conductive films was a natural step. There are many issues, though, in manufacturing quality imaging materials with water-soluble materials, not the least of which is their unacceptable behavior when wet (the dielectric layer and hence image can slide off the film!).

The conductivity of these layers is dependent upon the inherent conductivity of the chemical mix, its thickness (coat weight), the content of water in the layer, and the uniformity of the coating layer itself. The first is a simple design issue, but the loss of conductivity when binders are added was a major impediment to providing an archival cost-effective film. Coat weight is a normal manufacturing parameter, but an exceptionally high level of uniformity is necessary—these are thin layers in which small differences will show up as imaging artifacts.

The most difficult aspect of achieving and maintaining proper conductivity has been ensuring consistent moisture content. Unlike paper, polyester film is neither a source of water nor is it permeable to water vapor. Thus the required moisture level must either remain in the layer after coating (generally beyond the capability of most film coaters) or be added to a separate operation by passing the film through a steamer. Unfortunately, moisture gain varies with changes in web speed, steam level, temperature, and dielectric thickness. The goal was never adequately met. Additionally, the film could pick up or lose moisture at the end user site if not properly stored and handled.

Coupled with these factors is the propensity of the conductive polymers to induce image defects, for example, by migrating through hydrophilic pathways in the dielectric layer (8), or from gels in the coating process. Quaternary ammonium polymers and other water-soluble conductives were thus quickly abandoned when better and more cost-effective technology became available.

Kodak introduced electrographic film with a thin polyaniline conductive treatment (38). It produced good images and performed reliably, especially as it is an electronic conductor and thereby independent of water content and relative humidity. This Kodak product was the first truly RH-independent electrographic imaging medium. The primary drawback of the polyanilines is their green/grey color. That fact, coupled with high cost, limited the film to a small sector of the market.

A film with similar properties was made using sputter coated, copper doped tin oxide (37). This dielectric film had an attractive golden tint, but its commercial life was short due to the introduction of films coated with a slurry of antimony doped tin oxide (ATO).

Ref. 3 describes film made with ITO-coated silica. This chemical is a reliable semi-conductive material with few factors other than composition affecting its electrical properties. It is water insoluble and compatible with many binders. The primary impediment to its use in electrographic films was its particle size as supplied. The powder is opaque and contains particles that can protrude through the dielectric layer. Thus special grinding and dispersion techniques are needed to reduce the material to a much finer powder. Particle diameters must be less than 5 μm to avoid penetrating the dielectric layer, and even smaller to prevent light diffraction in the layer. For this, the particle size must be under 100 nm. Both Atheron (9) and Katsen (10) describe methods for size reduction.

ATO is now the conductive treatment of choice, having been commercialized by the three dominant manufacturers: Kimoto, Arkwright (9), and Rexam Graphics (10).

Dielectric Coatings

Critical requirements of the dielectric layer are the same as any paper substrate: high charge acceptance, low charge decay, proper spacing, proper nib cleaning without excessive generation of artifacts, low stain, toner adhesion, protection of the wet toner layer, and adhesion to the conductive base. On top of this, there may be special needs to satisfy the end use application. For example, CAD films must accept common drawing office pens and pencils, be erasable, and also be tolerant of desk accidents such as spilled coffee. The formulations developed over the years have been continually refined to meet these challenges, and they have by and large succeeded.

Dielectric coating resins (often with plasticizer) are essentially the same for films as those used in paper coating. They generally comprise 80 to 90% of the coating mass, as a low P:B ratio is essential to good clarity. In addition to accepting and holding the charge, the resins serve to bind the toner.

A mixture of pigments—such as precipitated or ground calcium carbonate and amorphous or crystalline silica—is normal. Plastic pigments may also be used for clear films (12) because, like the silica, their refractive index is similar to the resins, so light scattering is minimal. Blends are chosen to give the proper relationship between abrasion and spacing. Although profilometry is the most precise measurement of smoothness and pigment concentration, Sheffield smoothness is still the common roughness test. Typically a roughness of 100 to 120 mL/min is optimum; it ensures a 6 to 10 μm gap for nib discharge during writing. It also protects the wet toner leaving the toning station. As stated earlier, there should be sufficient abrasion to maintain the nibs in a good firing state while at the same time minimizing the frequency of highly abrasive events from oversize or excessively hard particles, which result in flare and spurious nib writing.

Different approaches to this balance are described in the patent literature (9–11,54). The Atherton (9) approach tends to have the abrasive event leave the nib with good emissivity for several firings, because it relies on a moderate concentration of hard materials. The Katsen (10) approach prefers to have a greater number of less abrasive events, each capable of ensuring emissivity for only one or two firings. Dot size analysis demonstrates the lower frequency of flaring and hence the better image quality. The drawback with plastic pigments is their low abrasiveness. Dot dropout is a common issue. A sufficient content of fine amorphous silica in the coating left on top of the larger pigments can provide the necessary microabrasion to prevent line dropout.

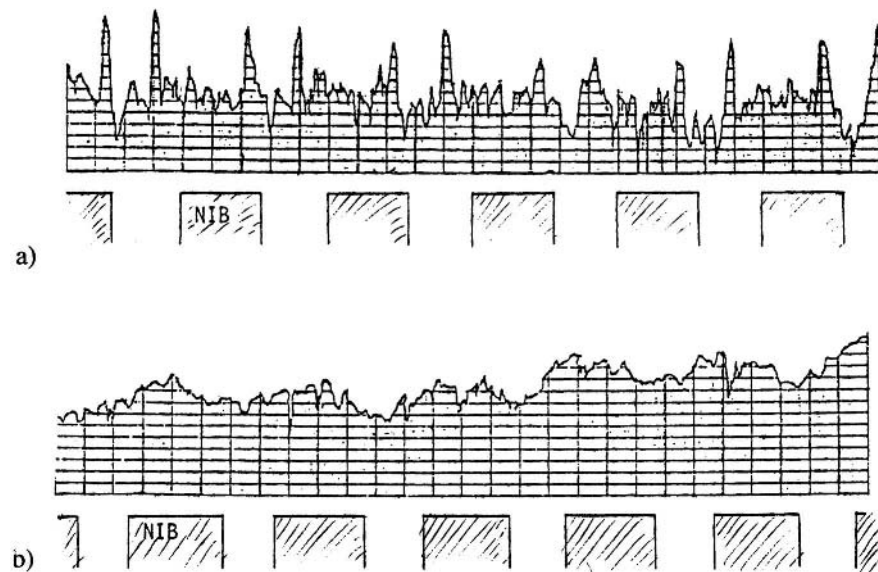


Figure 8.28 Effect of high and low abrasion pigments on the writing head: (a) new film with high-density silica; (b) old film.

Edge Grounding Stripes

The insulating nature of polyester film blocks direct grounding of the countercharge that forms in the conductive layer on deposition of the latent image. Therefore, to prevent capacitive grounding via the toner fountain and the generation of leading edge fog, an alternative grounding method is needed. All electrographic films require edge stripes of highly conductive ink that can provide a pathway between the conductive layer and the printer ground. The usual stripe composition contains carbon black dispersed in a dielectric resin binder. The SER of this layer is typically 10^4 to $10^5 \Omega/\square$. A grounding surface is provided in the printer to contact the image side of the film. Printers with drums perform better if the stripe is also on the film end (called *wraparound striping*), so that contact between the conductive layer and the back is assured. Prior to the introduction of ping-pong writing it was advantageous to have an unbalanced relationship between the stripes on the side where image writing began and where it ended (61).

The grounding stripes themselves are only effective if they can remove the charge at a rate comparable to that at which it is formed without the potential over the toner fountain rising by more than a few volts. There are two factors that determine the effectiveness of stripes: the relative distance from the center of the film to the edge compared with that to the toner station, and the speed of the printer. With the introduction of wider printers, the problem grew worse; higher printer speed also exacerbated the problem. Xerox solved this in the 8500 Series printers by applying a controlled positive potential to the stripes, the so-called *ghostbuster* technology (62).

For the Raster Graphics DCS 5400 series it is customary to minimize fog by separating the writing pass from the toning pass. This gives sufficient time for the surplus charge to bleed off so that good quality images can be obtained. A similar practice is embodied

in the high-speed Xerox printers but is possible only with materials that exhibit good charge retention.

Single-pass printers such as the Synergy machines do not have the same ability to bleed off charge via edge stripes, simply because they were never designed to run dielectric film. When attempts were made to write on film, leading edge fog appeared to a degree proportional to image area coverage. Images with large solids invariably showed heavy leading edge fog. The problem could be eliminated by installing bias plates at each end of the writing head and applying about +10 to +20 volts DC. Several printers were so adapted for specific customers.

Back Side Coatings

Polyester films, like most plastics, generate static when transported across many materials. This static will stay with the film for extended periods of time—as much as months. When the film is passed through the toner development system of the plotter, toner will be attracted to the areas where the static resides, causing an objectionable background pattern. More familiarly, polyester film also draws dust and dirt, while in large diazo duplicating machines it may cause jams, because the film master and the copy paper fail to separate. To eliminate static buildup it is customary to apply an antistatic coating to the reverse side (60). This is the case not only for clear and opaque films but also for those with a matte coating. Provided the SER is about 108 to 1010 MΩ/□ at 50% RH, static is usually not an issue. The quaternary ammonium nitrate compound Cyastat SN® (American Cyanamid) is a common antistatic agent. ATO can also be used (10).

Prevention of blocking and improvement in transport requires a degree of roughness that the drive rolls can grip. Amorphous silica provides this in many antistatic formulations that use a resin binder to bond particles to the film. Most film coaters have antistatic antiblocking coatings suitable for clear and opaque electrographic film.

Matte coatings can be applied to the back for drafting applications. The coatings are usually derived from drafting film compositions and modified only to accommodate different antistatic levels, opacity, or transport requirements.

8.7.2 Pressure-Sensitive Vinyl Films

Vinyl films are ubiquitous—they are used for advertising, decoration, protection, and direction. Direct imaging on pressure-sensitive adhesive vinyl has been an ideal; developments with ATO conductive materials have solved some of the critical performance factors allowing such materials to be introduced. Penetration of the transfer technologies into signage, flags and banners, fleet graphics, and other wide-format markets brought the market to a scale sufficient to make direct-write vinyl films affordable.

Structure

The structure of pressure-sensitive vinyls is similar to electrographic film except that a composite of vinyl film, pressure-sensitive adhesive, and release liner replace the polyester. The structure comprises the following elements (see Fig. 8.29):

1. The dielectric layer and edge stripes
2. The conductive layer
3. The vinyl film
4. The pressure-sensitive adhesive
5. The release liner

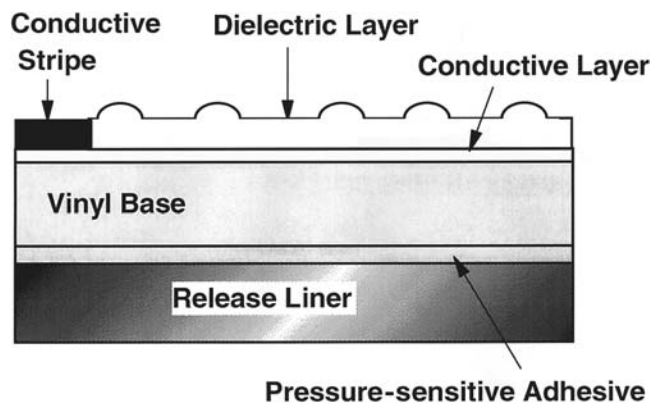


Figure 8.29 Schematic diagram showing the structure of direct-write, self-adhesive dielectric vinyl.

The structure is typically assembled on the release liner. A pressure-sensitive adhesive is first coated onto the liner, and in the same operation the vinyl film is laminated to the liner using a pressure-sensitive adhesive. Because the vinyl has a high surface energy, the adhesive bonds preferentially to it. Next, the conductive and dielectric coatings are applied. Conductive striping, slitting, and rewinding into finished rolls complete the process.

Release Liner

Release liners are generally paper materials of about 50 to 70 lb with a release layer on one side. The release layer is a low surface energy silicone polymer often coated from monomer and cured by radiation. The silicone layer may be applied directly to the paper or on top of another coating. The paper may be coated on both sides with polyethylene coatings to make it waterproof and hence suitable for wet installing. The cost is related to the quality of materials used and whether the liner is water resistant.

Adhesive

There exist a wide variety of pressure-sensitive adhesives that serve many different demands. The adhesive may be “repositionable” so that the vinyl can be moved around during installation until the position is proper. Controltac®, a product of 3M, features weak adhesion until the position is finalized; then permanent bonding is achieved using heavy pressure. Options exist for removable or permanent bonding, as well as for special surfaces such as glass. One of the dilemmas facing the manufacturer of electrographic vinyl is the choice of adhesive.

Vinyl Layer

A white cast vinyl is the preferred substrate (the value added by conversion to an electrographic medium does not warrant the use of calendered vinyl). This material is made by dissolving polyvinyl chloride in a solvent such as MEK (methylethyl ketone) and casting it (coating) onto a heavy release coated paper. This material has a low tensile strength and is elastic, so that it does not lend itself to traditional solution or dispersion coating. Instead, the paper-backed vinyl is brought together with the adhesive-coated release liner, and the backing upon which the vinyl is cast is then removed.

Conductive Layer

The vinyl is opaque, permitting the use of a water-insensitive conductive layer based upon a pigment such as doped tin oxide. It is not necessary to obtain a haze-free coating as for clear polyester films. An average pigment particle size of about 0.5 μm is preferred for such films versus the 0.1 μm of transparent coatings. Without the requirement for opacity the formulator can also run to higher coat weights, giving the benefit of higher binder contents and tougher coatings.

Dielectric Coating

The opacity of these vinyl films affords some latitude to the formulator of the dielectric layer. These can be similar to paper coatings with higher pigment loadings and easier topological control.

Conductive Grounding Stripes

Conductive striping is similar to those used on polyester film.

Performance

The use of direct-write vinyl films has never blossomed. Image quality is generally useful, although spurious nib writing and flare are issues. Leading edge fog is often seen, and although it can be dealt with by separating the writing and toning sequences, this solution doubles the printing time. Only a limited range is available. Transfer techniques are still needed to obtain electrographic images on most vinyl types and for special applications such as window film.

Manufacturer

Kimoto and 3M (with a product developed by Azon) (63) have entries in the direct-write pressure-sensitive vinyl market. A similar product, using opaque polyester, has also been discussed (64).

8.7.3 Direct Imaging Dielectric Fabrics and Nonwovens

A direct-write polyester fabric was brought to market by Xerox but later withdrawn. This material was intended for banners and flags but (1) lacked sufficient image quality, (2) was generally considered to be priced too high, and (3) various transfer techniques proved a better alternative.

du Pont's popular Tyvek® can also be made into a direct-write material (65).

8.8 FUTURE OUTLOOK

Liquid-toner-based electrographic printing, as portrayed in this chapter, remains an important imaging process among competing technologies. Compared to ink jet printing, for example, it is faster, has better image permanence, and generally costs less in terms of imaging material (ink jet ink versus toner). Keeping this in mind, and despite the demise of certain printer OEMs (e.g., CalComp, Phoenix Precision Graphics, Precision Image, and Synergy) there is no doubt that this technology will continue to serve many applications in the present decade.

To its advantages we must add the availability of a wide selection of dielectric papers and films and the growth of sublimation transfer applications. Today's polyester-

based receptor coatings have made it possible to place near-photographic quality images on textiles, garments, drums, tambourines, floor coverings, ceramic tiles, shower enclosures, pools and spas, and other architectural surfaces. Image permanence is a proven fact, as electrographic prints withstand sunlight exposure, weather, and swimming pool and spa chemicals.

Admittedly, ink jet printers are available at a fraction of the cost of electrographic machines, but their low productivity is a drawback for many print shops and service bureaus. The impending solution for ink jet—the pagewide array printhead—will certainly increase imaging speed but will also bring a quantum leap in hardware cost. Thus the economics of wide-format printing will likely continue to favor electrography.

Wide-format, digital color printing continues to exhibit rapid growth. It dominates a few key applications and promises to capture many others where it has yet to be tried. Electrography is still being used creatively, although it has become a mature technology.

One cannot ignore the existing installed base of electrographic printers, a vast population that requires large quantities of consumables. This business volume is sufficient to sustain innovation and support ventures into novel applications. Indeed, it will be a long time before the last electrographic printer is retired.

ACKNOWLEDGMENTS

The knowledge we are sharing here was accumulated over the years we have spent with electrography. Much of it came from informal, open, and frank discussions with our colleagues from throughout the industry. It is too large a task to recognize all of these people directly. We trust they will accept our thanks this way.

In the preparation of the chapter we can recognize people who have been especially cooperative and who have ensured that their organizations have been supportive: Vern Rylander at 3M Commercial Graphics, Frank Perry and Frank Shah of Xerox ColorgrafX Systems, Rak Kumar of Raster Graphics Inc., Don Balbinder of Hilord Chemical, Romit Bhattacharya of Specialty Toner Corp., Boyd Jones and Gene Day of Phoenix Precision Graphics, and Rich Himmelwright of Rexam Graphics.

Dene Taylor wishes especially to recognize Don Brault, his colleague at Rexam Graphics, who foresaw the market that exists today, who knew it could not happen without media, and who drove for the provision of them. The industry would not be the same without his vision.

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9

Photoreceptors: The Chalcogenides

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9.1 INTRODUCTION

The commercial importance of amorphous selenium (a-Se) and its various alloys at present lies in their use as xerographic photoreceptor materials (e.g., Se–Te alloys and As_2Se_3) and more recently as x-ray photoconductors in x-ray imaging though, in the past, crystalline selenium has had successful applications in photocells, solar cells, and rectifier diodes. In a much smaller quantity, amorphous Se–Te–As alloys are also used in Hitachi's Saticon TV pickup tubes (Goto et al., 1974; Maruyama, 1982). The xerographic photoreceptors over the last decade have been progressively using more organic photoconductors rather than selenium alloys, and this trend is expected to continue (Schein, 1988; Springett, 1989, 1994). Some large-volume copying applications still use a-Se alloys since they provide many copies per drum. Another challenge to the chalcogenide photoreceptor comes from a-Si:H photoreceptors, which have good sensitivity in the red and IR regions and exceptionally long machine lifetimes, as is discussed by Mort (Chapter 16) and Joslyn (Chapter 11) in this handbook. Recent research on x-ray imaging systems utilizing the x-ray sensitivity of a-Se photoconductors, however, suggests that the x-ray photoconductor usage is likely to experience substantial growth, as will be discussed later in this chapter. There are currently a number of potential applications for selenium-based amorphous semiconductors in high-sensitivity TV pickup tubes, called the HARPICON (Tanioka et al., 1988), in large area x-ray sensitive vidicons for medical imaging, called the X-icon (Luhta and Rowlands, 1991), in ELIC (electrophotographic light-to-image converter) imaging devices (Kempter et al., 1983), in optical storage (Koshino et al., 1985; Matsushita et al., 1987), in IR fiber optics (Klocek et al., 1987) and in optical recording of images via selective

photodeposition of a-Se films from a colloid (the Selor process), as demonstrated by Peled and coworkers (Peled and Dror, 1988; Peled et al., 1992).

The xerographic process and the basic photoreceptor requirements for xerography are summarized in this handbook by Borsenberger and Weiss as well as by numerous authors in the past (see, e.g., Tabak et al., 1973; Mort and Chen, 1975; Schaffert, 1975; Weigl, 1977; Berger et al., 1979; Mort, 1984; Scharfe, 1984; Williams, 1984; Pai and Melnyk, 1986; Burland and Schein, 1986; Mort, 1989; Pai and Springett, 1993). There is also an extensive literature on the physics and technology of selenium based photoreceptors (Berkes, 1974; Cheung et al., 1982; Springett, 1984, 1988). In its simplest form, a xerographic photoreceptor consists of an amorphous selenium (a-Se) alloy film deposited by vacuum evaporation techniques onto an aluminum drum. Vitreous selenium alloys are normally thermally evaporated from long stainless steel boats onto heated cylindrical aluminum substrates, which are rotated during deposition. Typically the a-Se film is 50–70 μm in thickness and 100 cm^2 in surface area, though areas as large as 1 m^2 are used in the largest machines. The fabrication of many photoreceptor drums requires special vacuum coaters that can accommodate a large number of drums (e.g., 50 or more) and can achieve the required film composition and xerographic characteristics with high yield.

Many aspects of selenium alloy photoreceptor fabrication are poorly understood, especially in the case of Se–Te and Se–As based alloys, where fractionation effects dominate (e.g., Berkes, 1974; Schottmiller, 1975; Springett, 1988). There are still a number of photocopying and printing machines that use either a- As_2Se_3 or a- $\text{Se}_{1-x}\text{Te}_x$ alloy films. Amorphous $\text{Se}_{1-x}\text{Te}_x$ photoconductors contain various amounts of Te alloying and are either in monolayer form or in multilayer geometries. The major reason for alloying with Te is to shift the spectral response of a-Se toward the red region of the spectrum to match the photoreceptor spectral sensitivity with the efficiency of the light source used in the copier or printer. In laser printer applications, the laser light wavelength is invariably beyond the visible red region and demands appreciable Te alloying to bring the photosensitivity of the photoreceptor into the source wavelength band. With as high as $\sim 25\%$ Te alloying, many additional problems arise in the xerographic performance of the photoreceptor, such as rapid dark discharge and high residual potentials, which must be overcome. The solution has been to utilize multilayer photoreceptor geometries incorporating a selenium-rich charge transport layer (CTL) on the Al substrate, a Se–Te alloy based photogeneration layer (PGL) on the CTL, and a Se–As alloy type protection or overcoating layer (OL) on the PGL. In addition, various amounts of halogenation are used to attain specific xerographic criteria. These multilayer geometries have interesting xerographic properties that have been investigated during the 1980s, as is discussed below (Kiyota et al., 1980; Taniguchi et al., 1981; Cheung et al., 1982; Melnyk et al., 1982; Tateishi and Hoshino, 1984). The advantage of a- As_2Se_3 photoreceptors is that they have a wide spectral photosensitivity extending from the blue region to ~ 700 nm.

9.2 PROPERTIES OF SELENIUM AS AN IMAGING MATERIAL

9.2.1 Structure of Selenium

The structure of amorphous selenium has been the subject of many discussions in the literature, inasmuch as for a long time it was believed that the amorphous phase consisted of selenium chain, Se_n , and 8-ring, Se_8 , and perhaps 6-ring, Se_6 , structures mixed together.

This model essentially arose from the fact that in the crystalline phase, selenium can exist in two forms, α -monoclinic Se (α -Se) and trigonal Se (γ -Se). The former has Se_8 rings and the latter Se_n chains, and therefore it was quite natural to seek a structure for the amorphous phase based on a mixture of ring and chain members. Recent structural studies on selenium and its alloys however favor a ‘random chain model’ in which all the atoms are in twofold coordinated chain structure and the dihedral angle ϕ is constant in magnitude but changes in sign randomly (Lucovsky, 1979; Lucovsky and Galeener, 1980; Feltz, 1993).

The dihedral angle, as illustrated in Fig. 9.1, is defined as the angle between two adjacent bonding planes. Its definition therefore involves four atoms, say 1, 2, 3, and 4, so that it is observed as shown in Fig. 9.1 by looking down the bond connecting atoms 2 and 3. In the crystal, the positions of all the atoms are fixed by the symmetry and the bond length r and the bond angle θ ; consequently the magnitude of ϕ is constrained as a function of bond length and angle. In the trigonal form, the dihedral angle rotates in the same sense in moving along a chain to give a spiral pitch of three atoms. In the Se_8 molecular unit, however, its sign alternates in moving around the ring. Thus in a-Se, the change in the sign of the dihedral angle ϕ leads to regions that are ringlike or to regions that are chainlike, depending on a particular sequence of ϕ . If + or – is used to indicate the relative phase of the dihedral angles between adjacent bonding planes, then a sequence of the type $+-+-$ has been termed a ringlike and a sequence of $+++$ or $---$ chainlike by Lucovsky (1979).

The local order shown in Fig. 9.2, for example, can be characterized as $+++-+--$. This model, which assumes only local molecular order within a selenium chain, has been used successfully to explain the vibrational spectra of a-Se to account for the presence of various Se_8 -like spectral features in the infrared absorption and Raman scattering spectra without invoking a mixture of Se_n and Se_8 members for the structure. Other structural studies of a-Se, in particular those by Meek (1976), Robertson (1976), and Long et al. (1976), generally support the random chain model.

An important common feature of nearly all the chalcogenide glasses is the fact that these materials contain thermodynamically derived charged structural defects, called valence alternation pairs (VAP), which correspond to some of the chalcogen atoms being

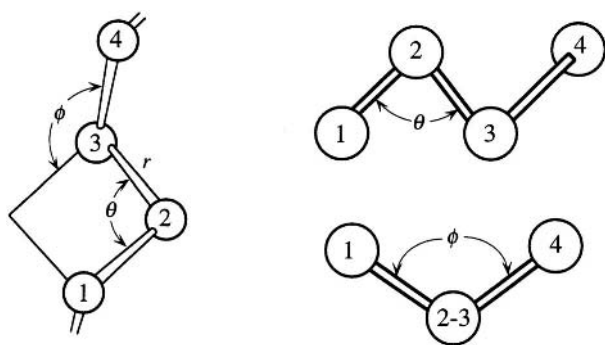


Figure 9.1 Selenium chain molecule and definition of the dihedral angle ϕ . The definition involves an angle between planes and thus four atoms labeled 1, 2, 3, and 4. It is observed looking down the bond joining atoms 2 and 3.

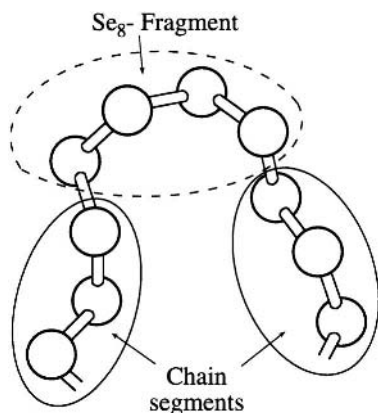


Figure 9.2 Local molecular order in a selenium chain in which there are segments characterized by repetition of the same dihedral angle (“chainlike” in the sense of trigonal Se) and segments characterized by alternating dihedral angles (“ringlike” in the sense of Se_8 molecules). (From Lucovsky, 1979.)

under- and overcoordinated (Kastner et al., 1976; Adler, 1977; Fritzsche, 1977; Kastner, 1977, 1978; Feltz, 1993). The absence of electron spin resonance (ESR) signal in chalcogenide glasses (Abkowitz, 1967; Agarwal, 1973) has indicated that the lowest energy defect in these glasses does not have a dangling bond. The lowest energy defects are charged centers in the structure that have their electrons paired. For example, in the a-Se structure, the Se_2 is the lowest energy configuration for the Se atom and represents the normal bonding configuration. The lowest energy structural defect, however, is not a singly bonded neutral Se atom, Se_1^0 , or a triply bonded neutral atom, Se_3^0 , but a pair of charged centers of the type Se_1^- and Se_3^+ . If the atoms of the pair are in close proximity, they will form an intimate valence alternation pair (IVAP).

The VAP model is essentially based on the fact that it is energetically more favorable to form a diamagnetic pair of charged over- and undercoordinated chalcogenide centers, Se_1^- , Se_3^+ , than to form paramagnetic singly or triply coordinated defects, Se_1^0 or Se_3^0 . The latter are unstable. For example, a dangling bond, Se_1^0 , can lower its energy by approaching the lone pair on the normally coordinated Se_2 atom and generate an IVAP. The diffusion of the resulting species can further reduce the Gibbs free energy. Thus the reaction $\text{Se}_1^0 + \text{Se}_2^0 \rightarrow \text{Se}_1^- + \text{Se}_3^+$ is exothermic because lone pair electrons have been absorbed into dative bonding. Figure 9.3, a schematic representation of a typical a-Se structure with VAP centers, illustrates the nature of lowest energy defects in chalcogen glasses.

Many photoelectric properties of a-Se and its alloys can be at least qualitatively explained by using concepts based on VAP or IVAP centers and interconversions between the diamagnetic charged centers and the paramagnetic defects. The physics of such processes has been extensively discussed in the literature (see, e.g., Mott and Davis, 1979; Elliott, 1984, 1986). Their existence and the possible defect reactions that can occur in the structure have led to many important predictions and much insight into the behavior of chalcogenide semiconductors. For example, the linear dependence of the steady state photoconductivity on the light intensity for a-Se has been interpreted via photoinduced IVAP-type centers (Carles et al., 1984).

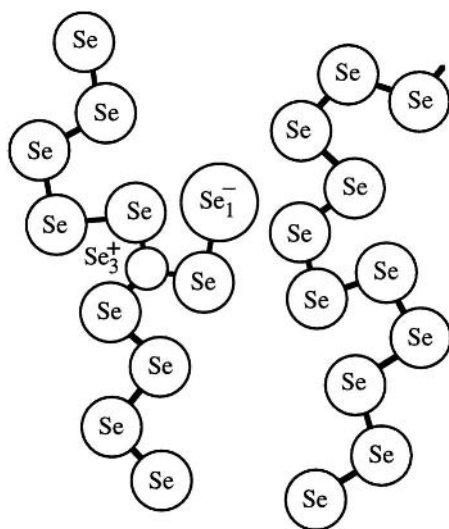


Figure 9.3 Schematic illustration of the amorphous selenium structure showing valence alternation pair (VAP) defects; Se_3^+ , Se_1^- .

9.2.2 Optical and Electrical Properties

During the 1960s and 1970s the optical and electrical properties of a-Se films were extensively studied by many authors. The experimental research at that time coincided with the lack of proper understanding of the physics of amorphous semiconductors, and many of the papers contained models and interpretations that were not fully applicable. Nonetheless, the wealth of experimental data was later put into perspective by various authors (Davis, 1970; Mott and Davis, 1979; Elliott, 1984). The optical absorption coefficient of a-Se exhibits an Urbach edge, of the form (Hartke and Regensburger, 1965) $\alpha = 7.35 \times 10^{-12} \exp[h\nu/0.058 \text{ eV}] \text{ (cm}^{-1}\text{)}$, whereas at high photon energies the absorption coefficient has been found (Davis, 1970; Mott and Davis, 1979; Al-Ani and Hogarth, 1984) to obey $(\alpha h\nu) \sim (h\nu - E_0)$, where $E_0 \approx 2.05 \text{ eV}$ is the optical “band gap” at room temperature. The latter behavior has been attributed to a sharp rise of the density of states at the band edges. A dependence following Tauc’s law $(\alpha h\nu) \sim (h\nu - E_0)^2$ has been also found with an optical bandgap E_0 of about 1.9 eV (Adachi and Kao, 1980; Chaudhuri et al., 1983; Nagels et al., 1994, 1996). Although the absorption coefficient indicates considerable absorption at photon energies above 2 eV, the quantum efficiency (defined as the number of electron–hole pairs collected per absorbed photon) has been found to evince a strong field and photon energy dependence even above the fundamental band edge. Figure 9.4 shows the dependence of the absorption coefficient α and the quantum efficiency η on the photon energy $h\nu$, where it is clear that the quantum efficiency reaches a xerographically acceptable value only at high electric fields and photon energies above the fundamental edge.

The mechanism for the field-dependent quantum efficiency observed for a-Se is common to other molecular solids and can be explained by the Onsager theory for the dissociation of an electron–hole pair (Pai and Enck, 1975). In essence, the Onsager theory calculates the probability that an electron–hole pair will diffuse apart under an electric

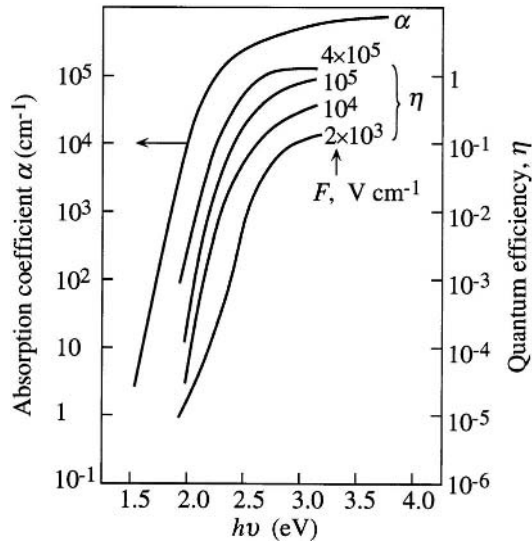


Figure 9.4 Absorption coefficient α and quantum efficiency η , as a function of incident photon energy $h\nu$ at various applied fields F . (Data from Hartke and Regensburger, 1965; Ing and Neyhart, 1972; Pai and Enck, 1975.)

field. The quantum efficiency depends on the electric field F , the temperature T , and the initial separation of the photogenerated electron–hole pair r_0 , the thermalization length. The quantum efficiency η is thus given by

$$\eta = \eta_0 f(F, T, r_0) \quad (1)$$

where $f(F, T, r_0)$ is the probability that the electron–hole pair will separate and $\eta_0(h\nu)$ is the quantum efficiency of the intrinsic photogeneration processes. The significance of the field and photon energy dependence of the quantum efficiency is that the xerographic design has to consider the charging voltage together with the spectrum of the illumination to obtain optimal performance from the photoreceptor. The quantum efficiency affects the nature of photoinduced xerographic discharge and thus the contrast potential. For example, the transit time of photogenerated holes across the thickness of an a-Se based photoreceptor is invariably much shorter than the exposure time, which means that the photoinduced discharge mechanism is emission limited (Mort and Chen, 1975). As the field in the photoreceptor decays, the photogeneration rate diminishes, by virtue of the field dependence of the quantum efficiency. Consequently the total number of photogenerated charge carriers is not simply proportional to the exposure, which makes gray scale images more difficult to replicate.

It is instructive to mention that recently Moses (1992, 1996) has challenged the Onsager interpretation of the quantum efficiency in a-Se. He carried out subnanosecond transient photoconductivity experiments using a matched microwave stripline technique and a very short laser pulse (25 ps at 1.8–2.29 eV photon energy). The quantum efficiency as inferred from the peak photocurrent in the subnanosecond time scale shows no field or temperature dependence, in contrast to that inferred from TOF transient photoconductiv-

ity and xerographic photoinduced discharge experiments (i.e., as that shown in Fig. 9.5) in the time scale of microseconds and above. The quantum efficiency interpretation in the latter, according to Moses, is a carrier supply yield rather than the intrinsic quantum efficiency. More careful experiments are now needed to clarify the present controversy.

Charge transport and trapping in a-Se and its alloys has been a subject of much interest and research inasmuch as it is the product of the charge carrier drift mobility and the trapping time (or lifetime), $\mu\tau$, termed the range of the carriers, which determines the xerographic performance of a photoreceptor. The nature of charge transport in a-Se alloys has been extensively studied by the time-of-flight (TOF) transient photoconductivity (TP) technique. The principle of the technique is illustrated in Fig. 9.5. The sample is sandwiched between two electrodes, typically Au and Al, the former being semitransparent. Since the external resistance R is much less than the sample resistance, the applied bias V appears across the thickness L of the specimen. A short light pulse of appropriate wavelength photogenerates a packet of electron-hole pairs near the surface of the specimen. The absorption depth $\delta(\lambda) = 1/\alpha(\lambda)$ is chosen to be much shorter than the thickness L . Electrons become neutralized almost immediately by reaching the top electrode, whereas holes drift toward the substrate, generating a transient current in the external circuit R . The circuit time constant $C_{\text{sample}}R$ is maintained much shorter than the transit time of the charge packet, $T_t = L^2/\mu V$, across the film, to ensure that the voltage signal across R is proportional to the photocurrent in the specimen. While the holes are drifting in the specimen, there is a photocurrent $i(t)$ in the sampling resistor R , and the shape of the photocur-

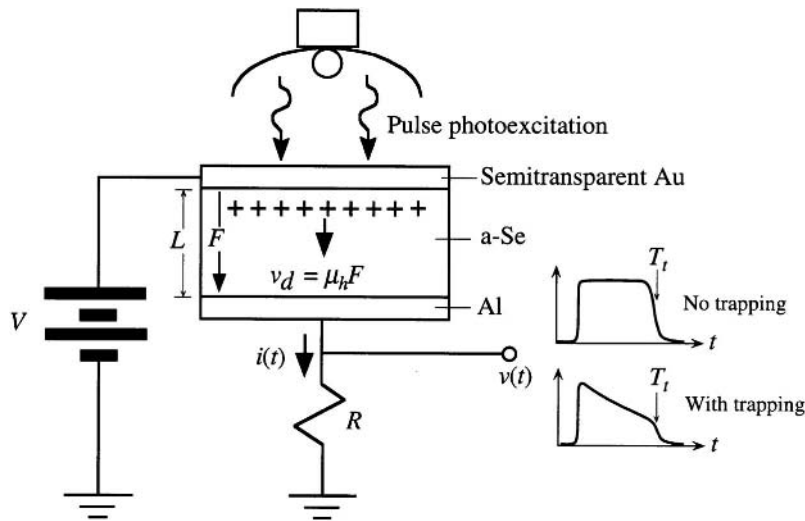


Figure 9.5 Schematic diagram illustrating the principle of time-of-flight (TOF) measurements. The top electrode is semitransparent. Following pulse photoexcitation, electron-hole pairs are generated within an absorption depth $1/\alpha(\lambda) \ll L$. As the holes drift across the specimen, they generate an external photocurrent $i(t)$. The shape of the photocurrent $i(t)$ depends on the nature of trapping within the solid. T_t is the transit time of the photoinjected holes across the sample thickness, L , and is given by $T_t = L/v_d$ where v_d is the drift velocity, $v_d = \mu_h F$, μ_h is the hole drift mobility, and F is the electric field (V/L).

rent waveform at any time represents not only the average concentration of mobile holes but also the mean velocity of the carriers at that instant, that is,

$$i(t) = eAp(t)v_d(t) \quad (2)$$

where $p(t)$ is the mean concentration of mobile holes in the specimen at time t , which is obtained by averaging the hole concentration $p(x, t)$ over the thickness L , and $v_d(t)$ is the drift velocity at time t .

Injected charge is normally much less than that on the electrodes, so that the electric field in the sample remains relatively unperturbed. Consequently, charge trapping and release events involving various distributions of traps in the material result in the transient photocurrent decaying with time. In the extreme case, when the trapping time is much shorter than the transit time and there is insignificant release from the traps over a time scale of the order of T_t , the observed photocurrent is an exponential-looking rapid decay without a transit time. The latter is termed trap-limited response. Many recent papers in the literature extract the distribution of localized states in the mobility gap from the shape of the TOF transient photocurrent. Some of these theories have been successfully applied to characterize the distribution of localized states in plasma-deposited amorphous silicon (a-Si:H) films, which is of interest in a-Si:H photoreceptor design. The virtue of the TOF measurement lies in its ability to monitor the motion of charge carriers across a photoreceptor film and so to provide a direct evidence of whether the photoinjected charges are making it across the sample.

Furthermore, by using an interrupted field time-of-flight (IFTOF) measurement, it is also possible to study the nature of trapping and release kinetics in the material at any location (Kasap et al., 1988, 1990c). This technique involves interrupting the electric field for a duration t_i during the flight of the photoinjected carriers. The field is removed when the charge carrier packet is at one location and is reapplied at the end of the interruption time t_i to extract the remaining carriers. The fractional change in the recovered photocurrent represents the trapped charge and allows the carrier lifetime, τ , to be evaluated at that location. Indeed, one can readily determine the variation of the carrier trapping time across a photoreceptor film and correlate this with the composition across the film (Kasap and Polischuk, 1995).

Figure 9.6 shows the temperature dependence of the drift mobility in various phases of selenium obtained mainly from transient photoconductivity measurements; the only exception consists of the drift mobility versus temperature data on trigonal Se (γ -Se), which was measured by the acoustoelectric current as well as the magnetoresistance methods (Mort, 1967; Mell and Stuke, 1967). It is immediately apparent from Figure 9.6 that, except in γ -Se, the drift mobilities at low temperatures in the liquid, monoclinic, and amorphous phases are thermally activated. In particular, the hole drift mobility activation energy in amorphous and α -monoclinic (α -) Se are comparable, though they encompass different temperature ranges. The basic interpretation of drift mobility–temperature data for both a-Se and α -Se has been a shallow trap–controlled transport mechanism in which the hole TOF drift mobility (or the effective drift mobility) is given by

$$\mu_h(T) = \mu_0(T) \frac{\tau_c}{\tau_c + \tau_r} = \mu_0(T) \left[1 + \frac{N_t}{N_v} \exp\left(\frac{E_t}{kT}\right) \right]^{-1} \quad (3)$$

where μ_0 is the microscopic (conductivity) mobility, τ_c and τ_r are the mean capture and the mean release times, respectively, N_t is the shallow trap concentration, N_v is the density

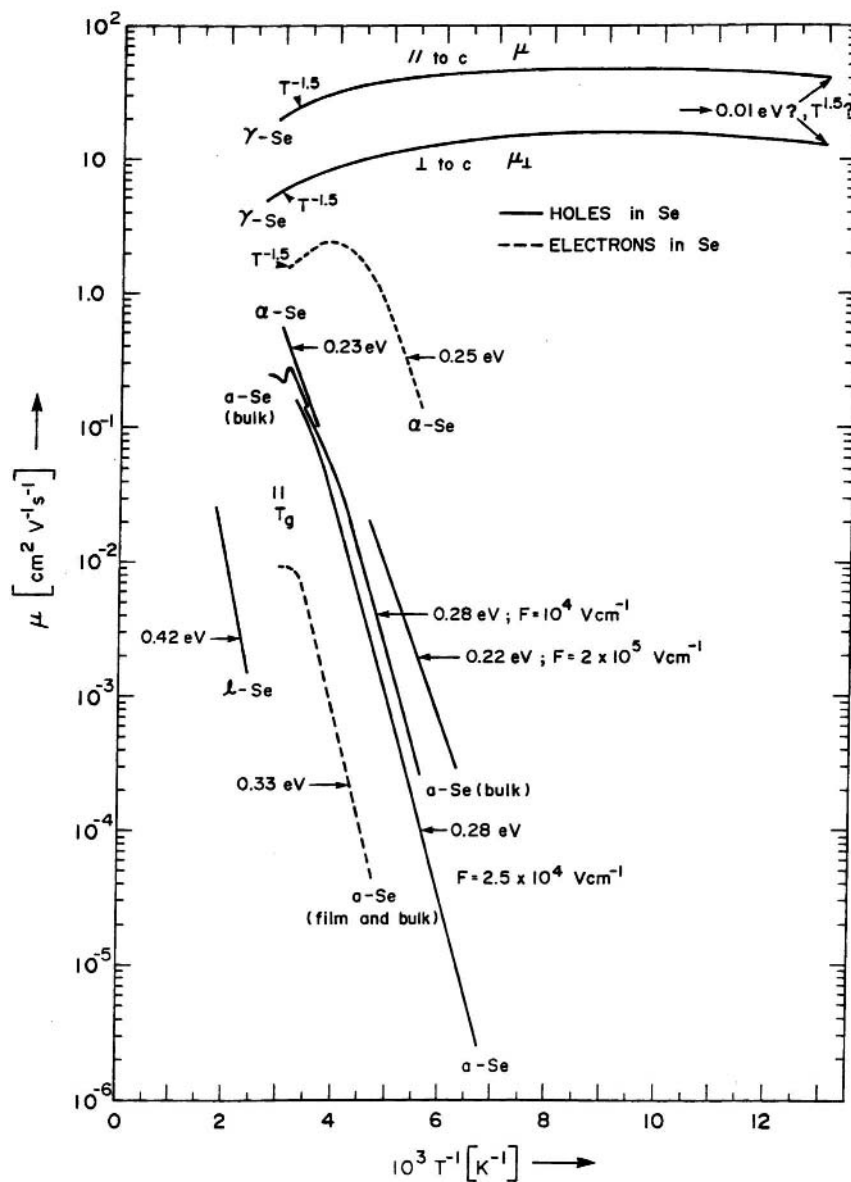


Figure 9.6 Hole and electron drift mobility in various phases of selenium: a-Se, amorphous Se; α -Se, α -monoclinic Se; γ -Se, trigonal Se; l -Se, liquid Se. (Data collected from Mort, 1967; Marshall et al., 1974; Spear, 1961; Juska et al., 1974; Marshall and Owen, 1972; Pfister, 1976; Marshall et al., 1974; Schottmiller et al., 1970; Juska and Vengris, 1974; and Abkowitz, 1979.)

of states at the valence band mobility edge E_v , and E_t is the energy depth of the shallow traps from E_v .

The nature of the basic microscopic conduction process, whether by extended state transport or by hopping—for example, in the localized tail states—has not been conclusively established. The lack of pressure dependence in the thermally activated drift mobility down to ~ 230 K has been used by various authors as evidence that the measured drift mobility does not represent a purely hopping transport process (Dolezalek and Spear, 1970). The temperature dependence of the microscopic mobility seems to follow a $\mu_o \sim T^n$ type of behavior, where n is an almost diffusive type of index ($n \approx 1$) (Kasap and Juhasz, 1985).

Figure 9.7 represents the presently accepted model for the electronic density of states for a-Se as developed mainly by Abkowitz and coworkers through various transient photoconductivity and electrophotographic measurements of cycled-up residual and dark discharge (Abkowitz, 1984a–c, 1985, 1987, 1988). There is a wealth of experimental evidence that the localized states, both shallow and deep, in the mobility gap are due to various structural defects that are thermodynamically stable at room temperature (Abkowitz, 1981, 1984a–c; Abkowitz and Markovics, 1984). Almost exponentially decaying shallow trap densities with discrete manifolds at certain energies near the transport bands have been determined from picosecond-resolution transient photoconductivity experiments using microwave stripline techniques (Orlowski and Abkowitz, 1986). The high concentration of traps at the relatively discrete energies ~ 0.29 eV above E_v and ~ 0.35 eV below E_c essentially control hole and electron drift mobility as originally proposed by Spear (1957, 1960) and Hartke (1962). Although these traps are known to be native defects, their exact nature has not been conclusively determined. Lucovsky and coworkers (Wong, Lucovsky, and Bernholc, 1985) proposed that they may be due to dihedral angle distortions in the random structure of a-Se in which the lone pair orbitals on adjacent Se atoms approach parallel alignment. The energy distribution of the deep localized hole states with

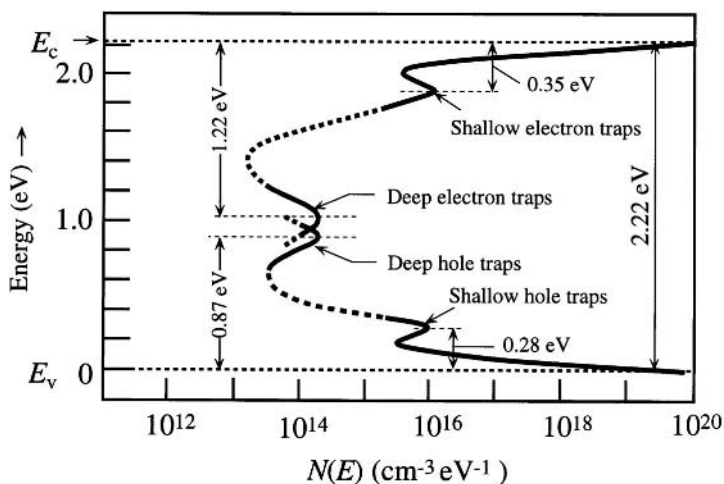


Figure 9.7 Density of states function $N(E)$ for a-Se derived from various optical, TOF, and xerographic measurements. (Adapted from Abkowitz, 1988.)

a peak around 0.85 eV has been also measured by cycled time-of-flight experiments as described by Veres and Juhasz (1993).

Early TOF measurements were quite successful in identifying the drastic effects of various impurities and alloying elements on the nature of charge transport in a-Se (Kolo-miets and Lebedev, 1966; Schottmiller et al., 1970; Tabak and Hillegas, 1972; Pai, 1974; Takahashi, 1979; Kasap and Juhasz, 1982; Takasaki et al., 1983; Baranovskii and Lebedev, 1985; Oda et al., 1986). It was shown, for example, that additions of halogens in small amounts to a-Se completely destroy electron transport. Halogens even in the parts per million range introduce sufficient concentration of electron traps to diminish electron transport. On the other hand, halogenation has been reported to improve the hole lifetime. The impurity effects in a-Se have been reasonably well documented. By appropriate chemical modification, it is possible to obtain an optimum xerographic performance from an a-Se based photoreceptor (Abkowitz and Jansen, 1983; Abkowitz et al., 1985b, 1986; Badesha et al., 1986).

9.2.3 Xerographic Properties

An optimal photoreceptor design will require, among many other factors, high charge acceptance, slow dark discharge, low first and cycled-up (saturated) residual voltages, and long charge carrier ranges ($\mu\tau$). The latter factor has been addressed above. There are essentially three important types of xerographic behavior, generally termed the dark discharge, first cycle residual, and the cycled-up residual voltage, which must be considered in evaluating the electrophotographic properties of a-Se and its alloys. The three xerographic properties are illustrated in Fig. 9.8.

Dark discharge rate must be sufficiently low to maintain ample amount of charge on the photoreceptor during the exposure and development steps. A high dark decay rate will limit the available contrast potential. The residual potential remaining after the xerographic cycle must be small enough not to impair the quality of the electrostatic image in the next cycle. Over many cycles, the cycled up residual potential should also be small, to avoid deterioration in the copy quality after many cycles. In the case of a-Se, these xerographic properties have been extensively studied (Abkowitz and Enck, 1980, 1982, 1983). In addition to the magnitude of the saturated residual voltage, the rate of decay and the temperature dependence of the cycled-up residual potential are important considerations, since they determine the time required for the photoreceptor to regain its first cycle xerographic properties.

Figure 9.9 displays the simplest experimental setup for xerographic measurements. The rotating photoreceptor drum is charged at station A by a corotron-type device. The surface potential is measured at B, and the photoreceptor is then exposed to a controlled wavelength and intensity illumination at station C, following which its surface potential is measured again at station D. In some systems, the surface potential is also monitored during exposure at C via a transparent electrometer probe to study the photoinduced discharge characteristics (PIDC). Normally, the charging voltage, speed of rotation, and exposure parameters (energy and wavelength) are user-adjustable.

Figure 9.10 shows typical positive and negative dark discharge curves for pure a-Se films prepared under different conditions (Schaffert, 1975), where it can be seen that the dark discharge rate depends on the substrate temperature. The presently accepted model for the dark decay in a-Se films is that which involves substrate injection as well as bulk

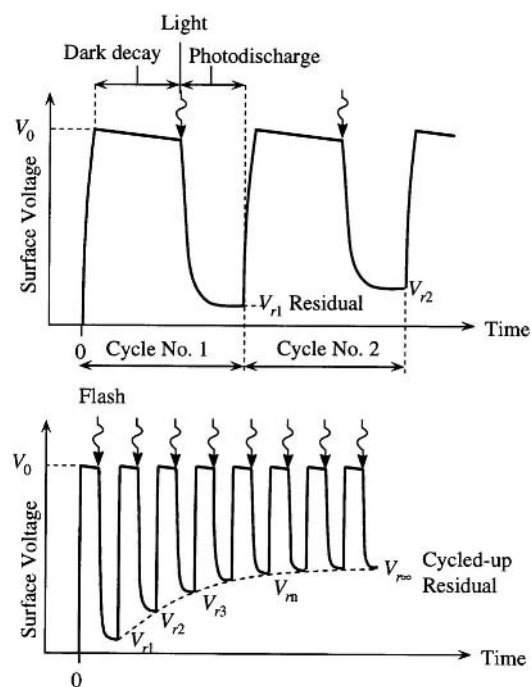


Figure 9.8 Typical photoreceptor behavior through xerographic cycles showing dark decay, first cycle residual potential V_{r1} , and cycled-up residual potential V_{res} , after many cycles.

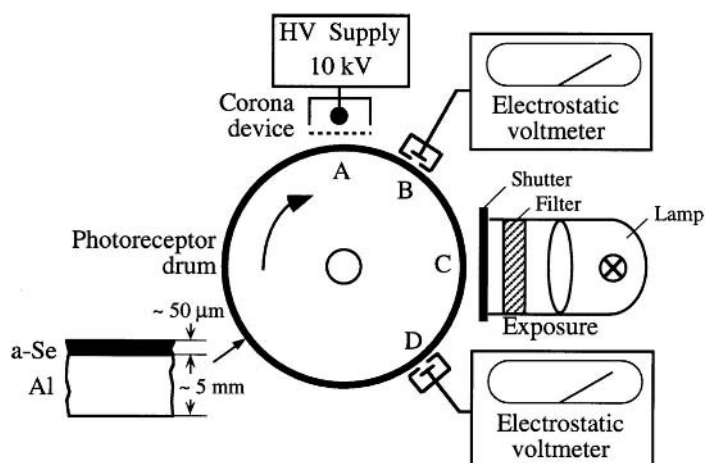


Figure 9.9 Simplified schematic diagram of a xerographic measurement. The photoreceptor is charged at A and exposed at C. Its surface potential is measured before and after exposure at B and D.

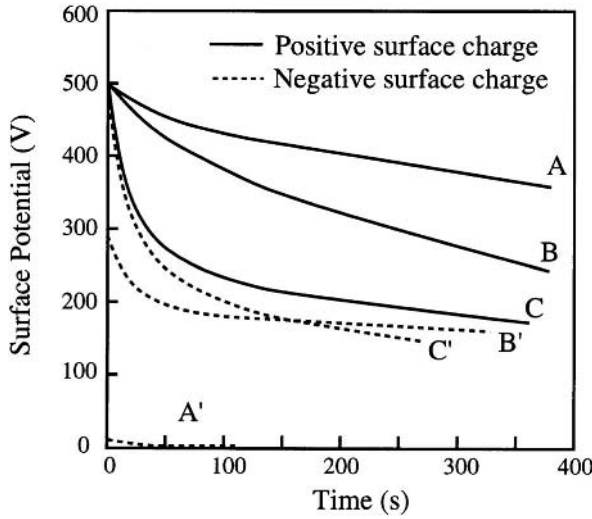


Figure 9.10 Dark discharge of surface potential on a-Se layers. A, B, and C involve a-Se deposition under different substrate temperature (T_{sb}) conditions: A and A' at $T_{sb} = 75^\circ\text{C}$; B and B' at $T_{sb} = 50\text{--}60^\circ\text{C}$; C and C' at $T_{sb} = 25\text{--}50^\circ\text{C}$ and uncontrolled. (From Schaffert, 1975.)

thermal generation and depletion. The latter process involves thermal generation of holes in the bulk and their sweepout from the sample by the internal field, leaving behind a bulk negative space charge (see Section 9.3.2). With thick films and a good blocking contact between a-Se and the preoxidized aluminum substrate, the latter phenomenon dominates. The main reasons for a-Se possessing good dark decay characteristics are (1) there are not many deep localized states in the mobility gap of a-Se; (2) the energy location of these localized states is deep in the mobility gap, so that the thermal generation process of holes (or electrons) from these centers is slow; (3) injection from the substrate can be reduced substantially by using oxidized Al substrates (Zhang and Champness, 1991).

Figure 9.11a displays the buildup of the residual voltage V_{ri} on an a-Se film with the number of xerographic cycles n . If blue light is used for the discharge process, then the absorption is very close to the charged surface, and one can assume that the discharge process involves the transport of photogenerated holes through the bulk. Trapping of these holes in the bulk then results in the observed first residual potential, V_{ri} . In the case of a-Se photoreceptor films it has been found that V_{ri} is well predicted by the simple Warter expression (Kasap et al., 1991a, b)

$$V_{ri} = \frac{L^2}{2 \mu_h \tau_h} \quad (4)$$

where L is the film thickness, μ_h is the hole drift mobility, τ_h is the hole lifetime, and $\mu_h \tau_h$ is the hole range.

It can be seen from Fig. 9.11a (and also from Fig. 9.8) that as the xerographic cycle is repeated many times at a constant repetition frequency, the residual voltage rises and eventually saturates. The saturated residual voltage $V_{r\infty}$ is much larger than the first cycle residual potential V_{ri} . Both the first residual and the cycled-up saturated residual potential, V_{ri} and $V_{r\infty}$, are sensitive to preillumination as well as to impurities and alloying. For

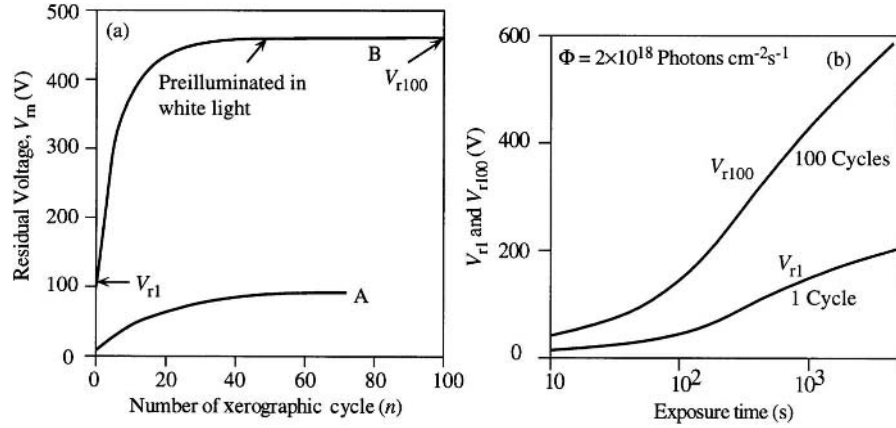


Figure 9.11 (a) Residual potential V_m as a function of the xerographic cycle n for pure a-Se films of comparable thickness ($L = 50\text{--}55\ \mu\text{m}$). A: dark rested specimen; B: specimen preilluminated with white light. (Data from Abkowitz and Enck, 1982, 1983.) (b) Dependence of the first and hundredth cycle residual potentials V_{r1} and V_{r100} on the exposure time under white light illumination. (From Abkowitz and Enck, 1983.)

example, when a-Se films are preilluminated with white light, the buildup of the residual potential occurs more rapidly toward a much higher saturated residual potential, as indicated by curve B in Fig. 9.11a. Furthermore, the residual potentials V_{r1} and $V_{r\infty}$ increase with the exposure time (Fig. 9.11b). It is clear from Fig. 9.11b that exposure to white light generates an appreciable concentration of deep hole traps. There are essentially two ways of accounting for the saturation of the residual voltage in Fig. 9.11a. First, the observed saturation may be due to the dynamic balance between trapping and release of charge carriers as the xerographic cycle is repeated. Alternatively, it may be due to the filling of the deep trap population so that the saturated residual potential is given by

$$V_{r\infty} = \frac{L^2 e N_t}{2\epsilon_0 \epsilon_r} \quad (5)$$

where N_t is the concentration of deep traps and ϵ_0 and ϵ_r are, respectively, the absolute permittivity and relative permittivity of the photoreceptor material.

The rate of decay and the temperature dependence of the saturated voltage can be used to obtain the concentration and energy distribution of the deep traps responsible for the residual voltage. Thus $V_{r\infty}$ provides a useful means of studying the nature of deep traps in amorphous semiconductors and has been successfully used to derive the energy distribution of deep localized states in the mobility gap of both a-Se and a-Si:H (Abkowitz and Enck, 1982; Abkowitz and Markovics, 1984; Imagawa et al., 1986).

Figure 9.12 shows the decay of the saturated residual potential on an a-Se film at the end of a large number cycles. As thermal release proceeds, holes are emitted and swept out from the specimen, resulting in the decrease of the measured surface potential. The decay rate of the saturated potential is strongly temperature dependent due to thermal release from deep mobility gap centers, which are $\sim 0.9\text{ eV}$ above E_v for holes. The discharge of the saturated potential due to electron trapping occurs much more slowly, as indicated in Fig. 9.12. The reason is that the energy depth of electron traps from E_c is about $\sim 1.2\text{ eV}$, which is greater than that of hole traps from E_v .

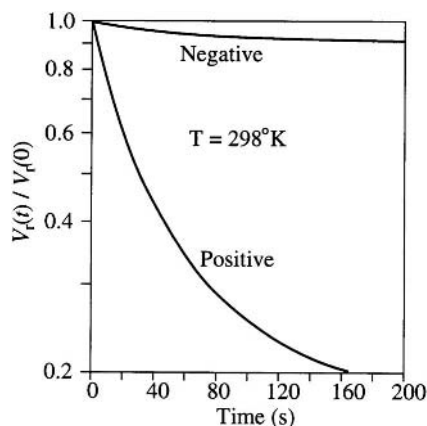


Figure 9.12 The decay of the saturated residual potential $V_{r\infty}$ with time following the cessation of xerographic cycling for positive charging and negative charging. The residual potential at time t is normalized to that at $t = 0$ marking the end of xerographic cycling.

9.2.4 Thermal Properties and Aging (Structural Relaxation)

Inasmuch as a-Se is basically an inorganic polymeric glass, it exhibits many of the properties of glassy polymers. Its glass transformation and crystallization behaviors have been extensively studied by numerous authors. Most thermal studies on a-Se and its alloys have used the differential scanning calorimeter (DSC) type of differential thermal analysis (DTA) measurements, which involves monitoring the rate of heat flow into the specimen as a function of sample temperature while the sample is heated at a constant rate.

Figure 9.13 shows a typical DSC thermogram on a pure a-Se film at a heating rate of $10^\circ\text{C min}^{-1}$ where the glass transformation, crystallization, and melting phenomena are clearly visible as endothermic, exothermic, and endothermic peaks, respectively. The glass transformation temperature T_g , the crystallization onset temperature T_o , the maxi-

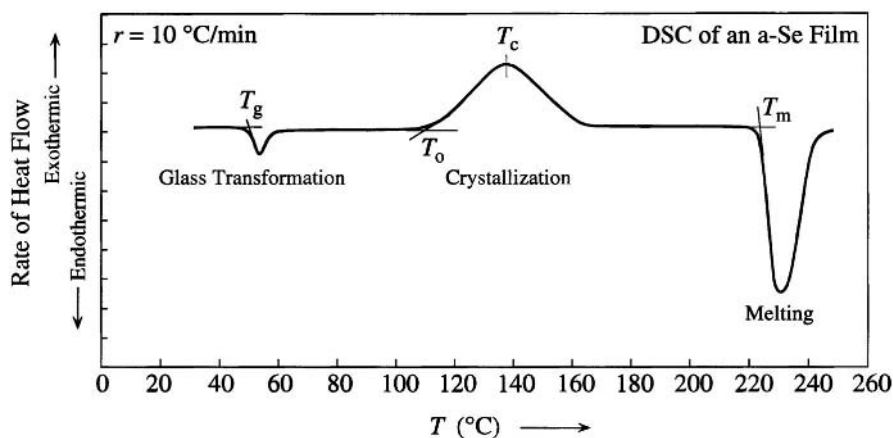


Figure 9.13 A typical DSC thermogram for an a-Se film showing the glass transition region, crystallization, and melting transitions. Heating rate, $r = 10^\circ\text{C/min}$. (From Kasap and Juhasz, 1986.)

imum crystallization rate temperature T_c , and the melting temperature T_m are defined in the figure.

The dependence of the glass transition temperature T_g on the heating rate r and the aging time t_A has been investigated by Stephens (1976, 1978) and Larmagnac et al. (1981) and can be readily explained by the enthalpy $H(T)$ vs. temperature behavior of a typical glass-forming material shown in Fig. 9.14. Once the glassy state G has been reached—by, for example, cooling from the melt—and the glass is at temperature T_A , the enthalpy will relax via structural relaxation toward the enthalpy of the metastable equilibrium state $H_E(T_A)$ at A. In the case of a-Se and in a number of other glassy polymers, several days of annealing at the room temperature brings the glass enthalpy close to $H_E(T_A)$, as evidenced by the endothermic peaks in the DSC thermograms at T_g . There is much evidence from a variety of experiments under thermal cycling conditions to indicate that following prolonged annealing (e.g., ~ 1000 hours) at room temperature, the thermodynamic state of a-Se corresponds almost to that of the supercooled metastable liquid at A (Abkowitz, 1981, 1984a–c, 1985, 1987).

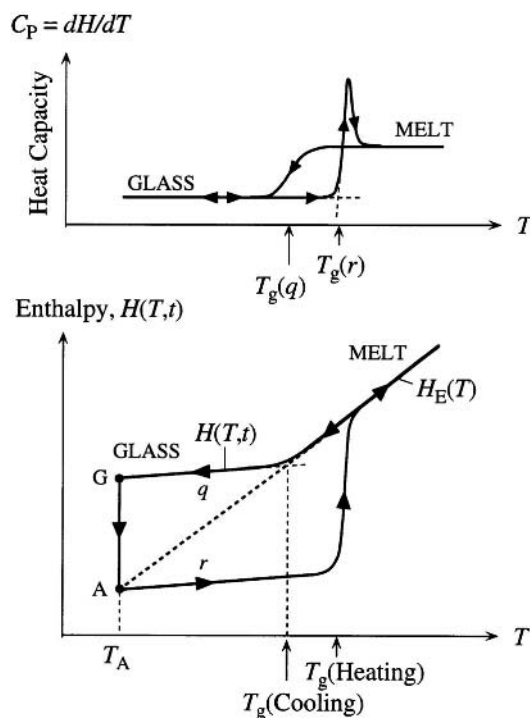


Figure 9.14 Enthalpy H versus temperature T for a typical glass-forming liquid. As the melt is cooled at a rate q , eventually the structure goes through a glass transformation at $T_g(q)$. The enthalpy of the glass is higher than the equilibrium liquidlike enthalpy $H_E(T)$. When the glass at point G at T_A is annealed, the structure relaxes toward the equilibriumlike metastable state at A. On reheating at a rate r , the glass enthalpy is retarded and recovers toward H_E at $T = T_g$ (heating) or $T_g(r)$. The upper curve shows the heat capacity versus temperature behavior observed during heating and cooling.

When the sample at $H(T_A)$ is heated at a constant rate r , the enthalpy of the system, as a result of long relaxation times at these low temperatures, follows the glass H - T curve until the structural relaxation rate is sufficiently rapid to allow the system to recover toward $H_E(T)$. This sharp change in $H(T)$ leads to the glass transformation endotherm in the DSC heating scan. The observed glass transition temperature T_g during heating depends not only on the heating rate but also on the initial state $H(T_A)$. On the other hand, during cooling (at a rate q) from the melt down to low temperatures one observes only a change in the base line, i.e., a change in the heat capacity. T_g during cooling depends only on the cooling rate q (for a-Se, see, for example, Kasap et al., 1990a).

The significance of the glass transformation behavior of a-Se is that as T_g is approached, many of the physical properties of the film exhibit sharp changes as a result of relaxation phenomena. For example, the hole range $\mu\tau$ evinces a sharp drop in the T_g region, which reflects as a deterioration of the xerographic performance. When the photoreceptor is returned to its normal operating temperature, the recovery of the various physical properties occurs over a time scale determined by the relaxation time at that temperature. The mean relaxation time τ for structural relaxations has a Vogel $\tau \sim \exp[A/(T - T_0)]$ type strong temperature dependence (Kasap et al., 1990a, 1990b). Relaxations at room temperature occur over a time scale ~ 1000 hours. The Vogel type of relaxation phenomenon exhibited by a-Se is typical of many organic polymers and is also consistent with the Williams-Landel-Ferry behavior observed for the dielectric relaxation in this material (Abkowitz et al., 1980). Nearly all the physical properties of a-Se evince an aging behavior, which means that the property changes with time as the film is left to anneal isothermally. For example, immediately after deposition, the Vickers microhardness H_V of an a-Se film may typically be about $25 \text{ kgf} \cdot \text{mm}^{-2}$, but H_V increases with aging, and after aging for several hundred hours H_V stabilizes at around $35 \text{ kgf} \cdot \text{mm}^{-2}$. The basic principle of the aging process can be explained by enthalpy-temperature or volume-temperature diagrams as illustrated in Fig. 9.14, which show structural relaxation toward the metastable liquidlike state $H_E(T_A)$ at A. Aging behavior has been reported for various properties of a-Se, e.g., density, heat capacity, density of structural defects, etc. (e.g., Das et al., 1972; Stephens, 1976, 1978; Larmagnac, et al., 1981; Abkowitz, 1985) and is a fundamental property of all glasses.

Crystallization of a-Se in bulk and film form has been extensively examined (see, e.g., Cooper and Westbury, 1974). It is well known that pure a-Se is sensitive to crystallization and invariably crystallizes at a rate determined by the nucleation process, the morphology of growth, and the temperature. Isothermal crystallization rate has been found to be well described by the Avrami equation. Crystallization data from a variety of experiments suggest that the growth rate during the crystallization process is inversely proportional to the melt viscosity and that the latter can be adequately described over a temperature range by a Vogel type of temperature dependence as originally proposed by Felty (1967). The effects of various impurities on the crystallization kinetics have been reported by many authors, as reviewed by Cooper and Westbury (1974).

Alloying a-Se with As has been found to be very effective in retarding the crystallization rate. In fact, once the As content has reached a few percent, the alloy is almost totally resistant to crystallization (Nemilov and Petrovskii, 1963a, b). During the 1960s it was found, essentially by experiments, that 0.3–1% As addition to a-Se is sufficient to diminish the crystallization rate but has the adverse effect of creating hole traps. The latter xerographic disadvantage was overcome by adding Cl in ppm amounts to compensate for

the As-induced traps (Tabak and Hillegas, 1972; Schottmiller, 1975). It should be mentioned that with As alloying the glass transformation temperature increases, which is a distinct advantage, and the films become mechanically more stable (Kasap and Juhasz, 1987). Although most a-Se based modern photoreceptors are essentially Se–Te alloys or a-As₂Se₃, chlorinated Se:0.5% As alloy is still in use as x-ray photoconductors in x-ray imaging applications, as will be discussed later, and often forms the overcoat layer in multilayer Se–Te based photoreceptors. Chlorinated Se:0.5% As alloy is typically referred as *stabilized* a-Se.

9.3 PROPERTIES OF SELENIUM ALLOYS

9.3.1 Selenium–Arsenic

It has been mentioned that alloying selenium with arsenic results in improvements in the thermal and mechanical properties. There are essentially two composition ranges for Se–As alloys that are useful for electrophotographic applications; the low As content end (As content <1 at%) and the near stoichiometric composition (As content 35–38 at%), which is simply termed As₂Se₃. The physical properties of the Se–As alloy system over a wide range of compositions have been extensively studied, as reviewed by Barisova (1981) and Feltz (1993), for example. There is also much literature on the electrophotographic properties of a-As₂Se₃ that examines its optical, charge transport, and xerographic properties (Tabak et al., 1973; Pfister and Morgan, 1975, 1980; Pfister et al., 1977; Pfister, 1979; Scharfe, 1984; Pinsler et al., 1986).

The major advantages of a-As₂Se₃ photoreceptors over those of a-Se:0.5% As and a-Se_{1-x}Te_x alloys are superior thermal and mechanical properties, as manifested in a higher glass transformation temperature, almost absent crystallization, and a considerably higher microhardness, as summarized in Table 9.1. The latter advantages naturally lead to a long operational lifetime for a-As₂Se₃ photoreceptors in large-volume copying applications. Interband absorption in a-As₂Se₃ starts at a photon energy of ~1.8 eV, which makes the photoreceptor almost panchromatically sensitive to the visible spectrum. Unity xerographic photosensitivity, for example, occurs around 500 nm for a-Se but at about 720 nm for a-As₂Se₃. Only holes are mobile in a-As₂Se₃, with an effective drift mobility (as determined by TOF type experiments) that is highly field dependent and nearly 3 to 4 orders of magnitude smaller than in a-Se. Consequently, the photoinduced discharge in a-As₂Se₃ photoreceptors is controlled mainly by bulk transport. Generally a-As₂Se₃ used as a photoreceptor material is also typically halogen doped (e.g., 1000 ppm Br) to increase the hole drift mobility (Pfister et al., 1977). It should be mentioned that the transport of photoinjected holes through an a-As₂Se₃ film is based on multiple trapping and release events involving a distribution of localized states in the mobility gap and cannot be simply described in terms of a constant drift mobility as in the case of a-Se. The dark decay of the surface potential is controlled by a depletion discharge process (Melnik, 1980) and has many similarities to that found for a-Se_{1-x}Te_x alloys, as is discussed in detail in the next section.

The xerographic properties of a-As₂Se₃ in terms of dark discharge and residual potential are generally worse than those for a-Se, essentially as a result of a high population of deep mobility gap states in a-As₂Se₃. Another shortcoming of a-As₂Se₃ is that in a monolayer form it is not generally suitable for laser printer applications requiring long

Table 9.1 Physical Properties of a-Se and a-As₂Se₃

Property	a-Se	a-As ₂ Se ₃
Density, g · cm ⁻³	4.29	4.55
Glass transformation temperature (DSC at 5°C/min)	50°C	~180°C
Crystallization temperature (DSC at 5°C/min)	100°C	~300°C
Melting temperature, °C	218	~360
Microhardness (Vickers hardness number kgf/mm ²)	40	~150
“Photoconduction band gap” (eV)	2.5	1.8
Wavelength for unity photosensitivity, nm	500	720
Dark resistivity (Ω · cm)	10 ¹⁴	10 ¹²
Hole drift mobility, cm ² /V · s (<i>F</i> is the electric field in V · cm ⁻¹)	0.16	~2 × 10 ⁻¹⁰ <i>F</i>
Electron drift mobility, cm ² /V · s	7 × 10 ⁻³	—
Quantum efficiency	Field dependent	Field dependent
Xerographic dark discharge	Depletion discharge	Depletion discharge

Sources: Barisova (1981, Ch. 1), Kasap and Juhasz (1987), Lutz (1987), Lutz and Reimer (1982), Scharfe (1984).

wavelength responsivity, since bulk absorption results in trapped electrons. By using a double-layer photoreceptor consisting of a thin As₂Se_{3-x}Te_x ($x < 0.5$) layer for photogeneration and a thick As₂Se₃ layer for charge transport, the photosensitivity can be shifted further into the long wavelengths (Pinsler et al., 1986).

The cyclic buildup of the residual potential in As₂Se₃ photoreceptors can be stabilized to ensure reproducible copy quality by employing light sources of various wavelengths for prefatiguing or erasure as described by Pinsler et al. (1986). In addition, the photoreceptor can be operated at a stable temperature, above the room temperature, to reduce variations in the xerographic performance due to temperature changes in the environment. Both dark discharge and residual potential depend on the population of deep localized states which are thermally generated structural defects. Thus the dark discharge and residual potential are highly temperature sensitive (Ing and Neyhart, 1972; Melnyk, 1980).

Figure 9.15 shows the effect of adding 0.5% As to a-Se on the charge transport and trapping properties from TOF measurements. Although the mobility is relatively unaffected, the trapping time becomes shorter, which leads to, for example, high residual potentials. With ppm amounts of Cl addition, however, the hole lifetime is restored. It was the success of this combinational doping to normalize the properties of a-Se that led to the continued use of a-Se as an imaging material. The physical process that restores the hole transport can be qualitatively accounted for by various possible defect reactions in the structure (Juhasz and Kasap, 1985); the compensation effects of As and Cl in a-Se is still a subject of topical interest (Pai, 1997), given the recent importance of this material as an x-ray photoconductor. The improvement in the hole lifetime when a-Se is doped with small amount of Cl is also apparent in xerographic measurements in which the residual potential, V_{r1} in Eq. (4), falls sharply with small amounts of Cl addition (<10 ppm) (Wang and Champness, 1995).

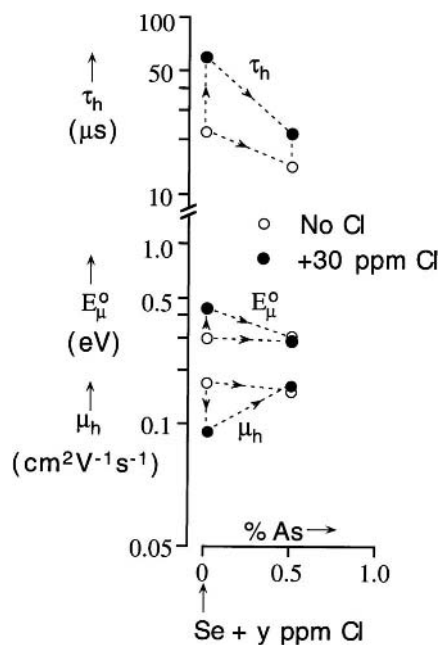


Figure 9.15 Hole transport parameters, namely hole drift mobility (μ_h), mobility activation energy (E_μ°), and hole lifetime (τ_h) in $a\text{-Se}_{1-x}\text{As}_x + y$ ppm Cl; solid points contain Cl. (From Juhasz and Kasap, 1985.)

9.3.2 Selenium–Tellurium

The central reason for alloying amorphous selenium with tellurium is the shift in the spectral response toward the red region with Te content, which allows the photosensitivity of the photoreceptor to be matched with the exposure spectrum; hence an improvement in the overall xerographic efficiency. Figure 9.16 shows that the optical band gap decreases almost linearly with Te addition, which leads to an appreciable increase in the quantum efficiency. For example, for ~ 20 at% Te alloy, the quantum efficiency is almost 3 orders of magnitude higher at a wavelength of 600 nm. The photosensitivity is also enhanced with Te alloying, as illustrated in Fig. 9.17. From both these figures it clear that there is a distinct advantage of alloying Se with Te, since the spectral response of the photoreceptor can be tailored to specific exposure needs.

Although $a\text{-Se}_{1-x}\text{Te}_x$ alloys have desirable spectral photosensitivity, their electro-photographic properties, especially when the Te content is high, are not suitable for monolayer photoreceptor applications. Monolayer $a\text{-Se}_{1-x}\text{Te}_x$ photoreceptors exhibit rapid dark decay and high residual potentials.

The decay of surface potential on $a\text{-Se}_{1-x}\text{Te}_x$ alloy films has been found to be controlled by the depletion discharge process (Abkowitz et al., 1985a; Baxendale and Juhasz, 1990; Kasap et al., 1991c). In essence, the xerographic depletion discharge model is based on bulk thermal generation involving the ionization of a deep mobility gap center to produce a mobile charge carrier of the same sign as the surface charge, and an oppositely charged ionic center. Assuming, as above, positive charging, a mobile hole would be thermally generated and the ionized center would be negative. As thermally generated

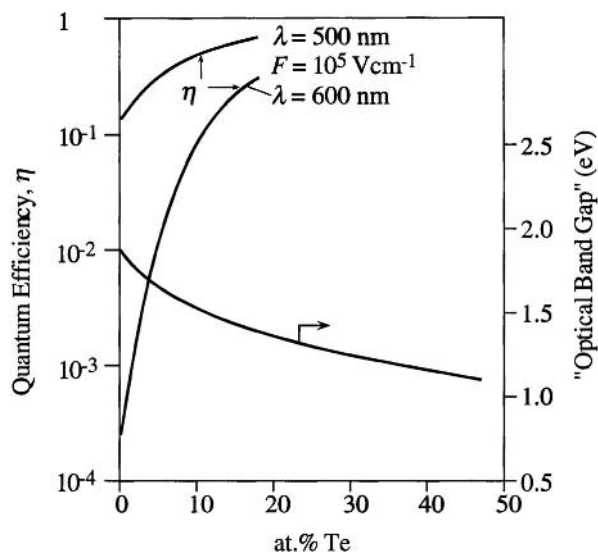


Figure 9.16 Quantum efficiency, $\eta(\lambda, F)$, at two wavelengths and “optical band gap” E_0 in $a\text{-Se}_{1-x}\text{Te}_x$ alloys as a function of Te content. Quantum efficiency data at a field F of 10^5 Vcm^{-1} . (From Hagen and Derks, 1984.) Optical band gap refers to E_0 in $(h\nu\alpha)^{1/2} \sim (h\nu - E_0)$. (As determined by Adachi and Kao, 1980.)

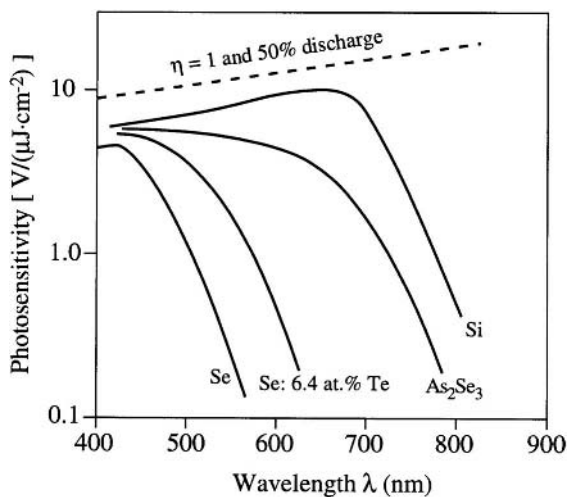


Figure 9.17 Photosensitivity versus wavelength for pure $a\text{-Se}$, $a\text{-Se}_{1-x}\text{Te}_x$, $a\text{-As}_2\text{Se}_3$, and $a\text{-Si}$: H photoreceptors. “Photosensitivity” is simply the amount of surface potential discharge per unit incident radiation energy, i.e., $\text{V}/(\text{J} \cdot \text{cm}^{-2})$. It is widely determined by measuring the required flux of radiation for 50% discharge. The absolute values of photosensitivity, however, can vary considerably depending on the experimental conditions used (e.g., initial charging voltage). The broken line is the theoretical photosensitivity for unity quantum efficiency and 50% surface potential discharge. (Data mainly from Lutz, 1987; Lutz and Reimer, 1982; and Nakayama et al., 1982.)

holes are swept out by the electric field, a negative bulk space charge builds up with time in the specimen, causing the surface potential to decay with time as shown in Fig. 9.18. If the buildup in the bulk negative charge density is spatially uniform, the internal electric field F falls linearly with distance from the top surface. At a certain time called the depletion time t_d , the electric field F at the grounded end of the sample becomes zero. From that time onward the field will be zero at a distance $X(t) < L$, the sample thickness, and consequently there will be a neutral region from X to L inasmuch as holes generated in $0 < x < X$ and arriving into $X < x < L$ will not be swept out. The shrinkage of the depleted volume with time $t > t_d$ means that t_d marks a functional change in the dark decay rate, as indicated in Fig. 9.18, and therefore is readily obtainable from dark discharge experiments.

Under low charging voltages the depletion time indicates the time required for the surface potential to decay to half its original value. Under high charging voltages, however, field-enhanced emission from the deep mobility gap centers also plays an important role, and the surface potential initially decays at a much faster rate so that at the depletion time the surface potential is in fact less than half the initial value (Kasap et al., 1991c). Figure 9.19 shows the dependence of the depletion time t_d and the half-time $t_{1/2}$ on the charging voltage V_0 , where it can be seen that at the highest charging voltages there is no improvement in $t_{1/2}$ with further increase in the charging voltage V_0 . Inasmuch as the dark decay in a-Se_{1-x}Te_x alloys is a bulk process, the rate of discharge increases with the square of thickness ($dV/dt \sim L^2$) and can be reduced only by using thin a-Se_{1-x}Te_x layers. The latter concept leads naturally to the design of multilayer photoreceptor structures.

The origin of the deep localized states in the mobility gap that control the dark decay has been attributed to structural native thermodynamic defects (Abkowitz, 1984a–c, 1985). Thermal cycling experiments of Abkowitz and coworkers show that the response of the depletion time to temperature steps is retarded, as would be expected when the structure relaxes toward its metastable liquidlike equilibrium state.

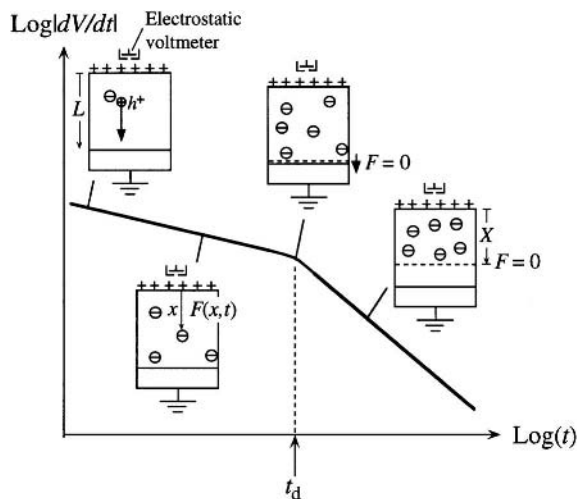


Figure 9.18 Typical log–log plot of the dark discharge rate versus time for an a-Se_{1-x}Te_x film. The break point identifies the depletion time t_d . Various stages in the depletion discharge model are also illustrated. F is the electric field. (From Kasap, 1989a.)

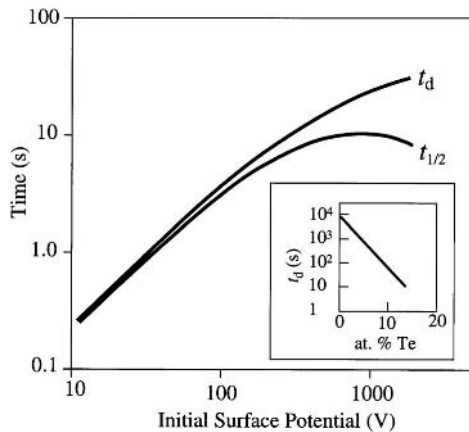


Figure 9.19 Log-log plots of the depletion time t_d and time for the surface potential to decay to its half value $t_{1/2}$ versus charging voltage V_0 for an a-Se:13 wt% Te photoreceptor film of thickness 70 μm . (From Kasap, 1989a.) The inset shows the dependence of the depletion time t_d on the Te content. (From Abkowitz et al., 1985b.)

Figure 9.20 illustrates the relaxation effect on the depletion time t_d as an a-Se:Te film is temperature stepped. When the temperature is stepped from 22°C to 35°C, the depletion time instantaneously drops from (a) to (b) to a value determined by the isostructural temperature dependence. Then as the structure relaxes toward the equilibrium state, t_d decreases further toward (c) until the structure has equilibrated. Stepping the temperature back to 22°C again results in an instantaneous change in t_d from (c) to (d), followed by a gradual increase toward its original value as the structure equilibrates. The only possible inference is that t_d must be controlled by structure-related thermodynamic defects. The generation of such defects is therefore thermally activated. It should also be noticed that a change of 13°C in the temperature has changed the depletion time, and hence the dark discharge time, by more than an order of magnitude: (a) to (c). We should note that since the depletion discharge mechanism involves the thermal emission of carriers from deep localized states, it is strongly temperature dependent. For example, t_d increases in an approximate Arrhenian fashion with decreasing temperature (Baxendale and Juhasz, 1990).

In addition to the deterioration of the dark decay, there is an increase in the residual potential associated with a-Se_{1-x}Te_x alloys. Figure 9.21 displays the $\mu\tau$ product for holes and electrons (Abkowitz and Markovics, 1982) determined from the xerographic residual potential in a-Se_{1-x}Te_x monolayer films, where it can be seen that even with very little Te alloying there is a considerable rise in both hole and electron deep traps. The relationship between the trapping time τ and the residual potential has been evaluated by Kanazawa and Batra (1972) and Kasap (1992). It can be seen that once the Te concentration exceeds 12 wt% Te, the residual potential is more than an order of magnitude larger than typical values for a-Se.

The relatively large residual potentials in a-Se_{1-x}Te_x alloys can be effectively reduced by doping the alloy with chlorine. Addition of chlorine even in the ppm range has been found to reduce drastically the residual potential, as shown in Fig. 9.22. On the other hand, both the charge acceptance, as indicated by the initial charging voltage V_0 , and the dark discharge, as indicated by the surface potential 1 second later, V_{01} , decrease with the

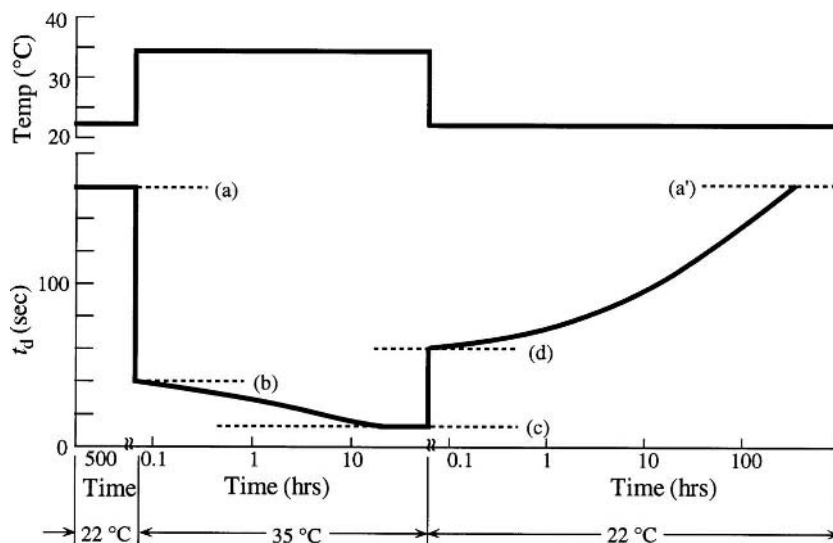


Figure 9.20 Time evolution of the depletion time t_d for an a-Se:12 wt% Te film 50 μm thick after temperature steps. The initial charging voltage was 100 V. Imposed thermal history is represented in the upper half of the figure. Almost instantaneous changes (a)–(b) and (c)–(d) in t_d are due to the isostructural dependence of t_d on the temperature. The much slower response (b)–(c) and (d)–(a') reflect the structural relaxation induced changes in t_d . (From Abkowitz, 1984a, b, 1985).

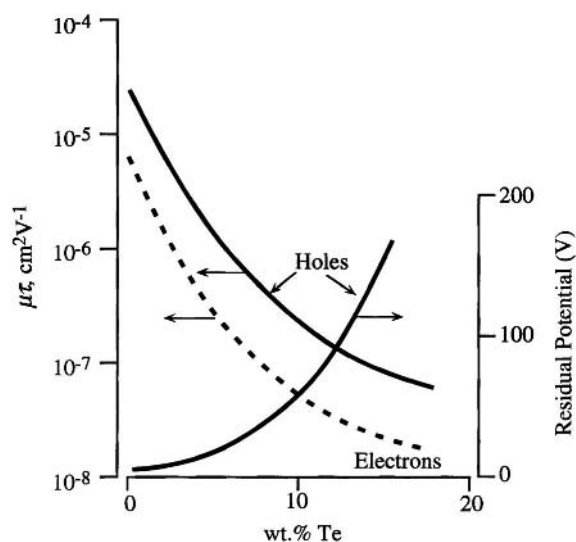


Figure 9.21 Hole and electron drift mobility lifetime product $\mu\tau$ and residual potential versus Te content in a-Se_{1-x}Te_x films. (The $\mu\tau$ product was xerographically measured by Abkowitz and Markovics, 1982; residual potential data from Onozuka et al., 1987.)

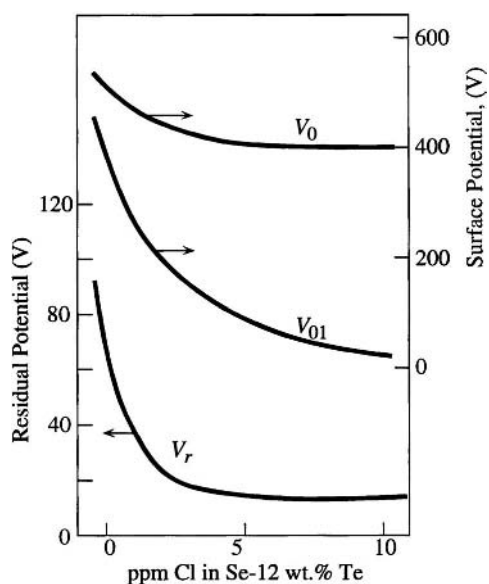


Figure 9.22 Effect of Cl doping on the residual potential, the initial voltage V_0 , and the dark surface potential after 1 second for a-Se:12 wt% Te films; $V_0 - V_{01}$ represents dark discharge in one second. (Data from Onozuka et al., 1987.)

Cl content. The dark decay, as gauged by $V_0 - V_{01}$ in Fig. 9.22, therefore increases sharply with chlorination in accordance with the effects of Cl addition to pure a-Se (Abkowitz et al., 1985b). The general xerographic effects of Cl addition to a-Se:12% Te films highlighted in Fig. 9.22 are also similarly observed for Cl addition to a-Se films (Wang and Champness, 1994, 1995).

Charge transport in a-Se_{1-x}Te_x alloys has been studied extensively by the TOF technique. Typical hole and electron TOF photocurrent waveforms are shown in Fig. 9.23. Compared with the a-Se case, where the TOF waveform is almost ideal, the photocurrents in Fig. 9.23 evince noticeable dispersion. Figure 9.24 summarizes the dependence of the hole and electron drift mobility and their activation energies in the alloy system a-Se_{1-x}Te_x with various amounts of chlorination in the ppm range. The electron drift mobility contin-

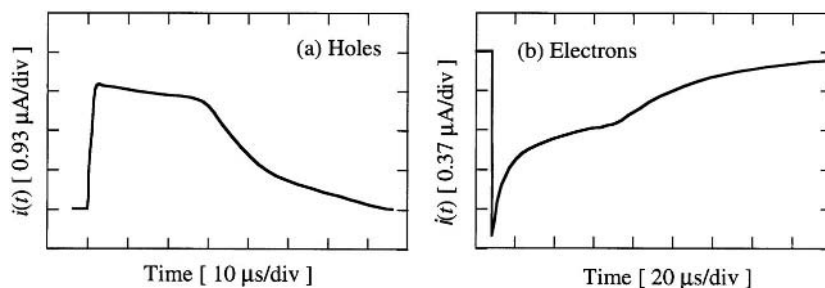


Figure 9.23 Time-of-flight hole and electron transient photocurrents in an a-Se_{0.966}Te_{0.034} alloy photoreceptor film. (From Kasap, 1989b; Kasap et al., 1991c.)

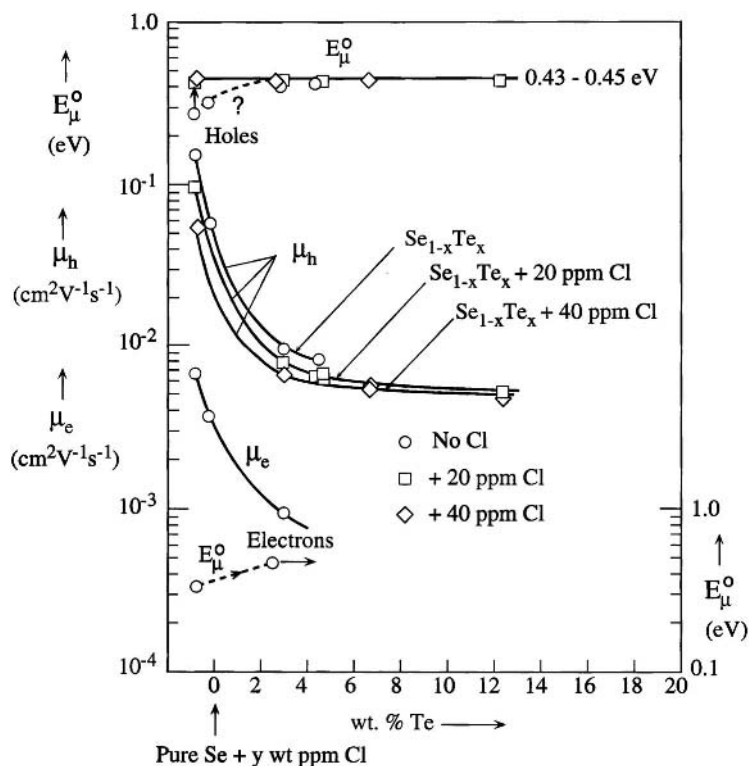


Figure 9.24 Charge transport parameters, namely drift mobility μ and zero field activation energy E_{μ}^0 , in chlorinated $a\text{-Se}_{1-x}\text{Te}_x$ alloys. (From Kasap, 1989b.)

ues to fall with Te addition. But the hole drift mobility, after an initial sharp decrease, saturates at a low value determined by the extent and concentration of localized states. As discussed by the present author (Kasap, 1989b), the charge transport mechanism in halogenated $a\text{-Se}_{1-x}\text{Te}_x$ films is most probably trap-controlled hopping in the band tail states similar to doped As_2Se_3 (Pfister and Morgan, 1980). The sharp drop in the drift mobility coupled with the rise in the population of deep traps as inferred from Fig. 9.21 mean that the charge carrier range in $a\text{-Se}_{1-x}\text{Te}_x$ alloys is shorter than that in pure $a\text{-Se}$ and leads to the rapid buildup of the saturated potential. The effect of deep traps can be reduced, though not completely eliminated, by doping with Cl, since it is well known that Cl addition enhances hole transport.

The exact way in which charge transport and trapping are controlled in $a\text{-Se}_{1-x}\text{Te}_x$ is not well understood, but there is no doubt that under- and overcoordinated charged structural defects, VAP-type centers, must play a key role. Recently, by considering the possible defect reactions in the $a\text{-Se}_{1-x}\text{Te}_x$ structure, it was shown, for example, that as the Te content is increased, there is an initial rapid rise in the population of localized states, which eventually saturates as the Te content becomes appreciable (Springett, 1990). The latter behavior is in qualitative agreement with the observed rapid fall and saturation of the hole drift mobility.

The alloying of Se with Te does not result in changes in the glass transformation and crystallization behavior as drastic as those observed for the Se–As glass system. The

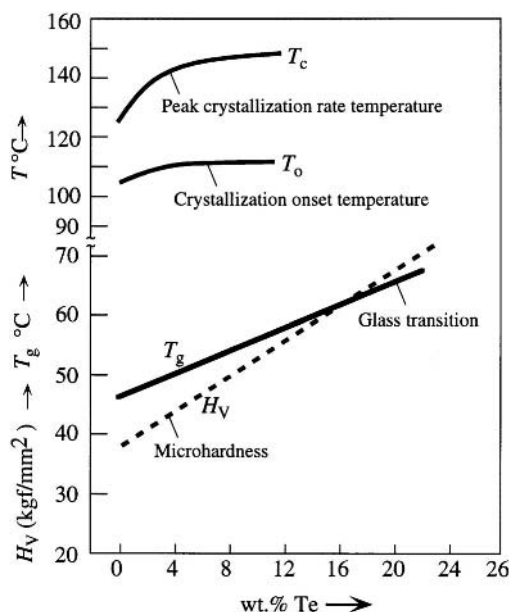


Figure 9.25 Thermal and mechanical properties of $a\text{-Se}_{1-x}\text{Te}_x$ alloy films from DSC and microhardness measurements. DSC data at a heating rate of $5^\circ\text{C}/\text{min}$; T_g = glass transition temperature; T_o = crystallization onset temperature, T_c = maximum crystallization rate temperature (defined in Fig. 9.13), H_v = Vickers microhardness. (From Kasap and Juhasz, 1986.)

glass transformation temperature increases almost linearly with the Te content, whereas the crystallization onset temperature has been reported to increase only slightly (Kasap and Juhasz, 1987).

Figure 9.25 summarizes the thermal and mechanical properties of $a\text{-Se}_{1-x}\text{Te}_x$ alloys over the xerographically useful alloy range. The improvements in the glass transition temperature T_g and the microhardness are a consequence of $a\text{-Se}_{1-x}\text{Te}_x$ having stronger secondary bonds between the Se–Te chains and the increase in the average mass of the chains with Te inclusion.

9.4 PHOTORECEPTOR DESIGNS

The basic electrophotographic requirements are high charge acceptance, slow dark decay, and low first and cycled-up residual potentials, assuming that the spectral response of the photoreceptor has been matched to that of the exposure lamp. With high Te content in the $a\text{-Se}_{1-x}\text{Te}_x$ film, both the dark decay rate and the residual potential are high, and the only practical alternative is to design multilayer photoreceptor structures in which the charge generation and charge transport functions have been separated, as is illustrated in Fig. 9.26, where single-, double-, and triple-layer photoreceptors are shown with typical structures that would be expected for copying and printing applications. The photogeneration layer (PGL) has a high Te composition and is made as thin as allowed by the penetration depth, $1/\alpha(\lambda)$, of the exposing radiation. Typically this layer is a few micrometers thick and has a Te content of 10–15% for copying applications and $\sim 25\%$ for laser printer

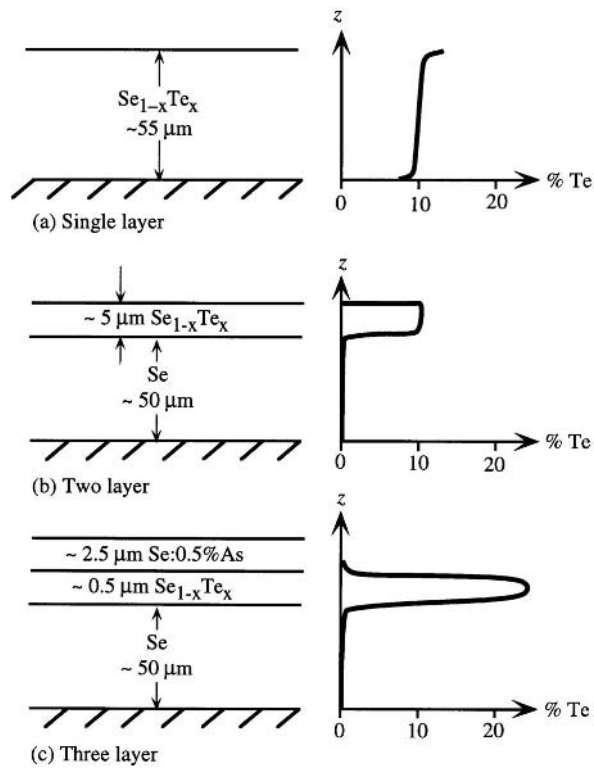


Figure 9.26 Typical single- and multilayer photoreceptor structures for copying and printing applications. (a) Single-layer photoreceptor for copying. (b) Double-layer photoreceptor for copying. (c) Triple-layer photoreceptor for printing. (From Cheung et al., 1982.)

applications. The printer-type photoreceptor also needs an overcoating layer (OL) to attain the required xerographic charge acceptance, to prevent surface injection and conduction at these high Te content levels. The overcoating layer also serves as a protection layer, since it often has some As added to enhance the thermal and mechanical stability.

With the high Te containing PGL region confined to a limited thickness, both the dark decay rate and the residual potential are reduced. The photosensitivity versus wavelength behavior, however, depends on whether the photoreceptor structure is a double- or a triple-layer type, and on the thickness of the photogeneration and overcoating layers. Figure 9.27 shows the xerographic photosensitivity of a typical three-layer photoreceptor as a function of wavelength for various overcoating thicknesses; it is obvious that the photosensitivity has been extended to the wavelength region of AlGaAs solid state lasers. It should be remarked that the photosensitivity axis in Fig. 9.27 cannot be directly compared with that in Fig. 9.17 inasmuch as the definition used in Fig. 9.27 is based on the quadratic-field-dependent generation model for the photoinduced discharge characteristics (Scharfe, 1984). It is interesting to mention that because of a large difference between the Te contents of the PGL and the OL, the photosensitivity exhibits a “gap” around the ~ 560 nm region when OL becomes “thick.” This gap is actually attributable to the failure of the 500–600 nm photons absorbed by the overcoating layer to result in photoconduction,

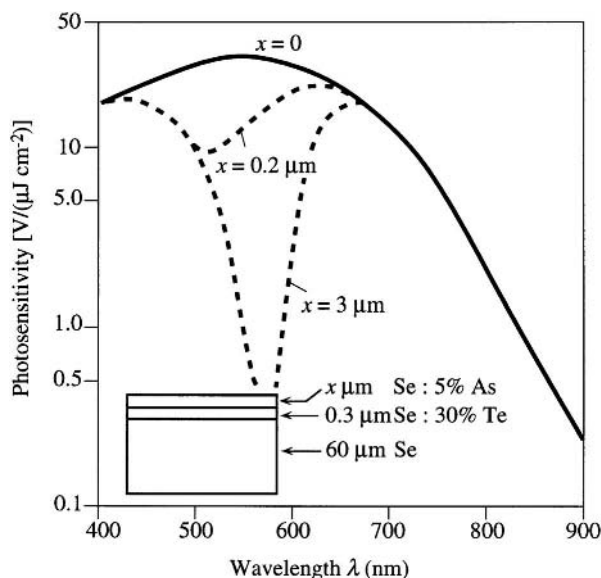


Figure 9.27 Photosensitivity of a triple-layer a-Se:Te:As-type photoreceptor as a function of wavelength for various thicknesses ($x \mu\text{m}$) of Se:5%As overcoating layer. The definition of photosensitivity differs from that shown in Fig. 9.16 and is based on the quadratic-field-dependent generation model. (From Melnyk et al., 1982.)

as was discussed in Section 9.2.2. Since the prime application in this case was for a printer utilizing an 825 nm solid state laser source, such a wavelength gap in the photosensitivity has no adverse effect on the xerographic printing performance of the photoreceptor.

The multilayer photoreceptor structures shown in Fig. 9.26 give the impression that the Te concentration profile changes sharply from one layer to another. This is not actually the case, however, since during the fabrication process there are fractionation and interdiffusion effects that tend to prevent sharp Te concentration changes. Nonetheless, there is the possibility that the interface between the layers may be electronically active: it can thermally generate and capture charges simply because strain in this region, as a result of some atomic mismatch due to the density change, can lead to structural defects. The properties of such interfaces between the various layers have not been studied in sufficient detail to permit the formulation of a general multilayer photoreceptor theory. It seems that a sharp change in the Te concentration is not desirable inasmuch as it will lead to more interfacial strain and thus to more interface localized states. Pinsler (1988) reported a xerographic TOF study of 15 wt% Te:Se/Se double-layer photoreceptor to conclude that the nature of charge transport in the CTL can be fully accounted by trapping and release kinetics and dispersion in the PGL without any evidence of interfacial traps. In other experiments, however, some evidence for trapping at the interface has been reported from the saturated residual potential on double-layer photoreceptors (Kasap et al., 1991c).

The main drawback of such multilayer PR designs is that they add to the complexity of the fabrication process, eliminating the simplicity of evaporating the alloy from a single boat with only basic source temperature and deposition controls. Not only must additional boats be used, but they must be properly shuttered or need careful control of the evaporation process to achieve the required Te profile across the film. Given unavoidable fraction-

ation effects, which are not well characterized, the established evaporation methods are essentially empirical.

9.5 PHOTORECEPTOR FABRICATION

The requirement of a $\sim 60\ \mu\text{m}$ thick photoreceptor coating for xerographic applications implies that the most efficient method of depositing the photoreceptor films is by thermal evaporation. Vitreous Se alloy pellets are simply loaded into stainless steel boats and evaporated at temperatures around $300\text{--}350^\circ\text{C}$ onto drum substrates held above the typical glass transformation temperature of the alloy. Figure 9.28a illustrates schematically the principle of thermal evaporation for depositing a-Se alloy photoreceptor films. Typical deposition rates reported in the literature have been around $2\ \mu\text{m}/\text{min}$, which indicates an evaporation process lasting about 30 minutes. During this time the material is continuously evaporated from the boat, and there are many changes taking place not only in the source material but also in the vapor composition and in the film deposited. There have not been any detailed studies of the evaporation kinetics of Se–Te alloys, although the Se–As sys-

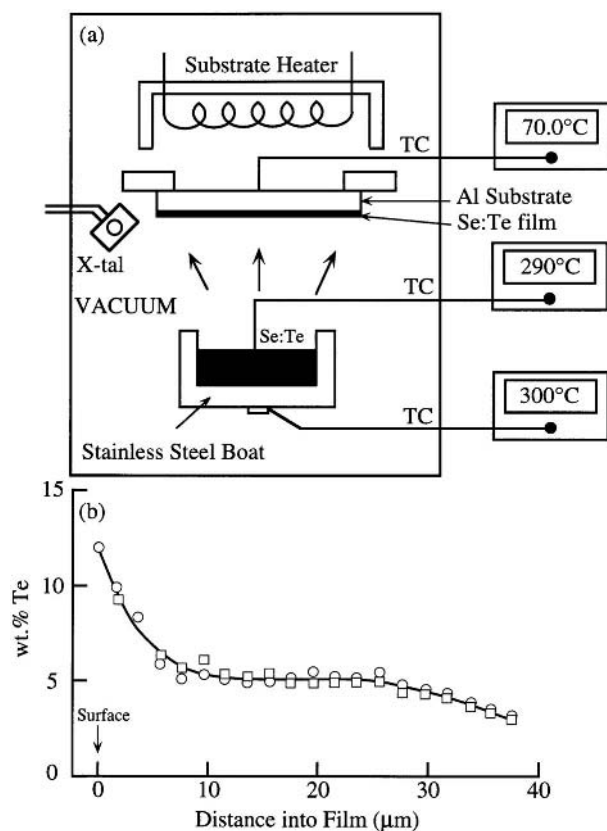


Figure 9.28 (a) Schematic sketch of a-Se_{1-x}Te_x photoreceptor film fabrication by vacuum deposition. Evaporation is often from a directly heated open boat. The substrates are normally Al drums that are heated and rotated during evaporation. TC means a thermocouple. (b) Fractionation in a-Se_{1-x}Te_x alloy photoreceptor films; plot shows a typical Te content across the film thickness.

tem has been examined by Sigai (1975) and Hordon (1989). Sigai, for example, was able to explain at least qualitatively the As composition variation across the photoreceptor film in terms of the evaporation process occurring in the boat. The Se–Te case however is poorly documented, and very little information is available on fractionation effects.

Figure 9.28b shows the Te composition of a $\text{Se}_{1-x}\text{Te}_x$ photoreceptor film deposited by a typical evaporation process from an open stainless steel boat. It should be noticed that fractionation effects cause the Te concentration to vary significantly across the film thickness, being Se-rich near the substrate and having a Te concentration 2 to 3 times as much on the surface. The latter concentration has been found to depend on the deposition rate. The composition of the condensed material at any time during the deposition depends on the partial pressures of Se and Te in the vapor. Deviations from Raoult's law result in condensed layers having different compositions (i.e., fractionation effects). The vapor pressure of Te over the $\text{Se}_{1-x}\text{Te}_x$ alloy is lower than its Raoult partial pressure because the latter occurs in an ideal solution in which all the bonds, Se–Se, Se–Te, and Te–Te, are assumed to be alike. Inasmuch as these bond energies are given by $E_{\text{Se–Se}} = 1.91$ eV, $E_{\text{Te–Te}} = 1.43$ eV, and $E_{\text{Se–Te}} = 1.8$ eV, the Te atoms in the $\text{Se}_{1-x}\text{Te}_x$ are more tightly bound than those in the parent (pure Te) material; consequently, their escape tendency is reduced in the $\text{Se}_{1-x}\text{Te}_x$ alloy, resulting in a lower Te partial pressure than the Raoult value. Fractionation effects are therefore a thermodynamic necessity of the evaporation process.

The actual fractionation that occurs during deposition depends in a much more complex way on the evaporation process, since temperature nonuniformities in the boat, finite material thermal conductivity, and limited diffusion in the source material all contribute to fractionation. As the evaporation proceeds, the Se-rich initial vapor leaves the surface region of the source rich in Te, which then results in an inhomogeneous source material. It may be that the constant Te concentration in the mid-bulk region of the photoreceptor film in Fig. 9.28b is a consequence of a dynamic equilibrium between the evaporation process and the diffusion process between the bulk of the source material and its Te-rich surface region.

It is apparent from the discussions above that fractionation effects result in inhomogeneous photoreceptor films. Inasmuch as many physical properties (e.g., density, drift mobility, deep trap concentration, glass transformation) depend strongly on Te concentration, the resulting film will have these properties varying along the film thickness. Very high Te concentrations on the surface can reduce the charge acceptance and accelerate the dark decay. Furthermore, the surface and substrate regions of the photoreceptor will structurally relax at different rates in response to a temperature change, resulting in unpredictable behavior. It should be remarked that although fractionation and noncongruent evaporation effects can be overcome by using flash evaporation techniques (Jansen 1982), such methods do not transfer directly to volume fabrication of photoreceptor drums.

9.6 TV PICKUP TUBES

A well known and successful application of amorphous Se–As–Te alloys is in Hitachi's Saticon (Goto et al., 1974), which is a commercially available TV pickup tube. Figure 9.29 displays the structure of a typical a-Se Saticon, which utilizes the high panchromatic photosensitivity of the Se–Te alloy and the relatively fast hole drift mobility of a-Se. Layers of CeO_2 and Sb_2S_3 act as hole and electron blocking contacts, respectively. Electrons injected by the scanning electron beam become trapped in the Sb_2S_3 layer, forming

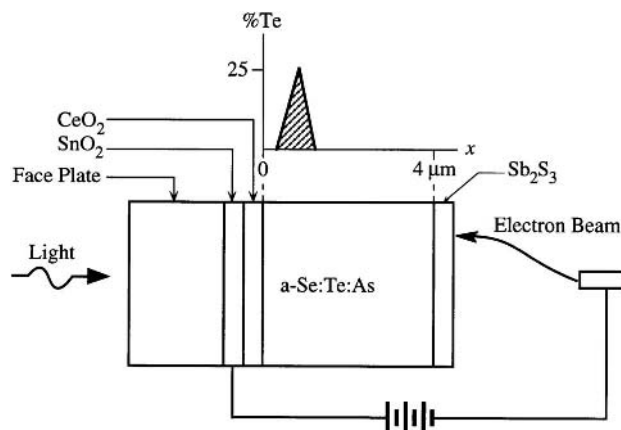


Figure 9.29 Schematic diagram of a Saticon TV image pickup tube utilizing an a-Se:Te:As alloy. The Te composition is concentrated in a narrow region, whereas the bulk is mainly a-Se:As . (From Maruyama, 1982.)

a negative space charge in this layer. Photogenerated holes in a-Se , from exposure to the image, transit across toward Sb_2S_3 to recombine with the electrons trapped in Sb_2S_3 . The photogeneration is contained in a region of high Te concentration. The crystallization of a-Se is inhibited by the addition of $\sim 1\%$ As to a-Se . Inasmuch as Saticon uses an amorphous material (i.e., grainless and uniform material), it exhibits high resolution. Further details on the fabrication and operation of the Saticon may be found in Maruyama (1982).

Recently Tanioka and coworkers (Tanioka et al., 1987, 1988; Takasaki et al., 1988; Tsuji et al., 1991) have developed a super-sensitive photoconductive target called the HARP (“high-gain avalanche rushing photoconductor”) for use in HDTV (high-definition television) camera pickup tubes. The vidicon using the HARP target has been called the HARPICON or a-Se avalanche vidicon. The basic structure of the HARP target and the principle of operation are schematically illustrated in Fig. 9.30. The entire target is typically about $2\text{ }\mu\text{m}$ thick though it may be thicker in ultrasensitive targets. The transparent signal electrode (SnO_2) is biased positively with respect to the cathode. The CeO_2 and

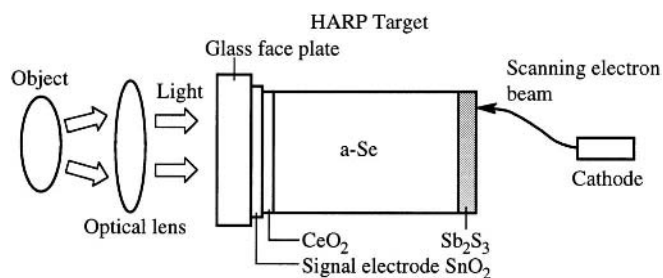


Figure 9.30 Schematic illustration of the structure of the HARP target and the principle of operation of the HARPICON. Avalanche multiplication occurs in the a-Se layer where the electric field exceeds $80\text{ V}/\mu\text{m}$ and causes hole multiplication by impact ionization. (Adapted from Tanioka et al., 1988.)

SbS₃ layers, as in the Saticon, act as blocking contacts for hole and electron injection, respectively. The incident light from the object is absorbed mainly in the a-Se layer. The electron-hole pairs photogenerated in the a-Se layer are then drifted by the applied electric field and constitute the signal current. As holes drift through the a-Se layer towards the back electrode, as a result of the large applied electric field (greater than 8×10^5 V/cm or 80 V/μm), they experience avalanche multiplication and hence yield a quantum efficiency greater than unity. The effective quantum efficiency resulting from avalanche multiplication depends on the fields as well as the photoconductor thickness. For example, in the 2 μm thick HARP target the quantum efficiency is about 10 at a field of 120 V/μm, whereas the quantum efficiency is about 1000 in an a-Se target of thickness 24.8 μm at a field of 100V/μm operating at a wavelength of 400 nm (Tsuji et al., 1991). TV pickup tubes using such HARP targets clearly have far superior sensitivity than conventional TV pickup tubes and accordingly constitute ultrahigh sensitive image pickup tubes.

9.7 X-RAY IMAGING

The use and properties of stabilized a-Se (a-Se:0.2–0.5% As doped with 5–20 ppm Cl) layers on Al substrates for x-ray imaging by xeroradiography is well documented (Boag, 1973; Leiga, 1990), but this system suffers from the difficulties and noise associated with the powder development technique. Xeroradiography is no longer competitive because of the toner readout method, not the underlying properties of the a-Se photoconductor. By replacing the toner readout with an electronic readout, a-Se has again become the basis of a clinical imaging system, and the commercial interest in a-Se has recently been revived. Recent research at the Sunnybrook Health Science Centre (University of Toronto) by Rowlands and coworkers (Rowlands et al., 1991, 1992; Zhao et al., 1995; Que and Rowlands, 1995; Yaffe and Rowlands, 1997), at Philips in Germany (Schiebel et al., 1986; Hillen et al., 1988), at Dupont de Nemours in the U.S. (Lee et al., 1995), and at Thompson CSF in France (De Monts and Beaumont, 1989) has shown that an x-ray imaging system based on the x-ray sensitivity of a-Se:As photoconductors has enormous potential for digital radiographic applications in medical diagnosis. Further, within the last few years commercial x-ray medical diagnostic imaging systems have been introduced into the market that are based on using the x-ray sensitivity of a-Se:As photoconductive layers (Neitzel et al., 1994) (e.g., Philips). In addition, two significant patents (e.g. U.S. Patent 5,396,072, May 1995, and 5,319,206, June 1994) have been filed by major corporate laboratories that use an a-Se:As layer vacuum coated onto a thin film transistor (TFT) active matrix array (AMA) and use this plate as an x-ray image detector. Images obtainable have been potentially superior to film based radiology, and the technique renders itself inherently to digital processing and storage.

Very recent research has shown clearly that one of the most promising digital radiographic systems is based on using a large area TFT matrix array (as used in flat panel displays for example) with an electroded x-ray photoconductor (e.g., Zhao et al., 1995; Zhao and Rowlands, 1995; Lee et al., 1995; Rowlands and Kasap, 1997). Figure 9.31 illustrates how a TFT-AMA can be used to read the amount of charge on each pixel electrode. Each pixel electrode carries an amount of charge that is proportional to the amount of incident x-ray radiation. All FETs in a row have their gates connected, whereas all FETs in a column have their sources connected. When gate line *i* is activated, all FETs in that row are turned ON and *N* data lines from *j* = 1 to *N* then read the charges on the pixel electrodes in row *i*. The parallel data are multiplexed into a series data and then

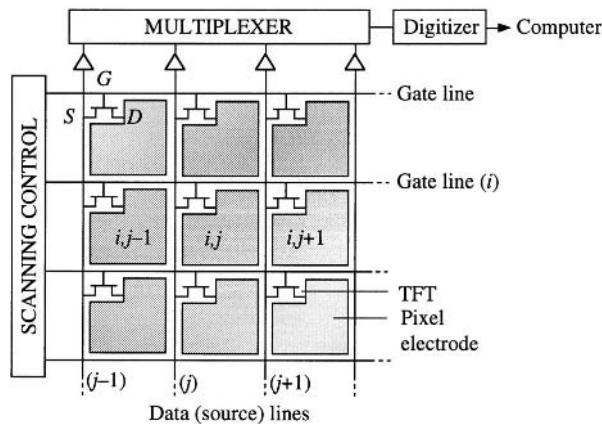


Figure 9.31 Thin film transistor (TFT) active matrix array (AMA) for use in x-ray image detectors with self-scanned electronic readout. (After Zhao et al., 1995.)

digitized and fed into a computer for imaging. The scanning control then activates the next row, $i + 1$, and all the pixel charges in this row are then read and multiplexed so on until the whole matrix has been read from the first to the last row.

The basic structure of an a-Se based TFT-AMA digital x-ray image detector is shown schematically as a cross section in Fig. 9.32. The a-Se layer is vacuum coated onto the TFT-AMA and carries a top electrode (A). Each pixel (i, j) carries a charge collection electrode, B, connected to a signal storage capacitor, C_{ij} , whose charge can be read through properly addressing the TFT (i, j) via the gate (i) and drain (j) lines. An external readout electronics and software, by proper self-scanning, converts the charges read on the C_{ij} to a digital image. The electron-hole pairs (EHPs) that are generated in the photoconductor by the absorption of an x-ray photon travel *along* the field lines. Holes accumulate on the storage capacitor C_{ij} and thereby provide a charge-signal q_{ij} that can be read during self-scanning. In this type of a-Se coated TFT-AMA image detector shown in Fig. 9.32, the resolution is determined by the pixel size, which in present experimental image detectors

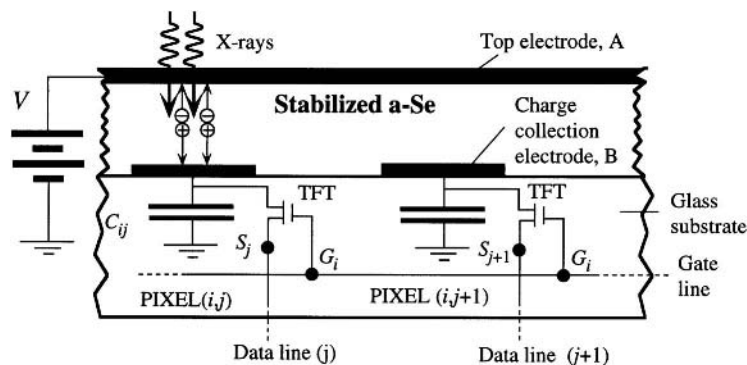


Figure 9.32 A simplified schematic diagram illustrating two neighboring pixels (i, j) and $(i, j + 1)$ and the formation of a charge image in pixel i, j .

is typically $\sim 150\ \mu\text{m}$ but is expected to be smaller than $50\ \mu\text{m}$ in future detectors to achieve a better resolution than the current film based systems for mammography.

Ideally the photoconductive layer should possess the following material properties: (1) There should be no dark current, which means that contact A should be hole injection blocking and contact B should be electron injection blocking. (2) There should be no deep trapping of EHPs, which means that for both electrons and holes the Schubweg $\mu\tau F \gg L$ holds, where μ is the drift mobility, τ is the deep trapping time (lifetime), F is the electric field, and L is the photoconductor thickness. (3) There should be no recombination, since EHPs are generated in the bulk of the a-Se layer. (4) EHP x-ray photogeneration efficiency, as gauged by the reciprocal of the energy required to create a free EHP (E_{EHP}) should be at a maximum. (5) The above should not change or deteriorate with time as a consequence of repeated exposure to x-rays, i.e., x-ray fatigue and x-ray damage should be zero. (6) The photoconductor should be easily coated onto the AMA panel, for example, by conventional vacuum techniques. Special processes are generally more expensive.

Provided that both holes and electrons have long ranges (i.e., $\mu\tau F \gg L$; L is the a-Se layer thickness), which will be the case for good quality a-Se material, the x-ray sensitivity of a given thickness photoconductor layer is then determined by the energy required to create a free electron-hole pair, E_{EHP} . This energy decreases with the electric field because at high fields more EHPs can escape recombination. At a field of $10\ \text{V}/\mu\text{m}$, E_{EHP} is about $50\ \text{eV}$. Experiments indicate that at sufficiently high fields, E_{EHP} may be expected to saturate at about 4 to $6\ \text{eV}$, which represents operation at maximum efficiency (Kasap et al., 1998).

There have been no systematic and fundamental studies in the literature that address the material properties of a-Se related to medical x-ray imaging requirements, even though all experiments, including commercialized systems and patents, indicate that it is an excellent x-ray photoconductor. It is quite likely that x-ray imaging will be one of the major uses of a-Se in the near future (Rowlands and Kasap, 1997).

ADDED IN PROOF

Recent work (Song, H. Z., et al., *Phys. Rev. B*, 59, 10610) examining the post-transit transient photocurrent in time-of-flight photoconductivity experiments has suggested a distinctly different density of states (DOS) distribution than that shown in Figure 9.7. This recent DOS model shows that there are two peaks at $0.40\ \text{eV}$ above E_v and $0.55\ \text{eV}$ below E_c . The most interesting feature in this model is the fact that these peaks are roughly close to the theoretical expectations for valence alternation pair defects at $\frac{1}{4}E_g$ ($= 0.55\ \text{eV}$) and $\frac{1}{3}E_g$ ($= 0.74\ \text{eV}$) from band edges as further discussed in Kasap, S.O. and Rowlands, J. A., 2000, *J. Mater. Sci. Elec.* 11; 179.

ACKNOWLEDGMENTS

The author is grateful to NSERC for their continuing support of his research program in amorphous semiconductor materials and devices since 1986.

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10

Photoreceptors: Organic Photoconductors

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10.1 INTRODUCTION

The research and development of organic photoreceptors for xerography has received considerable emphasis during the past two decades. The interest in these materials is primarily due to three considerations. First, these can be readily fabricated in large areas on a web or drum substrate; as a result, there is flexibility in designing the copier or printer architecture. Second, the electronic properties, particularly the dark resistivity and photoconductivity, are well suited for xerography. Third, relative to competitive technologies such as α -Si and the chalcogenide glasses, organic materials offer significant cost and environmental advantages. In the past two decades, organic materials have been increasingly employed and are currently used in most applications. At present, the annual revenues of these materials are approximately \$5 billion. This is the major photoelectronic application of organic materials.

The first organic photoreceptor used in a copier was based on the charge-transfer complex formed between poly(N-vinylcarbazole) (PVK) and 2,3,7-trinitro-9-fluorenone (TNF), introduced in the IBM Copier I in 1970. In 1975, Eastman Kodak Company introduced the dye-polymer aggregate photoreceptor in the Kodak Ektaprint 100 copier. Both the PVK:TNF and the aggregate photoreceptors were coated on a flexible web substrate

[†] Deceased

and then fabricated into a loop configuration. The PVK:TNF and dye–polymer aggregate technologies demonstrated the suitability of organic photoreceptors for high-volume, high-quality xerographic applications.

The next significant development was the introduction of the dual-layer photoreceptor configuration. In this format, the charge generation and transport functions are separated into two adjacent layers. These are described as the generation and transport layers. Dual-layer photoreceptors offer the advantages of higher sensitivity and extended process lifetimes. This configuration was introduced by Kalle in 1976. In the late 1970s, IBM replaced the PVK:TNF photoreceptor with a dual-layer photoreceptor containing a generation layer based on the bisazo pigment Chlorodiane Blue. In 1980, Eastman Kodak Company introduced a dual-layer photoreceptor containing a dye–polymer aggregate generation layer. By the late 1980s, most organic photoreceptors were prepared in the dual-layer configuration.

During the 1980s, there was increasing emphasis on the development of photoreceptors based on pigment-containing generation layers. These can be provided in large quantities, with acceptable levels of purity at low cost. Further, many of these materials show high sensitivity in the near infrared. Pigment-based generation layers are usually prepared by dispersion coating techniques. These materials are widely used for both copier and printer applications.

This chapter discusses the use of organic photoreceptors for xerography. The general photoreceptor requirements are described. A brief review of the photoelectronic properties of organic materials is given. Fabrication techniques are discussed. The xerographic properties are reviewed with emphasis on the materials used for generation and transport layers.

For further reviews of organic photoreceptors, see Pai and Melnyk (1986), Abkowitz and Stolka (1988), Melnyk and Pai (1990), Pai (1991), Borsenberger and Weiss (1993, 1998), Law (1993), Pai and Springett (1993), Stolka and Mort (1994), and Stolka (1995). For reviews of xerography, see Schaffert (1975), Williams (1984), Burland and Schein (1986), and Schein (1995).

10.2 PHOTORECEPTOR REQUIREMENTS FOR XEROGRAPHY

10.2.1 The Xerographic Process

The xerographic process involves the formation of an electrostatic latent image on the surface of a photoconductive insulator. The latent image is made visible by toner particles, transferred to a receiver, and then made permanent by a fusing process. The overall process can involve as many as seven steps, as illustrated in Fig. 10.1. In step 1, a uniform electrostatic charge is deposited on the photoreceptor surface. This can be accomplished by a corotron or a roller charging device. In the second step, the photoreceptor is exposed with a reflected or digitally rendered image. This selectively dissipates the surface charge in the exposed regions and creates a latent image in the form of an electrostatic charge pattern. In step 3, electrostatically charged toner particles are brought into contact with the latent image. The toner particles are transferred to a paper receiver in step 4 and then fused in step 5. Fusing is normally accomplished by passing the paper receiver through a set of heated rollers. In step 6, the remaining toner particles are removed from the photoreceptor surface, usually by means of a rotating brush. Finally, in step 7, the photoreceptor is uniformly exposed to remove any remaining surface charges. Following step 7, the process can be repeated.

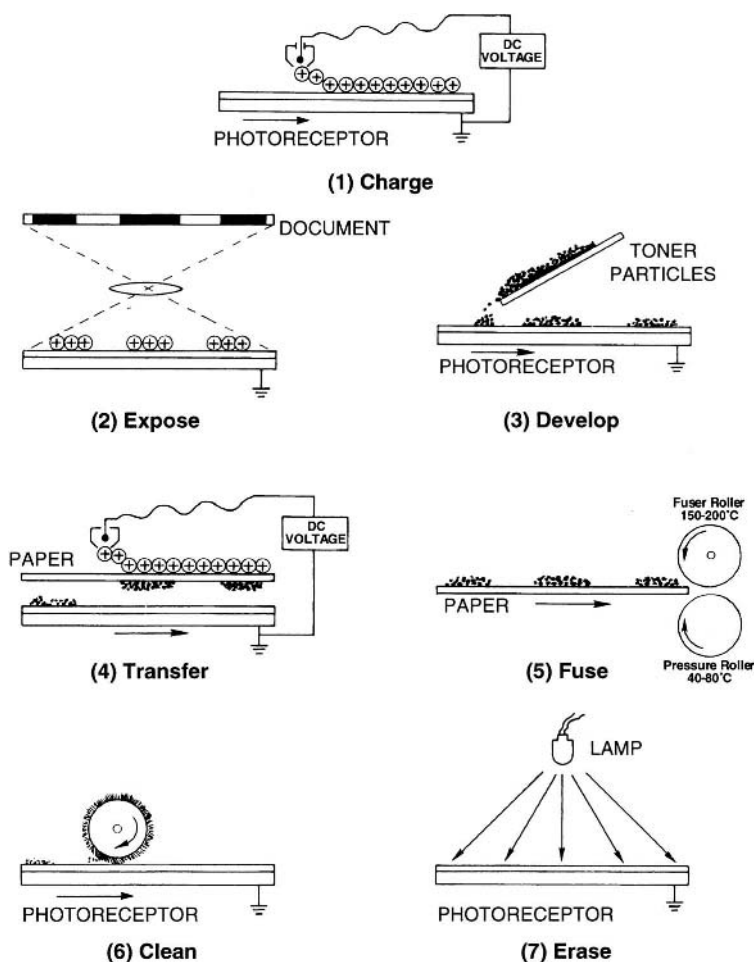


Figure 10.1 The various steps in the xerographic process.

The processes outlined in Fig. 10.1 can be carried out by either charged-area-development (CAD) (Fig. 10.2) or discharged-area-development (DAD) (Fig. 10.3) processes. In CAD, the toner particles are charged to the opposite polarity of the photoreceptor surface. The toner particles are thus attracted to the charged, or unexposed, regions of the photoreceptor. CAD processes are widely used for optical copiers. CAD exposures are usually obtained from a Xe-filled lamp for flash exposures or a quartz-halogen or fluorescent lamp for continuous or scan exposures. In DAD, the toner particles are of the same polarity as the photoreceptor surface. By means of a biased development electrode, the toner particles are attracted to the discharged regions of the photoreceptor. DAD processes are commonly used for printers. Exposures for DAD processes are usually derived from a laser or an array of light-emitting diodes. Figures 10.2 and 10.3 illustrate the CAD and DAD processes. In CAD, the photoreceptor areas that are exposed correspond to the background areas of the image that is to be reproduced. In DAD, the exposed regions correspond to the image areas. The development potential is the potential difference be-

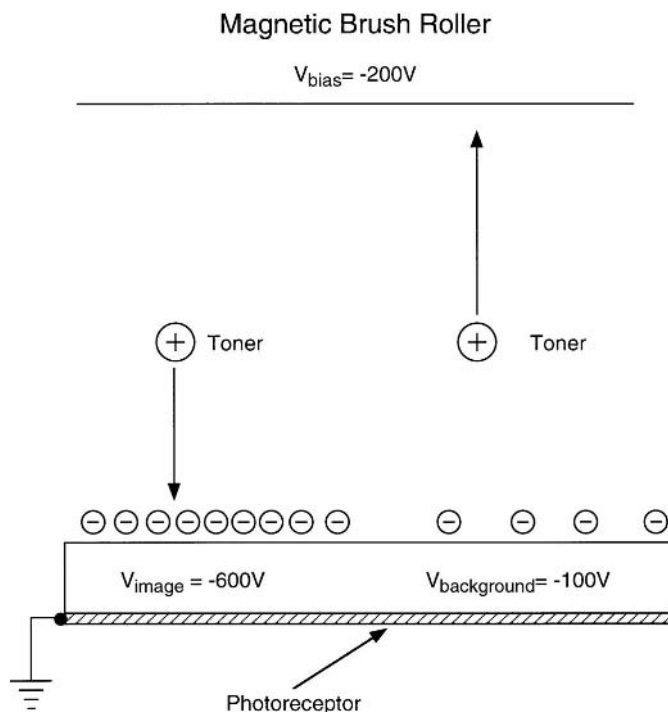


Figure 10.2 The charged-area-development (CAD) process.

tween the image and bias potentials. Photoreceptor requirements that are specific to DAD processes have been discussed by Chen (1990), Lutz (1995), Mort (1995), Jeyadev and Pai (1996), and Pai (1995).

The xerographic process places several fundamental requirements on the photoreceptor. The key requirements are that (1) the rate of thermal generation of free carriers must be extremely low, (2) the photoreceptor must have high sensitivity throughout the appropriate region of the spectrum, (3) the charge-transport processes must occur in the absence of deep trapping over an extended range of fields, and (4) the electronic properties must be stable to highly oxidizing corona atmospheres under high field and exposure conditions. Finally, the photoreceptor must have good mechanical properties, high abrasion resistance, and be amenable to large-area, low-cost manufacturing processes. These are separately discussed in the sections that follow.

10.2.2 Dark Discharge

The initial step in the xerographic process involves the deposition of electrostatic charges on the photoreceptor surface. To sustain the latent image for a period of time sufficient for the desired process development, the rate of dark discharge of the surface potential must be extremely low.

There have been many dark discharge models described in the literature. For a review, see Borsenberger and Weiss (1993, 1998). Most are premised on the assumption that the thermal generation process creates a free and deeply trapped carrier of opposite sign. The discharge that occurs under these conditions is described as depletion discharge and has been treated by Abkowitz and coworkers (Abkowitz and Markovics, 1982, 1984;

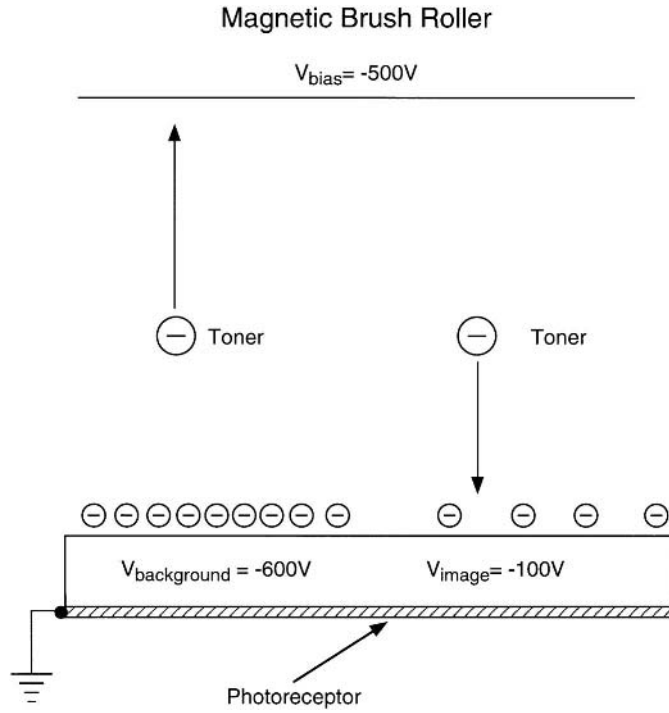


Figure 10.3 The discharged-area-development (DAD) process.

Abkowitz and Jansen, 1983; Abkowitz et al., 1985; Abkowitz, 1987, 1987a; Abkowitz and Maitra, 1987). The results are described in two time zones, $t \leq t_d$. Here t_d is a depletion time, defined as the time when the thermally generated bulk space charge is equal to one-half of the charge initially deposited on the surface. For $t < t_d$,

$$\frac{dV}{dt} = -\frac{L^2}{2\epsilon\epsilon_0} apt^{p-1} \quad (1)$$

For $t > t_d$,

$$\frac{dV}{dt} = -\frac{\epsilon\epsilon_0}{2a} \left(\frac{V_0}{L}\right)^2 pt^{-p-1} \quad (2)$$

At $t = t_d$,

$$\rho(t_d) = \frac{\epsilon\epsilon_0 V_0}{L^2} \quad (3)$$

and

$$t_d = \left(\frac{2V_d\epsilon\epsilon_0}{aL^2}\right)^{1/p} = \left(\frac{\epsilon\epsilon_0 V_0}{aL^2}\right)^{1/p} \quad (4)$$

In Eqs. (1) to (4), L is the thickness, ϵ the dielectric constant, ϵ_0 the permittivity of free space, V_0 the initial potential, and a and p are constants. For an exponential distribution

of energies, p is inversely proportional to the width of the distribution. For a discrete energy, $p = 1$. The key assumption of the model is a field-independent thermal generation process that creates a free and deeply trapped carrier of opposite sign.

For other treatments of dark discharge, see Kasap et al. (1987, 1992), Kasap (1989), and Scott and Lo (1990). For treatments of the charge acceptance, see Pai (1988), Jeyadev and Pai (1995), and Mishra and Pai (1996).

10.2.3 Photogeneration

To form an electrostatic latent image, a photoreceptor is charged to an initial potential and then exposed to a pattern of radiation that corresponds to the image that is to be reproduced. The absorption of the image exposure creates bound electron-hole pairs, a fraction of which separate and migrate to the appropriate surfaces. The exposure required to create the latent image is determined by the efficiency by which free electron-hole pairs are created in conjunction with any loss mechanisms, such as recombination or trapping. A key parameter is the photogeneration efficiency, the ratio of the number of free electron-hole pairs created to the number of photons absorbed. The models that have been most widely used to describe photogeneration phenomena of organic materials are based on surface-enhanced exciton dissociation or geminate recombination. For reviews, see Pope and Swenberg (1982, 1984), Pope (1989), Silinsh (1989), and Silinsh and Capek (1994).

Surface-enhanced exciton dissociation arguments are premised on the assumption that the absorption of a photon creates an exciton that diffuses to the surface where it either recombines or dissociates into a free electron-hole pair, or a free and a deeply trapped carrier of opposite sign. These arguments were first proposed in the early 1960s. Many early studies of anthracene were described by surface dissociation models. These were usually based on the assumption that the dissociation occurred at surface sites occupied by O_2 that act as deep electron traps. Most studies of the phthalocyanines have been explained by surface-enhanced exciton dissociation arguments, and usually attributed to the presence of O_2 . For a review of exciton dissociation processes in the phthalocyanines, see Mizuguchi (1987). Photogeneration has also been described by surface-enhanced exciton dissociation arguments involving charge transport molecules (Umeda and Hashimoto, 1992; Umeda et al., 1993; Umeda, 1994, 1998, 1999; Umeda and Niimi, 1994, 1994a; O'Regan et al., 1995, 1996; Molaire et al., 1997; Umeda and Yokoyama, 1997; Popovic et al., 1999).

The limitation of exciton dissociation models is that they are based solely on exciton diffusion length considerations and provide little further insight into the physical processes involved in photogeneration. Further, these do not address the field or temperature dependencies of the photogeneration process, which are of central relevance to xerography.

Geminate recombination is the recombination of an electron with its parent cation. Geminate recombination arguments are based on the assumption that the formation of a free electron-hole pair involves the dissociation of an intermediate charge-transfer state. There are many references in the literature to geminate recombination in organic solids, as well as organic liquids, α -Se, and α -Si. The most widely cited are based on theories due to Onsager (1934, 1938).

The Onsager theories are derived from the Smoluchowski (1916) equations that describe the escape probability of an electron from its parent cation in the presence of a field. In models based on the Onsager theories, free carriers are assumed to be created by a two-step process. The first involves photon absorption and the creation of a charge-transfer state. The probability of creating the state is described by a primary quantum

yield η_0 . In the second step, the state can either dissociate into a free electron and a free hole, or recombine. The photogeneration efficiency η is then given as the product of the efficiency of creating the state η_0 and the dissociation probability.

The Onsager expression for the photogeneration efficiency is

$$\eta = \eta_0 \left(1 - \frac{kT}{eEr_0} \sum_{j=0}^{\infty} I_j \frac{eEr_0}{kT} \right) \quad (5)$$

where

$$I_j(x) = I_{j-1}(x) - \frac{\exp(-x)x^j}{j!} \quad (6)$$

$$I_0(x) = 1 - \exp(-x) \quad (7)$$

and E is the field and r_0 the electron–hole separation distance of the charge-transfer state. The derivation of Eq. (5) is based on the assumption that the distribution of electron–hole separation distances can be described by an isotropic δ -function. In the literature, r_0 is usually described as a thermalization distance. The Onsager formalism leads to strongly field-dependent photogeneration efficiencies that approach nonzero values as the field goes to zero. At high fields, the efficiencies approach a limiting value. Field-dependent photogeneration was first described in the mid 1960s and has since been observed in virtually all organic materials described in the literature.

In the past two decades, most photogeneration studies of organic solids have been described by the Onsager theories. The limitations of the formalism are that the Onsager solutions to the Smoluchowski equations are based on a somewhat arbitrary set of boundary conditions and the absence of a theory to describe the thermalization process. Most models based on the Onsager theories are premised on the assumption that the thermalization distance is independent of field and temperature. These are highly questionable assumptions. For alternative treatments of geminate recombination, see Rackovsky and Scher (1984, 1988), Silinsh and Jurgis (1985), Ries and Bässler (1987), Berlin et al. (1990), Racovsky (1991), Arkhipov and Nikitenko (1993), Scher (1993), and Albrecht and Bässler (1995). For a review, see Pai (1985).

10.2.4 Charge Transport

Xerographic photoreceptors can be prepared in the single- or dual-layer configuration, as shown in Figs. 10.4 and 10.5. For either configuration, the photoinduced discharge must occur in the absence of trapping and within a time commensurate with the process development requirements. The photoreceptor property that determines the discharge time is the mobility, the ratio of the carrier drift velocity to the field. For complete discharge in a range of 10 ms, mobilities in excess of $10^{-5} \text{ cm}^2/\text{Vs}$ are typically required.

In the past decade, most studies of organic materials have been described by a formalism based on disorder, due to Bässler and coworkers (Bässler, 1993, 1994, 1994a, 1994b; Hartenstein and Bässler, 1995; Hartenstein et al., 1996; Borsenberger et al., 1998; Wolf et al., 1997; Visser et al., 1999). The disorder formalism is premised on the argument that charge transport occurs by hopping through a manifold of localized states that are distributed in energy and distance. The principal assumptions are that (1) the distributions of site energies and distances are Gaussian, (2) hops to higher site energies are scaled by a Boltzmann probability, while hops to lower energies occur with a probability of unity, (3) polaronic effects can be neglected, and (4) the process is incoherent and phase memory

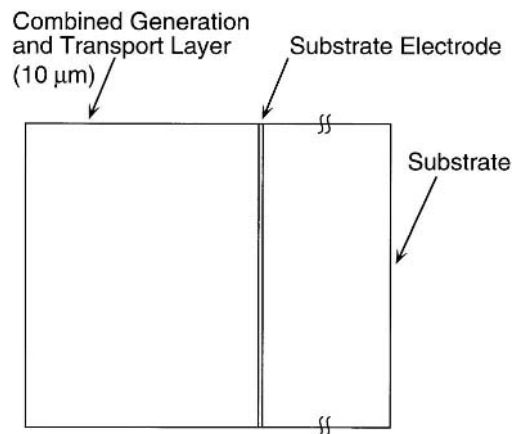


Figure 10.4 The single-layer photoreceptor configuration. Thickness of single-layer photoreceptors are typically 10 to 15 μm . The substrate serves as the electrode in drum photoreceptors. In this configuration, the photoreceptor can be discharged with either a positive or a negative potential.

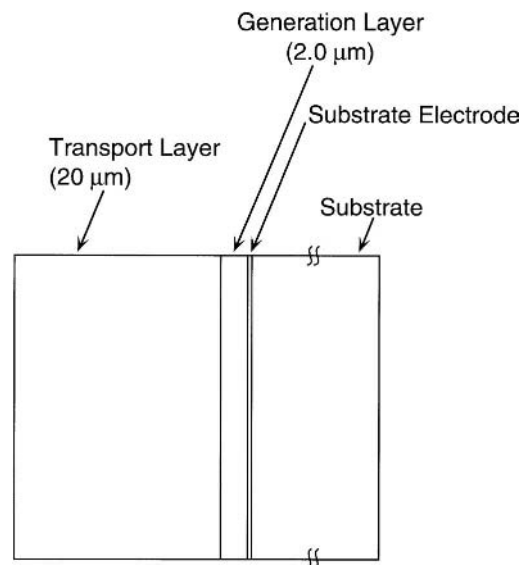


Figure 10.5 The dual-layer photoreceptor configuration. Transport layer thicknesses are typically 15 to 30 μm . Generation layers are usually between 0.5 and 5.0 μm . The substrate serves as the electrode in drum photoreceptors. In the configuration illustrated, the polarity of the surface potential must be opposite to the conductivity type of the transport layer. Hole transport layers require negative surface potentials and vice versa.

is lost after every jump. Of these, the key assumption is the formalism for computing the hopping rates. The validity of this approach has been reviewed by Kenkre and Dunlap (1992) and Dunlap (1995). Due to the asymmetry in the hopping rates, any analytic treatment becomes difficult, particularly for the case of a Gaussian distribution of site energies. For this reason, predictions of the formalism have been largely derived from Monte Carlo simulations. For a discussion of the simulation procedures, see Bäessler (1993). At high fields, the simulations give (Borsenberger et al., 1991)

$$\mu(\hat{\sigma}, \Sigma, E) = \mu_0 \exp \left[- \left(\frac{2\hat{\sigma}}{3} \right)^2 \right] \exp [C(\hat{\sigma}^2 - \Sigma^2)E^{1/2}] \quad (8)$$

where μ is the mobility, σ the energy width of the hopping site manifold, $\hat{\sigma} = \sigma/kT$, Σ the degree of positional disorder, E the field, μ_0 a prefactor mobility, C an empirical constant of $2.9 \times 10^{-4} \text{ (cm/V)}^{1/2}$, and kT has its usual meaning. Equation (10.8) is valid only for fields above a few multiples of 10^5 V/cm and $T_g > T > T_c$, where T_g is the glass transition temperature and T_c the nondispersive-to-dispersive transition temperature. At low fields, the mobility is field independent or, in the case of large Σ , increases as the field is further reduced. The materials parameters of the formalism are σ , μ_0 , and Σ .

From Equation (8), the basic predictions of the formalism are the field and temperature dependencies of the mobility and the temperature dependence of the field dependencies of the mobility. These agree with experimental results reported for a wide range of molecularly doped polymers, main chain and pendant group polymers, as well as vapor-deposited molecular glasses (Borsenberger et al., 1993).

For other treatments of transport, see Sahyun (1984), Movaghar (1987, 1991), Kenkre and Dunlap (1992), Schein (1992), Dunlap and Kenkre (1993), Novikov and Vannikov (1993, 1994, 1994a), Bäessler et al. (1994), Gartstein and Conwell (1994, 1994a, 1995), Dunlap (1995a, 1996, 1997), Parris (1995, 1996, 1997), Gartstein et al. (1995), Dunlap et al. (1996), Parris et al. (1997), and Novikov et al. (1998).

10.2.5 Recombination

Electron-hole recombination depends on the product of the electron and hole concentrations and thus may become important for high-intensity exposures. In low mobility materials, recombination is usually explained by a theory due to Langevin (1903). Langevin recombination arguments are based on the assumption that the recombination process is diffusion controlled. This requires that the electron and hole mean free paths be small compared to the Coulomb radius.

Recombination-limited discharge models have been described by Collins (1974), Fox (1974), Kerr and Rokos (1977), Chen (1978), and Mey et al. (1979). Recombination plays an important role in determining the photodischarge characteristics with high-intensity exposures such as those used in certain digital applications.

10.2.6 Photoreceptor Evaluation

Latent image formation involves the creation of free electron-hole pairs by the absorption of an image exposure and the displacement of these carriers by a field. These processes are determined by the photogeneration efficiency and mobility. Experimental techniques for their characterization are thus of considerable importance to xerography.

Photogeneration efficiencies are usually derived from potential discharge measure-

ments. These can be made with continuous or flash exposures. The distinction is based on the transit time. Continuous exposures are long compared to the transit time, while flash exposures are short compared to the transit time. Continuous exposures are usually monochromatic. The results can be described by the xerographic gain. The gain is defined as the ratio of the rate of decrease of the surface charge density to the incident photon flux,

$$G_x = -\frac{\epsilon \epsilon_0}{LeI} \left(\frac{dV}{dt} \right) \quad (9)$$

where I is the photon flux and dV/dt the rate of photoinduced discharge. As defined in Eq. (9), the maximum gain is unity. In the absence of trapping and recombination, the gain is equal to the photogeneration efficiency η when normalized to the absorbed photon flux. The gain is commonly used to characterize the spectral dependence of the sensitivity.

Flash exposures are usually made with constant initial potentials and multiple exposures of different intensities. The surface potentials are sampled at a time well in excess of the transit time, typically 1 to 2 s. Normally, the sample is erased after each exposure. The results are usually described by the exposure required to discharge the photoreceptor from an initial potential V_0 to an arbitrary potential, typically $V_0/2$, at a specified time after the exposure. The exposures are usually expressed in erg/cm^2 or $\mu\text{J/cm}^2$. The wavelength, the exposure time, the time at which the potential is sampled, and the erase conditions must be specified. Results of these measurements can also be used to determine the photogeneration efficiency, although the analysis is somewhat more complex than for continuous exposures. The sensitivity is a useful metric for the evaluation of photoreceptors. Comparisons are difficult, however, when measurements are made with different conditions. For practical evaluations, it is usually necessary to evaluate the gain or sensitivity with cycling. Commercial instrumentation has been developed for this purpose (Tse, 1994, 1996).

Potential discharge measurements are also used for image evaluation. By dividing the overall xerographic process into the different subsystems and then describing each subsystem with a transfer function, the output image density can be related to the input density through a four-quadrant plot (Paxton, 1978; Pai and Melnyk, 1986). In this manner, the effects of changes in the various subsystems on the output density can be determined.

The standard method for measuring mobilities in materials with long dielectric relaxation times is the time-of-flight photocurrent technique, first described by Haynes and Shockley (1951) and Lawrance and Gibson (1952). These techniques were developed in considerable detail during the 1950s and 1960s by Brown (1955), Spear (1957, 1960), Kepler (1960), Le Blanc (1960), and others who successfully applied these techniques to a wide range of both crystalline and amorphous solids. By this method, the time for a sheet of carriers generated by a short flash of radiation to transit a sample of known thickness L is measured. The mobility can then be determined from the expression

$$\mu = \frac{L^2}{t_0 V} \quad (10)$$

where t_0 is the transit time of the carrier sheet.

For a review of potential discharge and photocurrent transient techniques, see Melnyk and Pai (1993).

Digital xerography has placed new requirements on photoreceptor materials. Because most digital engines use DAD processes, any microscopic defects in unexposed areas will have lowered surface potentials, and small spots will be developed. These are

sometimes called breakdown spots because of the inability of these regions to maintain the surface charge. The need to examine photoreceptors for such defects has led to new measurement techniques. The evaluation of microscopic electrical defects has been treated by Popovic et al. (1991), Lin et al. (1993), Prichard and Uehara (1993), and Lin and Nozaki (1995). Technologies have also been developed to determine the presence of such defects by examining the photoreceptor toned image (Tse, 1994, 1996).

10.3 FABRICATION

Photoreceptor fabrication involves the sequential application of one or more layers onto a substrate. The coating methods depend on whether the substrate is a flexible web or a metal drum. Flexible webs, such as poly(ethylene terephthalate), are usually metallized; Ni or Al are common. The substrate conductivity requirements have been discussed by Chen (1993). Polymeric electrodes (Katsen et al., 1994) have been used in some applications. With metal drums, the drum itself serves as the electrode. In either case, the substrate sometimes receives a very thin preliminary polymer coating as an interlayer between the substrate and the photoconductive layers. The interlayer has several purposes. It may serve as a blocking layer to prevent charge injection, which would otherwise give rise to excessive dark discharge and/or localized breakdown. The interlayer may also serve as an adhesive to ensure adequate bonding of the subsequently applied photoreceptor layers. Finally, the interlayer may serve to smooth a rough substrate surface, or alternatively it may provide a roughened surface to prevent the formation of interference patterns. Because of these many features, the choice of interlayer materials depends on the characteristics desired. Polymers such as nylons, polyvinyl chlorides, and sarans have been used. An overcoat layer may also be provided to protect the photoreceptor from chemical and/or mechanical damage. Finally, to fabricate an image loop, the ends of the appropriate length sections must be joined. This can be accomplished by an adhesive splice or by ultrasonic bonding techniques. The seam region is positioned outside the image area to prevent the production of an image artifact. As long as the seam does not interfere with belt alignment or the development and cleaning subsystems, it can be neglected.

10.3.1 Solvent Coating Techniques

For research purposes, solutions or pigment dispersions can be readily coated by a doctor blade. For commercial applications, materials must be produced under more carefully controlled conditions. This necessitates the use of coating machines that permit the precise control of the many coating variables. Among the more important are web stability and velocity, solution delivery rate and geometry, and drying conditions. Solvent emission control is also an important component of the coating process. Because organic materials are generally water insoluble, organic solvents are commonly used. The factors influencing the choice of solvent are solubility, solvent evaporation rate, solution surface tension, and toxicity. Ketones (acetone and methyl ethyl ketone), alcohols (methanol), chlorinated hydrocarbons (dichloromethane or 1,2,2-trichloroethane), aromatics (toluene), ethers (tetrahydrofuran), esters (methyl acetate), and acetonitrile are commonly used. The *Federation Series on Coatings Technology* comprises relevant reviews including *Organic Pigments* by Lewis (1988), *Solvents* by Ellis (1986), *Coating Film Defects* by Pierce and Schoff (1988), and *Film Formation* by Wicks (1986). In addition, monographs such as *Coating and Drying Defects* by Guttoff and Cohen (1995) and *Organic Coatings: Science*

and Technology, Volumes 1 and 2 by Wicks et al. (1992, 1994) are excellent sources of practical information.

While there are several coating methods available, a common technique is to pump the coating solution or dispersion from a hopper through a slot and onto the web. The design of the hopper assembly, the shape of the hopper lip, and the relative position and distance from the web are all critical. The optimum conditions will be specific to the particular coating under investigation. There are many coating defects to be avoided. These include surface patterns, thickness variations, voids, cracks, streaks, blush, and mottle. These can frequently be eliminated by modifications of the coating conditions, such as the elimination of vibrations, the prevention of static discharge in the roller nip, adjustments of hopper geometry, and changes in coating speed and drying conditions. Other defects are best controlled by modifying the coating solution.

10.3.2 Dispersion Methods

Most photoreceptors have generation layers composed of pigment dispersions. These are fabricated by solvent coating methods. Techniques for the large-scale preparation of such dispersions are well known, especially for applications in the paint industry (Coulson and Richardson, 1983). The pigment is usually received as a powder cake or as crystal nuggets and must be crushed to a small size before milling. Mills of various types can reduce the pigment to submicron size. Devices commonly used are ball or vibrating mills, where small balls of a hard material such as stainless steel or a ceramic are placed in a slurry of the pigment in a nonsolvent. The action of rolling, or vibration, imparts sufficient energy to break the pigment into small primary particles. Roll mills are common in the paint industry. In these devices, two (or more) rollers move at different speeds in opposite directions. The pigment is circulated between the rollers until the desired combination of uniformity and particle size is attained. Other methods use centrifugal and sand or salt milling techniques. It is usually necessary to treat the milled pigment further to prepare the final dispersion solution. In the paint industry, the techniques are specific to each pigment due to the need to control pigment crystal structure, morphology, and surface characteristics as well as the extent of aggregation (McKay, 1989). Ball milling is the most commonly used technique for the preparation of photoreceptor dispersions. For environmental reasons, it is desirable to coat the generation layer from aqueous dispersions. Hoshino et al. (1990) discuss one such application.

10.3.3 Vapor Deposition Techniques

In some cases, generation layers can be prepared by vapor deposition techniques. Examples of materials that have been prepared by these methods include various phthalocyanine and perylene derivatives. The major advantage of these techniques is that a very thin layer can be deposited in a controlled manner with excellent uniformity. The principal disadvantage is that vapor-deposited pigment films are usually amorphous. To achieve optimum sensitivity, the material must be converted to a crystalline state. This requires a subsequent thermal or solvent conversion process. A further disadvantage is that vacuum deposition methods are slow and expensive compared to solvent coating techniques.

10.3.4 Drum Techniques

In principle, drum coating can be carried out in a manner similar to that of web coating. The simplest method is dip coating, where the drum is withdrawn from a coating solution.

The film thickness increases with increasing viscosity and withdrawal speed and decreases with increasing surface tension. An alternative technique is ring coating. In this method, the drum is slowly withdrawn through an annulus, which determines the coating thickness. In addition, various spray coating methods may be used. The preferred method must be selected for each application. Virtually all desktop printers use drums with diameters of approximately 30 mm. Larger diameter drums have been produced, however, such as the 140 mm drum used in the Xeikon Digital Color Press (De Schamphelaere et al., 1994).

10.3.5 Overcoat Layers

Organic photoreceptors are relatively soft and easily deformed, making them susceptible to physical damage and wear. Further, they are sensitive to the deleterious effects of corona exposures. Many overcoat technologies have been investigated in order to improve the photoreceptor stability and process life. The overcoat conductivity must be carefully controlled. If it is too insulating, a residual potential will develop during cycling. If it is too conductive, the latent image will spread. Therefore overcoats must be formulated for an optimized conductivity. Several approaches have been described and some commercialized.

Polymeric materials are one approach. Sato et al. (1992) described an overcoat composed of a polyurethane and a silicone. The best image quality was obtained by the use of a hydrophobic silica in an overcoat with a high urethane content. Yamamoto et al. (1982) described an overcoat composed of a polyester doped with 1,1'-dimethylferrocene. The overcoat was applied by spray coating and had a conductivity of approximately $10^{-10} (\Omega \text{ cm})^{-1}$. The photoreceptor had satisfactory image quality at elevated humidities.

Another approach involves the use of the polysiloxanes (Weiss et al., 1999). These materials are extremely tough and wear resistant. The conductivity must be carefully controlled by doping. An example of this technology is UltraShield™ from Optical Technologies Corp. (Cornelius, 1994). This material has been successfully used in both drum and web applications. A disadvantage of this material is that the dark conductivity is sensitive to environmental conditions, which can lead to latent image degradation. Polysiloxane overcoats are prepared from aqueous solutions using standard solvent coating technologies. These must be thermally cured to achieve the desired physical properties.

Another technique is to utilize a very thin layer of a refractory material such as SiC, SiN, or diamondlike carbon (DLC). These materials are usually prepared by plasma-enhanced chemical-vapor-deposition processes. Sato and Hisada (1996) described the use of a pulsed molecular beam process to prepare photoreceptor drums with DLC overcoats. DLC has been commercialized as Diamond 4™ (HDS Corp.) for drum applications. The dark conductivity of this layer must be controlled to minimize environmental effects. Kocchev et al. (1996) have compared DLC and polysiloxane overcoats.

10.4 XEROGRAPHIC PHOTORECEPTORS

10.4.1 Configuration

Organic photoreceptors are between 10 and 50 μm in thickness and can be prepared in a single- or a dual-layer configuration. Single-layer photoreceptors are composed of a pigment in a polymer doped with either a donor or an acceptor molecule and are typically between 10 and 15 μm in thickness. In the dual-layer configuration, the photoreceptor is prepared with two separate layers. The generation layer contains a pigment and is usually

coated adjacent to the substrate with the transport layer uppermost. Transport layers contain either a donor or an acceptor molecule in a polymer. Thicknesses of dual-layer photoreceptors are usually between 15 and 50 μm . Most transport layers are doped with donor molecules and thus transport only holes. For this reason, dual-layer photoreceptors are usually charged negatively. When it is desired to charge the photoreceptor positively, the layers may be inverted, so that the transport layer is coated on the substrate and the charge generation layer is uppermost.

10.4.2 Charge Generation Materials

Generation materials are generally classified according to their chemical structure. The physical forms may be molecular complexes or pigments. In either the single- or the dual-layer arrangement, both electrons and holes must transit the generation layer thickness in the absence of trapping to affect complete photodischarge. For this reason, generation layers usually contain high pigment concentrations and are fabricated as thin as possible while maintaining the desired absorption characteristics. Molecular complexes were widely used in early applications. More recently, pigments have received considerable attention. Both vapor-deposited and dispersion layers have been used.

Because of the long history of the synthesis and commercialization of pigments, the desired physical and chemical characteristics can be largely predicted and achieved. Most pigments exhibit polymorphism (Dunitz and Bernstein, 1995; Gavezzotti and Filippini, 1995), and the crystal form can be influenced by various finishing processes (Hunger and Merkle, 1983). Typical of these are solvent treatments, the introduction of surfactants, and thermal treatments. Because of the low solubilities of pigments, specialized purification technologies such as solvent extraction, acid pasting, and train sublimation are often used. Crystal modification is known to affect color, tinctorial strength, shade, and lightfastness. Other important factors are crystal morphology, degree of crystallinity, particle size distribution, and surface conditioning. The advent of semiconductor lasers and light-emitting diodes has necessitated generation layers with sensitivity in the near infrared. Thus there has been interest in predicting and producing crystal modifications with the desired absorption characteristics.

The properties of generation materials that are of principal interest are the useful spectral range and the sensitivity. The former is determined by the absorption spectrum and the latter by the efficiencies of carrier generation and injection into the transport layer. In the section that follows, we discuss different generation materials. These are classified as molecular complexes (donor-acceptor charge transfer and aggregates), pigments (polyazos, phthalocyanines, squaraines), polycyclic aromatics, and other materials.

Molecular Complexes

Charge-transfer complexes have a long history as generation materials. Charge-transfer complexes of various electron acceptors with poly(N-vinylcarbazole) (PVK) have been extensively studied. The complex formed between PVK and 2,4,7-trinitro-9-fluorenone (TNF) (Shattuck and Vahtra, 1969; Schaffert, 1971; Melz, 1972; Vahtra and Wolter, 1978) was the first organic photoreceptor to be used in a copier. The field and spectral dependencies of the xerographic gain have been described by the Onsager formalism (Melz, 1972; Kato et al., 1983; Andre et al., 1989). Values of the thermalization distance and primary quantum yield were approximately 35 Å and 0.20. The use of the fullerenes (C_{60} and C_{70}) as electron acceptors in sensitizing the photoconductivity of PVK (Wang, 1992; Chen et al., 1996) demonstrates the continuing interest in this class of materials.

Dye-polymer aggregate photoreceptors are a class of two-phase materials that con-

tain a light-sensitive crystalline phase dispersed in a polymer. Usually a donor molecule is added to enhance the sensitivity. Perlstein and Borsenberger (1982) have reviewed the photoelectronic properties of these materials. The dye–polymer aggregate phase is a highly colored filamentary structure. The dye can be any of several aryl-substituted pyrylium or thiapyrylium salts, while the polymer is bisphenol-A polycarbonate. The dye–polymer aggregate can be prepared by solvent fuming a homogeneous coating of a pyrylium or thiapyrylium dye and the polycarbonate. Aggregation shifts the absorption maximum from typically 580 to 680 nm. Substitution of the seleno- or telluropirylium dye for the thiapyrylium shifts the absorption maximum to longer wavelengths. Dye–polymer aggregate photoreceptors can be prepared in the single- or dual-layer configuration (Nguyen and Weiss, 1988, 1989). In the dual-layer format, the aggregate-containing layer comprises the generation layer.

Figure 10.6 shows the spectral dependencies of the xerographic gain of a mixture of 4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate, the polycarbonate, and the donor molecule 4,4'-bis-(diethylamino)-2,2'-dimethyltriphenylmethane before and after aggregation by fuming with dichloromethane. Aggregation results in a considerable increase in the gain. Both electrons and holes are mobile in the aggregate phase, while only holes are mobile in the homogeneous precursor. In the absence of carrier range limitations, the xerographic gain is symbatic with the absorption spectrum. Similar results are obtained for positive or negative potentials. The field dependence of the xerographic gain has been described by the Onsager theory with thermalization distances between 30 and 60 Å and a primary quantum yield of approximately 0.50. The thermalization distance

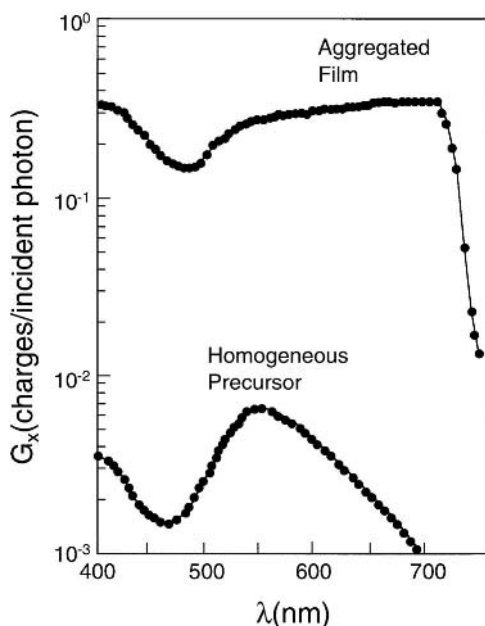


Figure 10.6 The spectral dependencies of the xerographic gain of a mixture of 4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate, bisphenol-A polycarbonate, and the donor molecule 4,4'-bis-(diethylamino)-2,2'-dimethyltriphenylmethane before and after solvent fuming with dichloromethane. The thickness was 20 μm , the temperature 296 K, and the field 4.0×10^5 V/cm. The measurements were made with a positive surface potential.

increases with increasing donor concentration. The photogeneration is believed to occur via a singlet exciton that diffuses to the interface between the crystalline and homogeneous phases and then dissociates into a free electron and a free hole via an interaction with the donor molecule (O'Regan et al., 1995, 1996; Molaire et al., 1997).

Reciprocity phenomena in aggregate materials have been described by Mey et al. (1979). A loss in sensitivity of 0.14 log ϵ was observed and explained by Langevin recombination.

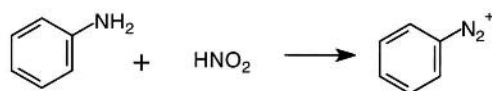
Polyazo Materials

Azo dyes and pigments have been important commercial products for the past century. Following the discovery of diazonium compounds in 1858, and the first azobenzene in 1861, this class of compounds was rapidly exploited for the production of dyes and pigments. One of the reasons for the success of this class is their relative ease of synthesis. Thus large numbers of compounds can be readily prepared in pure form. The basic synthetic steps, diazotization and coupling, are outlined in Fig. 10.7. The starting materials are primary aromatic amines, of which aniline (shown) is the simplest example, plus a coupling compound. For photoreceptor applications, the latter is typically an anilide of an *o*-hydroxyaromatic carboxylic acid. The example shown uses 2-hydroxy-3-naphthanilide. This compound is commercially available as Naphthol AS. The synthesis commences with the preparation of the diazonium salt from the amine. This is accomplished by reaction of the amine with cold aqueous nitrous acid. The coupling reaction is a classical electrophilic aromatic substitution. Being a very weak electrophile, the diazonium ion is most reactive toward activated (electron-rich) aromatics. Hydroxyl substituents are common. Depending on steric effects, such substituents direct the coupling to the *o* or *p* positions. In Fig. 10.7, only the *o* position is available. The final product is readily isolated from the reaction mixture in crystalline form. Subsequent treatments, such as stirring with hot dimethylformamide followed by water washing (Cort et al., 1983), yield the α -form. This pigment form is readily milled to produce stable dispersions.

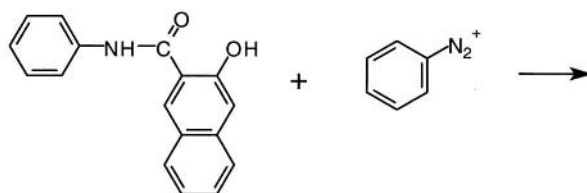
Azo compounds are classified according to the number of azo groups: mono, bis or dis, tris, and tetrakis. These are prepared from the appropriate mono-, di-, tri-, and tetraamino-substituted starting material. To describe the complex structures of the azo dyes used in generation layers, it is helpful to locate the portions of the molecule that were the original hydroxyaromatic coupling moiety, and the aromatic amine (I and II, respectively, in Fig. 10.7). In virtually all the literature on azo pigments as generation materials, the molecular structures are drawn as azo ($-\text{N}=\text{N}-$) compounds. Law et al. (1993), however, have shown that azo compounds prepared from 2-hydroxy-3-naphthanilide exist exclusively as the hydrazone tautomer. Pacansky and Waltman (1992) studied Chlorodiane Blue and came to the same conclusion. Ono et al. (1991) carried out similar studies on a series of bisazo pigments prepared from 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole and a variety of couplers. Thus the azo tautomers are not always accurate structural representations of these materials, although the molecules continue to be drawn in this manner because it is easier to identify the structural units. Figure 10.7 shows the hydroxy-azo to keto-hydrazone tautomerism.

Figure 10.8 shows representative azo pigments that have been used as generation layers (Nakanishi, 1987). Bisazo compounds dominate, although tris and tetrakis compounds are being increasingly used for applications that require sensitivity in the near infrared. The first use of an azo pigment as a photoreceptor was in Chlorodiane Blue. This material was used in early IBM copiers and printers. Both single- and dual-layer

Diazotization:



Coupling:



Azo Compound:

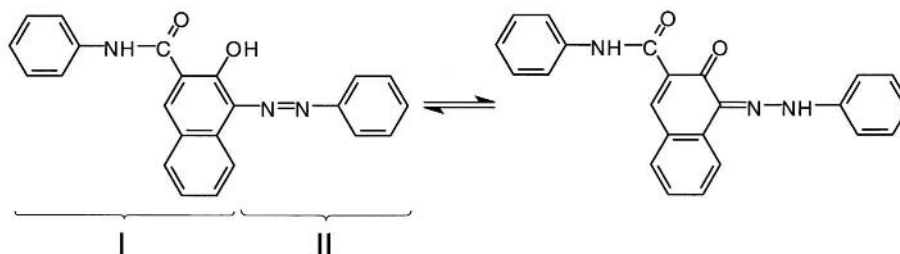


Figure 10.7 Azo compound synthesis and the molecular structure of the hydroxy-azo tautomer showing the positions of the coupler (I) and the amine (II) components. The keto-hydrazone tautomer is shown in equilibrium with the hydroxy-azo tautomer.

structures were used. The dual-layer configuration was preferred because of a considerable increase in lifetime and sensitivity (McMurty et al., 1984). Permanent fatigue occurred with excessive exposure to room light.

Single- and dual-layer photoreceptors using Chlorodiane Blue have been described by Khe et al. (1984). The sensitivity was improved by the addition of an indoline electron donor. Kakuta et al. (1981) showed that the sensitivity depends on the ionization potential of the donor molecule of the transport layer. Pacansky and Waltman (1992) reported that the pigment in the generation layer is in the azo tautomer, as initially coated from a solvent mixture of ethylenediamine and tetrahydrofuran, but it converts to the hydrazone tautomer

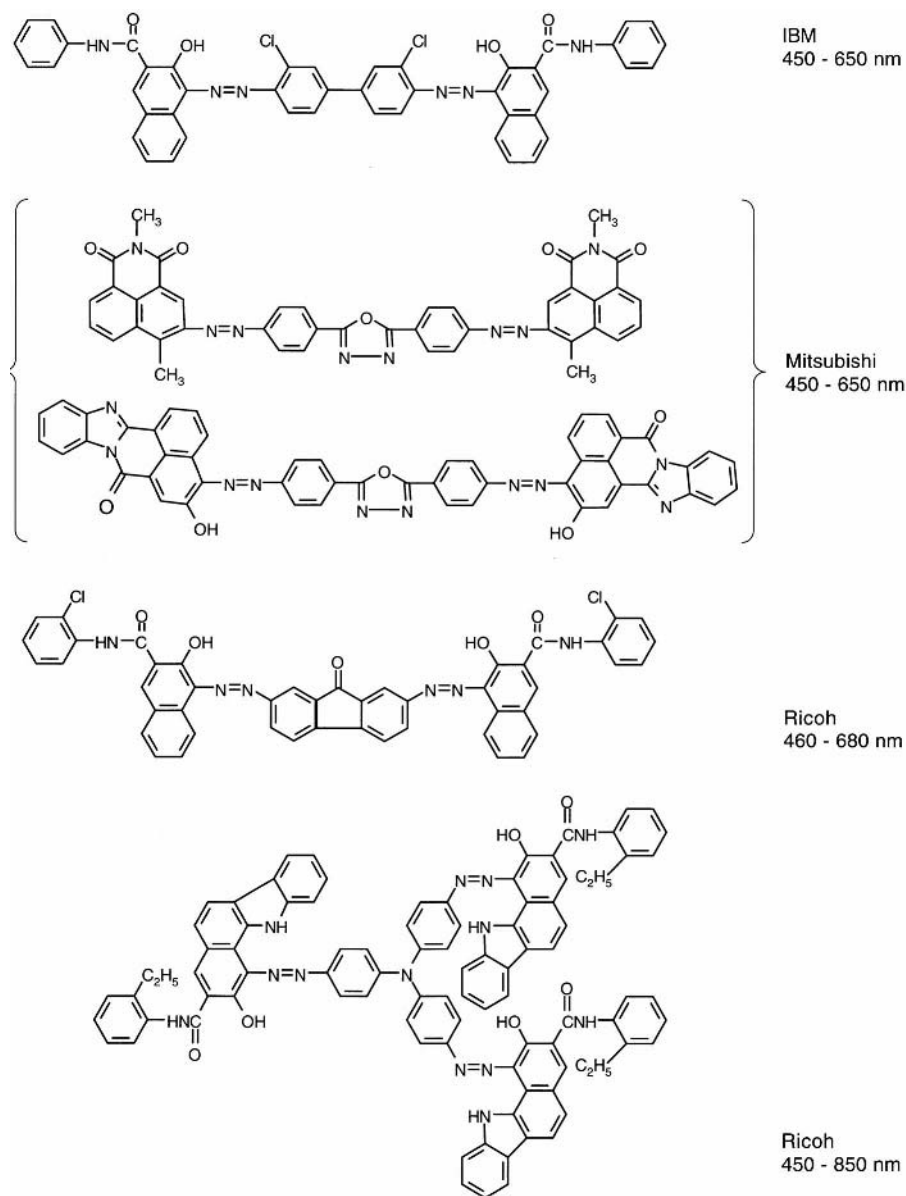
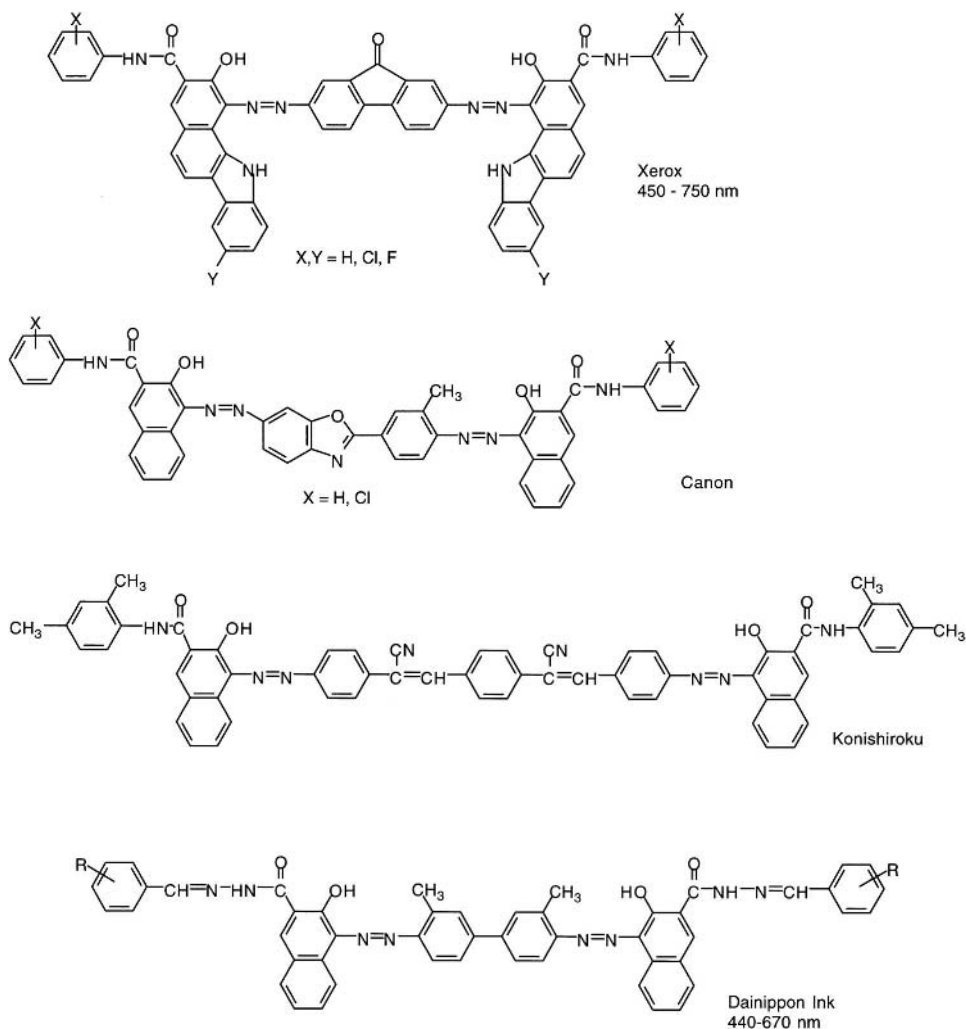


Figure 10.8 Polyazo compounds used in pigment dispersion charge generation layers.

during the subsequent transport layer overcoating process, which uses a solvent mixture of tetrahydrofuran and toluene.

The photoreceptors shown in Fig. 10.8 have been described by Nishijima (1985) and Ohta (1986). The trisazo material was used in a photoreceptor developed for printer applications (Seki et al., 1989). Umeda and Hashimoto (1992) and Umeda et al. (1993) have carried out extensive studies on the photogeneration mechanisms for this pigment. The more recently disclosed Mitsubishi materials have been developed for higher sensitiv-



ity and increased thermal and fatigue resistance (Otsuka et al., 1986). By using a coupling component that is a mixture of isomers, the perinone bisazo pigment is a mixture of three isomers. The x-ray diffraction peaks were very broad, indicative of low crystallinity and small particle size. Various treatments were unsuccessful in modifying these crystal properties. Dual-layer photoreceptors were prepared using generation layer dispersions. The transport layers contained mixtures of different hydrazones. These materials have significant blue absorption; thus the sensitivity decreased sharply for wavelengths below 470 nm. The xerographic gain was much less field dependent than for Chlorodiane Blue.

There are a few studies on the effects of different substituents with a given parent pigment and the importance of the crystal modification. In a study by Hashimoto (1986), several bisazo pigments based on diaminofluorenone were synthesized and characterized. Table 10.1 shows the results for pigments related to the bisazo Ricoh entry in Fig. 10.8. Here X refers to the Naphthol AS phenyl ring substituents. The long wavelength absorption edge and absorption maximum were not systematically altered by the phenyl substitu-

Table 10.1 The Effects of X Substituents on the Absorption and Sensitivity of a Series of Dual-Layer Photoreceptors Using Fluorenone-Based Bisazo Pigments in the Generation Layer, Fig. 8. The Sensitivity is the Energy Required to Discharge the Photoreceptor to $V_0/2$

X	Absorption edge (nm)	Absorption maximum (nm)	V_0 (V)	ϵ (erg/cm ²)
H	673	610	−1064	15.2
4-OCH ₃	678	620	−1246	24.4
2-CH ₃	665	620	−1090	6.4
3-CH ₃	682	620	−990	12.0
4-CH ₃	674	620	−1258	20.4
2-Cl	650	590	−690	1.9
3-Cl	655	590	−440	2.0
4-Cl	668	640	−844	8.6
2-NO ₂	684	640	−1192	4.9

Source: After Hashimoto, 1986. Reprinted from *Denshi Shashin (Electrophotography)*, 25:10. Copyright 1986, Japanese Electrophotography Society.

ents. There were, however, large differences in sensitivity. The generation layers were used with transport layers containing a hydrazone derivative. A Hammett free energy analysis showed a clear correlation between the sensitivity and increasing electronegativity of the anilide ring substituent. Interestingly, intramolecular hydrogen bonding also became stronger with substituent electronegativity. The compound with the 2-chloro substituent has recently received considerable attention in a series of papers by Niimi and Umeda (1993, 1994), Umeda and Niimi (1994, 1994a), and Umeda (1999).

There has been considerable activity in the preparation and study of new azo pigments. Law and Tarnawskyj (1993, 1995, 1995a) described pigments prepared with a variety of novel aromatic diamines, such as 2-nitro-4-4'-diaminodiphenylamine, 2,7-diaminofluorenone, and different 2-hydroxy-11(H)-benzo(a)carbazole-3-carboxanilide couplers, which extend the sensitivity into the near infrared. The sensitometry of many of these bisazo pigments have been described by DiPaola-Baranyi et al. (1990). Attempts have been made to understand the results in terms of structure–activity relationships (Law et al., 1994).

Phthalocyanines

From their discovery in Great Britain in 1927 to the present day, the phthalocyanines, Fig. 10.9, have been of significant commercial relevance. These materials have exceptional colorant characteristics, as well as stability to heat and light. Present applications extend from the traditional inks and paints (McKay, 1989) to xerographic photoreceptors (Gregory, 1991). Due to their importance as colorants, synthetic methods have been developed for their preparation on a large scale (Moser and Thomas, 1963, 1983; Thomas, 1990). Because the phthalocyanines are insoluble in most solvents, specialized isolation and purification methods have been developed. Phthalocyanines with many different central metal ions have been prepared and studied as generation materials. Since phthalocyanines containing ring substituents or polyaromatic rings are known, the number of possible compounds appears to be virtually limitless (Gregory, 1988).

The phthalocyanines can be used as vapor-deposited or dispersion layers. Of particular interest are those with strong absorption in the near infrared. Considerable effort has

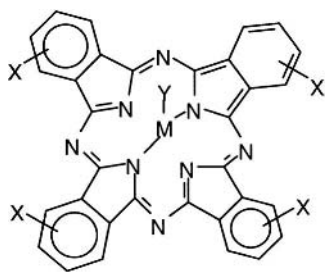


Figure 10.9 General molecular structure of a phthalocyanine (YM)(X₄-Pc).

gone into the synthesis of new compounds and the development of methods for the conversion of known phthalocyanines into morphologies that are infrared sensitive. This has been difficult, because the absorption spectra and generation characteristics depend on the chemical and crystal structure, particle size and morphology, and the presence of absorbed surface species (Sappok, 1978; Whitlock et al., 1992; Kubiak et al., 1995). Synthetic techniques and methods of photoreceptor fabrication must thus be designed to ensure that the desired characteristics are retained and/or induced (Mayo et al., 1994; Yao et al., 1995).

Because most phthalocyanines are insoluble in organic solvents, specialized methods of purification have been developed (Liebermann et al., 1988). Commonly used techniques are solvent extraction, acid pasting, and train sublimation. Solvent extraction is useful in removing trace organic contaminants. Acid pasting involves dissolving the material in concentrated mineral acid, typically sulfuric, followed by precipitation by the addition of cold water (Mayo, 1993). A limitation of this method is that some phthalocyanines (e.g., H₂Pc) may decompose during the acid pasting process. In addition, acid pasting may result in increased contamination by heavy metals such as Fe (Loutfy and Hsiao, 1979). A novel variation of acid pasting, carried out by dissolving the pigment in a solution of a Lewis acid and nitromethane, has been described by Hsieh and Melnyk (1996, 1998). Train sublimation is done by placing the pigment in one end of a quartz tube. The tube is placed in a furnace and the end containing the pigment is heated to the sublimation temperature. A flow of an inert gas, such as N₂ or Ar, is maintained from the high- to the low-temperature ends of the tube. The purified material is deposited in the cooler zones. This procedure has been described in detail by Wagner et al. (1982) and Kitamura et al. (1988).

Copper phthalocyanine (CuPC) was the first of this pigment class to be studied as a photoreceptor. Purity, crystal structure, morphology, and dispersion preparation conditions are important factors in the sensitometry. Effects of the polymer on the sensitometry of α - and β -CuPc dispersions have been described by Kishi et al. (1984). Other polymorphs, such as χ -CuPc (Sharp and Abkowitz, 1973) and σ -CuPc (Enokida and Hirohashi, 1991), have also been reported. Single-layer photoreceptors containing CuPc are of interest for positive-charging applications. A single-layer drum photoreceptor containing α -CuPc has been introduced by Kentek for applications that require near-infrared exposures (Decker et al., 1991). Fujimori et al. (1992) described the preparation of a single-layer photoreceptor with excellent cycling characteristics when α -CuPc is doped with nitrated CuPc. Dual-layer photoreceptors using α -CuPc, β -CuPc, ϵ -CuPc, and partly nitrated α -CuPc in the generation layer have been described by Enokida and Hirohashi (1992). The partly nitrated α -CuPc gave the best overall performance. Similarly substituted CuPc has also been bonded to polymers such as PVK (Chen et al., 1993; Wang et al., 1993, 1996).

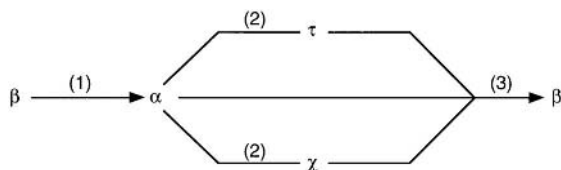


Figure 10.10 Polymorphic interconversions of H_2Pc .

Metal-free phthalocyanine (H_2Pc) has been prepared in several polymorphic forms: α (tetragonal), β (monoclinic), χ (hexagonal), and τ . Figure 10.10 shows the interconversions of these materials. For example, treatment of Monolite Fast Blue GS with hot dimethylformamide followed by ball milling in isopropyl alcohol yields the β -form as needles. Acid pasting produces the α -form as needles and flakes (Loutfy, 1981). Milling under different conditions yields the τ -form as needles or flakes (Takano et al., 1984; Kakuta et al., 1985) or the χ -form as needles (Sharp and Lardon, 1968; Hackett, 1971). The τ -form as rods has been produced directly by carrying out the synthesis in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene and seed crystals of the τ -form (Enokida and Ehashi, 1988). All of these morphologies convert to the stable β -form under equilibrium thermal, mechanical, or solvent conditions. The polymorphic forms are commonly identified by x-ray powder diffraction patterns and infrared absorption spectra. Enokida et al. (1991b) reported that cross-polarization magic-angle spinning ^{13}C NMR spectroscopy can be used to identify the various forms. Assignments have been problematic. Kubiak et al. (1995) argued that the χ -form is actually β - H_2Pc and that the α -forms of divalent metal phthalocyanines, such as $MgPc$, are complexes with N and O. This confusion is a recurring feature of phthalocyanine technology. Figures 10.11 and 10.12 show the absorption spectra of the four morphologies. Whatever their nature, the long-wavelength absorptions of the τ - and χ -forms are such that they are of interest for near-infrared applications. A dual-layer photoreceptor based on τ - H_2Pc has been described by Kakuta et al. (1985) and Shimada et al. (1987). The generation layer contained the τ -form in a polysiloxane or polycarbonate. The transport layer contained an oxazole derivative in the same polymers. Further refinements of the τ -form have been reported by Enokida et al. (1991a) and Endo et al. (1994).

Positively charged photoreceptors are of considerable interest for printer applications. Tsuchiya et al. (1995) described a single-layer photoreceptor prepared with χ - H_2Pc . Nakatani et al. (1985) reported that doping β - H_2Pc with electron acceptors, such as 2,4,5,7-tetranitrofluorenone, substantially enhanced the sensitivity. Similar observations were later reported by Kobayashi et al. (1996). A structure with the generation layer uppermost has been described by Takahashi and Yamamoto (1995). The generation layer was composed of χ - H_2Pc dispersed in a TiO_2 glass.

Generation layers composed of titanyl phthalocyanine (TiOPc) dispersions have received considerable recent attention. A procedure for photoreceptor fabrication described by Ohaku et al. (1988) involved first converting the as-synthesized pigment to the α -form by extended ball milling. A dispersion of the pigment and a polyester was used to prepare the generation layer. The transport layer contained an indoline derivative in a polycarbonate. The photoreceptor showed satisfactory charge acceptance and high sensitivity in the 520 to 900 nm spectral range. A similar photoreceptor prepared with β -TiOPc showed considerably higher dark discharge and lower sensitivity. Recent work has led to the identification of several new polymorphs, some of which have had commercial application.

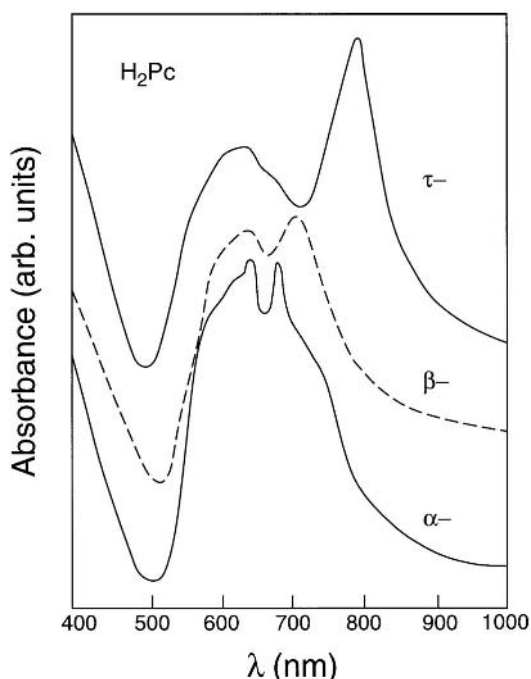


Figure 10.11 Absorption spectra for α -, β -, and τ -H₂Pc. (After Kakuta et al., 1985. Reprinted from *J. Imaging Technol.* 11:7. Copyright 1985, Society for Imaging Science and Technology.)

Unfortunately, different names are frequently given to what appear to be the same materials. Some of these may be small molecule complexes and not polymorphs. Enokida et al. (1990) described five forms of TiOPc (amorphous, α , β , m, and γ). Miyazaki et al. (1990) described the I-, M-, E-, G-, and H-forms. Takano et al. (1991) reported on Phases I, II, and III. Fujimaki (1991) and Fujimaki et al. (1991) described the A-, B-, D-, and Y-forms. Effects of ring substituents were described by Watanabe et al. (1993). Martin et al. (1995) studied Types I, II, III, IV, and X. Oka and Okada (1993) examined the relationship between crystal structure and sensitivities of Phases I and II and the C- and Y-forms. Hung et al. (1987) developed a ring-fluorinated TiOPc for use in dispersion-based generation layers with high sensitivity at 830 nm. Other TiOPc derivatives have been described by Suzuki et al. (1988).

Many other phthalocyanines have been investigated. Most undergo morphology changes upon solvent treatment, giving rise to new or enhanced absorptions (Hor and Loutfy, 1983) and increased sensitivity between 800 and 900 nm (Loutfy et al., 1985). Exposure to methylene chloride (fuming, ball milling, or overcoating) is typical, but other solvents such as acetone, toluene, tetrahydrofuran, and isopropyl alcohol will also induce polymorphic transformations. Table 10.2 lists the absorption maxima of vapor-deposited phthalocyanine films before and after exposure to methylene chloride. Tables 10.3 and 10.4 compare the sensitivities of dual-layer photoreceptors with dispersion and vapor-deposited generation layers. The transport layers contained N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) in a polycarbonate. The enhanced long-wavelength absorption and sensitivity were believed to be related to solvent-induced

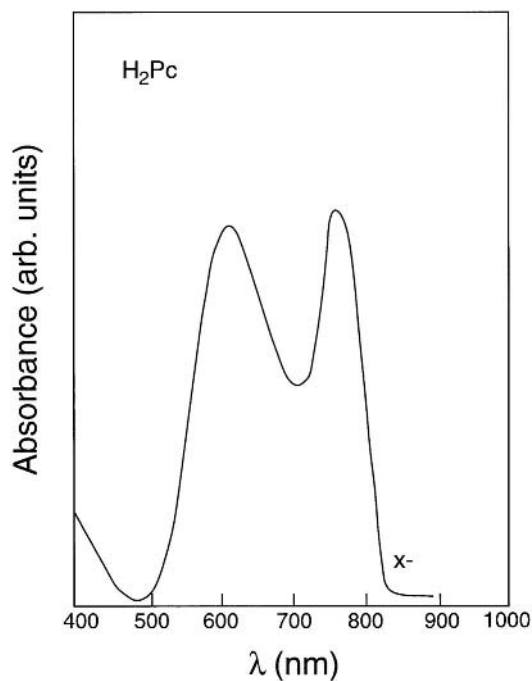


Figure 10.12 Absorption spectra of the x-H₂Pc. (After Loutfy, 1981. Reprinted from *Can. J. Chem.* 59:549. Copyright, Canadian Chemical Society, 1981.)

Table 10.2 The Absorption Maxima of a Series of 500 Å Vapor-Deposited Phthalocyanine Films Before and After Exposure to Methylene Chloride

Phthalocyanine	As deposited		After exposure to methylene chloride	
	$\lambda_{\max}$ (nm)	Optical density	$\lambda_{\max}$ (nm)	Optical density
MgPc	625	0.72	620	0.36
	695	1.00	700	0.46
			832	1.00
ZnPc	625	1.00	610	0.86
	700	0.83	700	1.00
			820	0.86
VOPc	630	0.56	630	0.52
	740	1.00	740	0.74
	830	0.77	830	1.00
ClAlPc	660	0.60	650	0.89
	730	1.00	720	0.96
			810	1.00

Source: After Loutfy et al., 1985. Reprinted with permission from *J. Imaging Sci.* 29:116. Copyright 1985, The Society for Imaging Science and Technology.

Table 10.3 The Sensitivity and Dark Discharge for a Series of Dual-Layer Photoreceptors with Phthalocyanine Dispersion-Based Generation Layers. The Sensitivity is the Energy Required to Discharge the Photoreceptor to $V_0/2$. The Wavelength Was 830 nm, and the Initial Potential -830 V. The Transport Layer Contained N-N'-Diphenyl-N-N'-bis(3-Methylphenyl)-[1,1'-Biphenyl]-4,4'-Diamine in a Polycarbonate

Phthalocyanine	Generation layer thickness (μm)	Dark discharge (V/s)	$\epsilon_{1/2}$ (erg/cm ²)
VOPc	0.40	30	4.1
τ -H ₂ Pc	0.30	20	5.0
TiOPc	0.30	30	5.6
HO ₂ GePc	0.50	60	7.0
ClInPc	1.40	60	8.0
ClAlPc	0.45	35	10.0
ClAlPcCl	0.45	25	11.0
MgPc	0.10	80	30.0

Source: After Loutfy et al., 1988. Reprinted from *Proceedings of the Fourth International Congress on Advances in Non-Impact Printing Technologies* (A. Jaffe, ed.). SPSE, Springfield, VA, p. 52. Copyright 1988, The Society for Imaging Science and Technology.

Table 10.4 The Xerographic Sensitivity and Dark Discharge for a Series of Dual-Layer Photoreceptors with 0.10 μm Vapor-Deposited Phthalocyanine Generation Layers. The Sensitivity is the Energy Required to Discharge the Photoreceptor to $V_0/2$. The Transport Layers Contained N-N'-Diphenyl-N-N'-bis(3-Methylphenyl)-[1,1'-Biphenyl]-4,4'-Diamine in a Polycarbonate. The Wavelength was 830 nm and the Initial Potential -830 V

Phthalocyanine	Dark discharge (V/s)	$\epsilon_{1/2}$ (erg/cm ²)
ClInPc	45	2.6
ClAlPc	40	6.0
PbPc	130	10.0
VOPc	30	16.0
Cl ₂ GePc	100	>100
FCrPc	26	>100
Cl ₂ SnPc	60	>100
SnPc	50	>100

Source: From Loutfy et al., 1988. Reprinted from *Proceedings of the Fourth International Congress on Advances in Non-Impact Printing Technologies* (A. Jaffe, ed.). SPSE, Springfield, VA, p. 52. Copyright 1988, The Society for Imaging Science and Technology.

changes in molecular stacking and spacing. Thus, α -MgPc has a 13.2 Å interplanar spacing and a 3.8 Å intermetal spacing along the phthalocyanine stacking axis. These distances are 11.6 and 3.5 Å after methylene chloride exposure. Similar changes occur with ClAlPc. Loutfy et al. (1985) used the term aggregation to describe these solvent-induced morphology changes. Generation layers prepared with vapor-deposited layers, Table 10.4, were converted to the infrared-sensitive morphology by overcoating with a methylene chloride solution of the transport layer (Loutfy et al., 1987).

Haloindium phthalocyanines have been used for dispersion (Hung et al., 1987a) and vapor-deposited (Kato et al., 1988) generation layers. Chloroindium phthalocyanine (ClInPc) shows near infrared absorption as synthesized. This was unchanged upon purification by train sublimation or ball milling in halogenated solvents or tetrahydrofuran (Loutfy et al., 1985a). The x-ray powder diffraction spectra likewise indicated that these materials were the same polymorph. Dispersion generation layers used with transport layers containing TPD in a polycarbonate showed increased 830 nm sensitivity and increased dark discharge as the thickness of the generation layer was increased. The results are summarized in Table 10.4.

Chloroindium phthalocyanine with ring chlorination, ClIn(Cl-Pc), has been described by Kato et al. (1985). The pigment was a mixture of the parent and the ring-chlorinated materials. Exposure to tetrahydrofuran vapors induced a modest absorption enhancement at longer wavelengths. Interestingly, the x-ray powder patterns for the as-synthesized material, and the vapor-deposited layers before and after tetrahydrofuran exposure, were identical. Thus ClIn(Cl-Pc) exists in one stable morphology.

In contrast to ClIn(Cl-Pc), the long-wavelength absorption maximum of vapor-deposited ClAl(Cl-Pc) undergoes a shift from 740 to 825 nm on immersion in tetrahydrofuran or acetone (Arishima et al., 1982). Generation layers of ClAl(Cl-Pc) of specific composition and x-ray powder patterns have been described by Nogami et al. (1988). These results, however, must now be viewed in light of the observation that ClAlPc forms a hydrate with spectral characteristics similar to those previously ascribed to polymorphism (Whitlock et al., 1992).

Vanadyl phthalocyanine (VOPc) exists in two crystal phases as characterized by absorption and emission spectroscopy (Huang and Sharp, 1982). Phase I, obtained by vapor deposition, has a long-wavelength absorption maximum at 725 nm. Acid pasting, milling in methylene chloride, and thermal treatments favor the formation of Phase II, which has a new absorption at 840 nm. A dual-layer photoreceptor with the generation layer uppermost showed high sensitivity from 400 to 900 nm (Grammatica and Mort, 1981). A soluble phthalocyanine, VO(t-Bu_{1.4}Pc), was fabricated into a single-layer photoreceptor (Law, 1988). The absorption spectrum had maxima at 650 and 694 nm, with a shoulder at 810 nm. Exposure to ethyl acetate vapor resulted in increased crystallinity, as evidenced in x-ray powder diffraction patterns and absorption spectra. Further, the intensity of the absorption at 810 nm was substantially increased. These changes were identified with Phases I and II as in VOPc. The Phase II film had a sensitivity at 600 nm in excess of 300 times that of Phase I. This was attributed to the crystalline nature of Phase II and the presence of a particular stacking structure with a close approach of neighboring molecules.

Hydroxygallium phthalocyanine (HOGaPc), with and without ring halogenation, has been described by Kato et al. (1986). The preparation and polymorphic transformations have been described by Mayo et al. (1994) and Daimon et al. (1996). Type I is formed during acid pasting and is converted to the more desirable Type V by subsequent milling

in *N,N*-dimethylformamide. Photoreceptors prepared with the latter showed high near-infrared sensitivity and good cyclic and environmental stability (Hsiao et al., 1994). A photoreceptor composed of a generation layer of HOGaPC in poly(vinyl butyral) and a transport layer of TPD in a polycarbonate had high sensitivity between 650 and 850 nm.

Naphthalocyanines have also been used as generation layers. Nikles et al. (1992) used an *n*-butanol soluble derivative, $[\text{RO}(\text{CH}_3)_2\text{SiO}]_2\text{SiNc}$, and prepared the generation layer by solution coating. Hayashi et al. (1992) described generation layers prepared from $[\text{C}_3\text{H}_7\text{-SiO}]_2\text{SiNc}$ as dispersions and as vapor-deposited layers with different transport layers. The best results were obtained with a vapor-deposited generation layer and a transport layer containing 1,1-bis(*p*-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene.

Molaire et al. (1997) described dual-layer photoreceptors prepared with tetrafluorinated titanylphthalocyanine $\text{TiO}(\text{F}_4\text{-Pc})$ generation layers. The transport layers contained tri-*p*-tolylamine doped into a polycarbonate. High sensitivity in the near-infrared and low dark discharge were reported. The spectral and field dependencies of the xerographic gain are shown in Figs. 10.13 and 10.14.

Finally, photoreceptors using mixed phthalocyanines (Wang et al., 1991, 1993; Itami et al., 1991; Hayashida et al., 1994) and phthalocyanines doped with C_{60} (Chen et al., 1995; Narushima et al., 1996) have been described.

Squaraines

Squaraines can be readily synthesized via the reaction of squaric acid (Treibs and Jacob, 1965) or its diester (Law and Bailey, 1986) with aromatic amines. Figure 10.15 shows

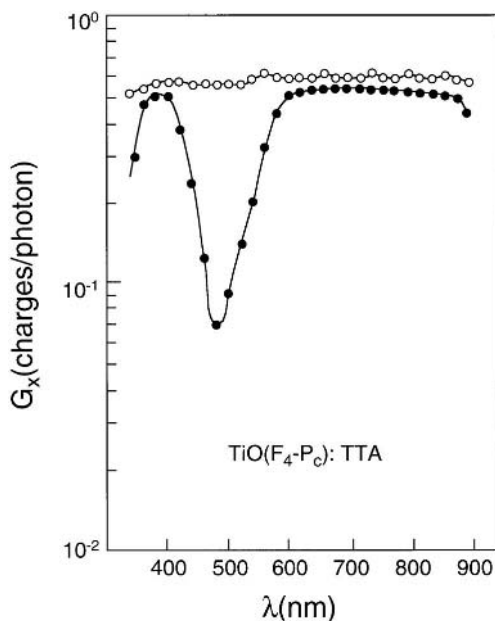


Figure 10.13 The spectral dependencies of the xerographic gain of a dual-layer photoreceptor computed on an absorbed (open circles) and incident (solid circles) photon basis. The generation layer contains a dispersion of a tetrafluorophthalocyanine in poly(vinyl butyral). The transport layer contains a mixture of 40% tri-*p*-tolylamine (TTA) and a polycarbonate (Molaire et al., 1997). The thickness was 20 μm , the field 4.0×10^5 V/cm, and the temperature 296 K.

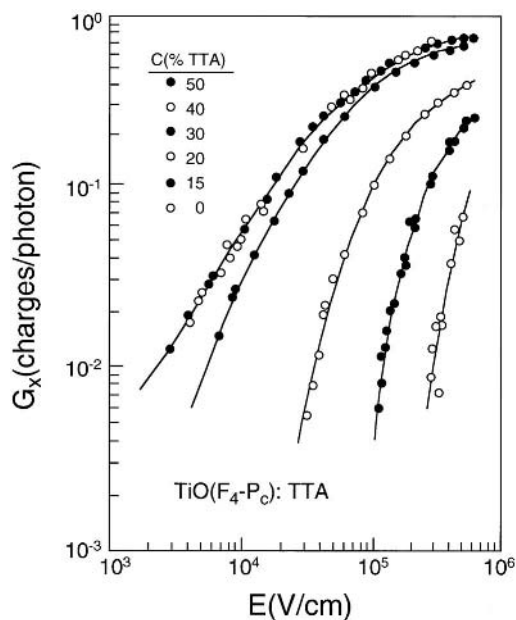


Figure 10.14 The field dependencies of the xerographic gain of a dual-layer photoreceptor. The generation layer contains a dispersion of a tetrafluorophthalocyanine in poly(vinyl butyral). The transport layer contains different concentrations of a mixture of tri-*p*-tolylamine (TTA) and a polycarbonate (Molaire et al., 1997). The thickness was 20 μm , the wavelength 680 nm, and the temperature 296 K.

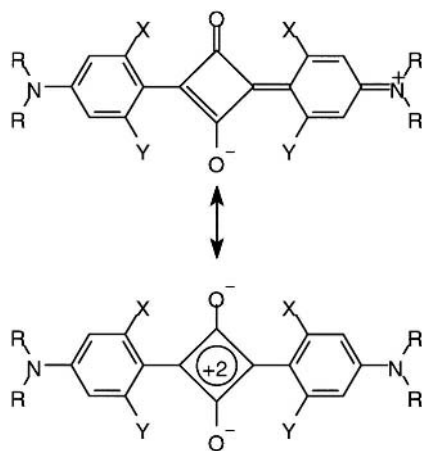


Figure 10.15 Molecular structures of two of the resonance forms of the parent squarylium molecule.

the molecular structure. Law and Bailey (1987) reported that squaraines prepared via the diester give enhanced sensitometry. This has been ascribed to the formation of a different crystal modification with a lower concentration of impurities. Other purification methods have been reported (Lin and Dudek, 1986). The synthesis of squaraines as generation layer materials has been widely studied during the past decade (Law and Bailey, 1988, 1991, 1992, 1993).

In the late 1970s, researchers at IBM developed dual-layer photoreceptors using squaraine dispersions as generation layers. The transport layers contained different pyrazoline and hydrazone doped polymers (Champ and Shattuck, 1974; Melz et al., 1977; Tam, 1980). A photoreceptor for laser printers has been described in some detail by Wingard (1982) and Champ (1987). An Al-coated polyester is the substrate. This was overcoated with a thin polyamide layer that serves as an adhesive for the generation layer as well as a blocking layer to prevent charge injection from the Al. The generation layer is an aggregated hydroxy-squarylium ($R = CH_3$, $X = OH$, $Y = H$). The transport layer is composed of *p*-diethylaminobenzaldehyde diphenylhydrazone (DEH) in a blend of a polycarbonate and a polyester plus polydimethylsiloxane, a surfactant for coating quality, and a dye to absorb fluorescent room light. The latter is required because the photoreceptor undergoes fatigue on exposure to room illumination. The action spectrum shows high sensitivity from 500 to 800 nm. The residual potential increases with cycling. The rate of increase is such that the useful lifetime was approximately 50,000 cycles. Schwartz (1991) has described a drum photoreceptor with similar composition that has been developed for use in a printer.

The photogeneration efficiency of the squaraines is related to their ability to form aggregates that have specific short-range intermolecular charge-transfer interactions (Law, 1988). Squaraines in solution exhibit narrow absorption bands with maxima between 500 and 600 nm. Materials that are useful in generation layers undergo aggregation, giving rise to very broad absorption spectra in the 400 to 1000 nm region. Law has reported several studies that correlated the sensitometry with solution electrochemistry (Law et al., 1990), fluorescence emission (Law, 1990), and state of aggregation (Law, 1992).

The effects of generation layer fabrication variables on the sensitivity of dual-layer photoreceptors prepared with bis(4-dimethylaminophenyl) squaraine ($R = CH_3$, $X = Y = H$) have been extensively investigated (Law, 1987). The dispersions were coated under humidity-controlled conditions. The transport layer contained TPD in a polycarbonate. The sensitivity was dependent on the generation layer polymer, milling conditions, pigment concentration, layer thicknesses, and the ambient humidity. The quality of the generation layer appeared to be of major importance. Some polymers produced unstable dispersions that precipitated large pigment agglomerates. Photoreceptors prepared with these polymers usually showed low charge acceptance and high residual potentials. Layers with the best dispersion quality, however, did not necessarily produce the highest sensitivity. Increased pigment concentration, or generation layer thickness, resulted in decreased charge acceptance, increased dark discharge, and increased sensitivity. Under high-humidity conditions, the dark discharge and charge acceptance were degraded. These effects were reversible. It was suggested that water absorption on the pigment surface gives rise to increased dark charge injection.

Table 10.5 compares several squaraines in a dual-layer configuration (Loutfy et al., 1988a). The generation layers were coated on an Al substrate prepared with a siloxane blocking layer. The transport layers were composed of a mixture of TPD in a polycarbonate. Increased squaraine solubility in the polymer (e.g., $R = Bu$) had a detrimental effect

Table 10.5 The Xerographic Sensitivity and Dark Discharge of a Series of Dual-Layer Photoreceptors with Different Squaraine Generation Layers. The Sensitivity is the Energy Required to Discharge the Photoreceptor to $V_0/2$. The Wavelength was 830 nm and the Initial Potential -830 V

X	Y	R	Dark discharge (V/s)	$\epsilon^{1/2}$ (erg/cm ²)
HO	H	CH ₃	35	3.0
H	H	CH ₃	42	3.5
F	H	CH ₃	70	3.5
F	CH ₃	CH ₃	35	5.5
HO	CH ₃	CH ₃	15	10.0
H	CH ₃	CH ₃	20	13.0
H	SCH ₃	CH ₃	40	33.0
HO	HO	CH ₃		Not photosensitive
H	OCH ₃	CH ₃		Not photosensitive
HO	H	Et		Not photosensitive
H	H	Et		Not photosensitive
HO	H	Bu		Not photosensitive
HO	CH ₃	Bu		Not photosensitive
HO	H	Julolidine	15	50.0
HO	HO	Julolidine	20	52.0

Source: After Loutfy et al. 1988a. Reprinted from *Pure Appl. Chem.* 60:1047. Copyright 1988, International Union of Pure and Applied Chemistry.

on the sensitivity and residual potential. Optimization of the photoreceptor with $R = CH_3$, $X = F$, $Y = H$ (Kazmaier et al., 1988) used poly(vinyl butyral) as the generation layer polymer. This material exhibited high sensitivity in the 500 to 900 nm spectral range, as well as good stability to temperature, humidity, and cycling.

The presence of certain phenols, such as 3,5-dihydroxytoluene (orcinol), during the synthesis of a squaraine corresponding to $R = CH_3$, $X = OH$, $Y = CH_3$ led to enhanced sensitivity (DiPaola-Baranyi et al., 1988). Thus a photoreceptor similar to those described in Table 10.5 showed a 6 times increase in sensitivity on doping with >20 mol% orcinol). Neither the spectral sensitivity nor the dark discharge was affected. Doping of the pigment dispersion prior to coating had no effect. This was ascribed to the isomorphic substitution of orcinol in the squaraine crystal lattice.

Unsymmetrical squaraines (Yanus and Limberg, 1986; Kazmaier et al., 1988a) prepared from two different aromatic amines have been compared to the corresponding symmetrical compounds (Kazmaier et al., 1988b). In the same study, a mixture of two aromatic amines was used in the reaction, resulting in a composite product mixture consisting of two symmetrical squaraines and the nonsymmetrical compound. Most of these materials showed high dark discharge and moderate near-infrared sensitivity. However, an unsymmetrical squaraine has been used in the development of a photoreceptor with excellent sensitometry (Law, 1992a). The pigment is the unsymmetrical fluorinated 3,4-dimethoxyphenyl-2'-fluoro-4'-(dimethylamino)phenylsquaraine. The generation layer polymer was poly(vinyl formal). The transport layer contained TPD in a polycarbonate. The photoreceptor showed low dark decay and high sensitivity from the visible into the near-infrared.

A squaraine prepared from N-chlorobenzyl-N-methylaniline and squaric acid has been used as a generation layer in a dual-layer photoreceptor with an inverted structure for positive charging applications (Yamamoto et al., 1986). The generation layer polymer was poly(vinyl acetate). The photoreceptor was prepared with a transport layer of TPD in a polycarbonate, an interface layer of a hydrolytically cured silane and zirconium, and an overcoat composed of tin oxide in a thermally cured polyurethane. The action spectrum was essentially constant from 400 to 900 nm. The photoreceptor exhibited full process stability with cycling.

There are many literature references to photoreceptors with generation layers based on dispersions of novel squaraine pigments. See, for example, Kin et al. (1986), Champ and Vollmer (1987), and Tanaka et al. (1987).

Polycyclic Aromatics and Other Compounds

Diimides of perylene-3,4,9,10-tetracarboxylic acid, Fig. 10.16, are frequently referred to as perylenes. These compounds are readily available, mainly because of their use in automotive finishes. As is the case with many pigments, the solid state absorption is red-shifted and broadened with respect to the solution absorption. This is believed to be due to specific intermolecular interactions in the crystal. Thus small changes in the structure of the R substituent give rise to absorption changes by influencing the crystal structure.

Several perylene pigments have been used in generation layer dispersions (Hor and Loutfy, 1986; Wiedemann et al., 1987; Kazmaier et al., 1988c; Staudenmayer and Regan, 1988). In one example, $R = R' = 2$ -phenethyl, conversion of the amorphous material occurs on overcoating with the transport layer. This results in a generation layer with enhanced absorption around 620 nm that shows high sensitivity and panchromatic response (Staudenmayer and Regan, 1988). A dual-layer photoreceptor with $R = R' = \text{CH}_3$ has been described by Schlosser (1978). The transport layer was 2,5-bis(4-diethylaminophenyl)-1,3,4-oxadiazole in a mixture of a polyester and poly(vinyl chloride).

A positively charged single-layer photoreceptor prepared with a dispersion of $R = R' = 3,5$ -dimethylphenyl in PVK has been described (Khe et al., 1984a). The as-synthesized pigment was observed to undergo a change in morphology with various milling techniques as well as exposure to organic solvent vapors. Good cyclic stability was reported. This pigment is used in single-layer drum applications (Matsumoto and Nakazawa, 1988). The effects of perylene structural modification on the sensitometry of vapor-deposited generation layers have been investigated by Loutfy et al. (1989) and Duff et al. (1990, 1991).

A near-infrared-sensitive photoreceptor based on 1,4-dithioketo-3,6-diphenylpyrrolo[3,4-c]pyrrole, Fig. 10.17, has been described by Mizuguchi and Rochat (1988). This material exists in three crystal forms: α , β , and Γ (Arita et al., 1991). Treatment of a sublimed film with solvent vapors, or pigment milling, results in conversion to the β -

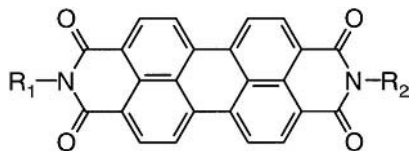


Figure 10.16 The molecular structure of perylene tetracarboxylic diimide.

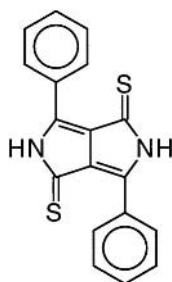


Figure 10.17 The molecular structure of 1,4-dithioketo-3,6-diphenylpyrrolo[3,4-c]pyrrole.

form with a shift in the absorption spectrum to longer wavelengths and the appearance of a new 830 nm absorption. Many solvents were successful, but acetone was preferred. The conversion also occurred upon ball milling in a mixture of xylene and ethylene glycol monomethylether. Both the converted and the nonconverted pigment forms were stable upon heating to 250°C. From transmission electron microscopy and x-ray diffraction patterns, the authors speculate that the conversion is due to a decrease in the interplanar separation in the crystal. It was further suggested that this stacking change permits enhanced intermolecular charge-transfer interactions, explaining the increase in the sensitivity of photoreceptors prepared with the converted material. Dual-layer photoreceptors with both vapor-deposited and dispersion-generation layers were prepared. The transport layers contained a mixture of DEH and a polycarbonate. The photoreceptors prepared with dispersion-generation layers showed a residual potential that increased with the generation layer thickness.

Takenouchi et al. (1988) described a dual-layer photoreceptor composed of a generation layer containing 2,7-dibromoanthanthrone, Fig. 10.18, dispersed in a polycarbonate. The transport layer contained a styryl triphenylamine derivative in a polycarbonate. The transport layer was degraded on exposure to ozone during corona charging. This resulted in a rising residual potential with cycling. Effects due to different halogen substituents on the pigment have also been studied (Allen et al., 1989). The unsubstituted parent compound had the highest sensitivity and the bromo- and iodo-substituted compounds the lowest. The results, however, depended on the donor component of the transport layer. The decreased sensitivity with bromine and iodine substituents was ascribed to a heavy atom effect, giving rise to enhanced rates of intersystem crossing from the singlet charge generating state to the triplet.

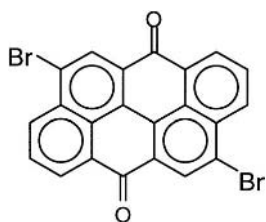


Figure 10.18 The molecular structure of 2,7-dibromoanthanthrone.

Generation layers composed of pigment mixtures have also been described. Nakazawa et al. (1994) reported that mixtures of phthalocyanines (H_2Pc , $CuPc$, $TiOPc$) with perylene, anthanthrone, or bisazo pigments offer enhanced sensitivity. Nishino et al. (1995) described a single-layer photoreceptor with $TiOPc$ and a perylene pigment. Cyanine dyes, aromatic polyenes, fullerenes (Mort et al., 1992; Hosoya et al., 1995), and similar large conjugated organic molecules have also been used.

10.4.3 Charge Transport Materials

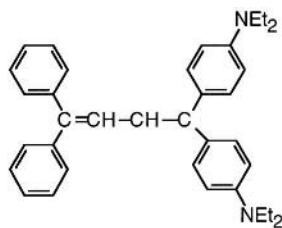
All photoreceptors contain donor or acceptor molecules to enhance the transport of holes or electrons. The donor or acceptor molecules can be doped into a polymer or chemically attached to the polymer. The former procedure is more common because it permits the greatest flexibility in the use of mixtures for optimum performance.

The basic requirement is the same for single- and for dual-layer photoreceptors. Charge transport must occur in the absence of trapping without a mobility limitation. The latter places requirements on both the transport material and the xerographic process (Pai and Yanus, 1983). The key requirement is that there be negligible residual surface potential. A residual potential can be due to either a mobility limitation or trapping. A mobility limitation arises when the transit time of electrons or holes created in the image exposure becomes comparable to the time between the exposure and development steps. There are several approaches to decreasing a mobility limitation. Increased donor or acceptor concentrations or reducing the photoreceptor thickness will reduce the residual potential. The same result can be obtained by increasing the time between the exposure and development processes or increasing the field. Traps may be present as a result of insufficient purification, chemical instability of the donor or acceptor molecule, or chemical instability induced by radiation or exposure to the chemicals associated with the corona discharge. When the potential discharge is trap-limited, the residual potential usually increases with cycling.

Hole Transport

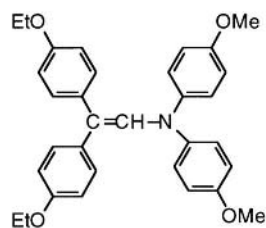
Figure 10.19 shows examples of different classes of donor molecules. In the literature, these are often referred to by their compound class: arylamines, enamines, hydrazones, oxadiazoles, triphenylmethanes, etc. This classification is convenient but misleading in that (with the exception of the polysilanes and polygermanes) it obscures the one basic feature common to all donor molecules, the presence of any arylamine substituent. That is, all these materials can be considered to be substituted aromatic amines. The presence of a nonbonding electron pair on a N atom gives rise to both a low oxidation potential, with the production of a chemically stable radical cation, and the potential for effective overlap of the nonbonding molecular orbitals of adjacent molecules. Both are important for efficient charge transport.

Some basic principles have been proposed in the design of molecules for hole transport. One is the presence of multiple conjugated arylamine moieties. This permits delocalization of the radical cation via resonance, thereby maximizing the probability for electron exchange with a neighboring donor molecule. To this end, there have been several studies on the effects of molecular orbital distributions on transport (Sugiuchi et al., 1990; Aratani et al., 1991, 1996; Kitamura and Yokoyama, 1991; Hirose et al., 1992; Okada, 1992; Hirano et al., 1995). The molecule should also be designed to prevent intramolecular ground state and/or excited state (excimer) dimer formation but at the same time maximize



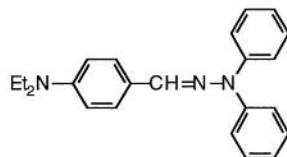
1,1-bis(4-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene
Aratani et al. (1990)

Butadienes



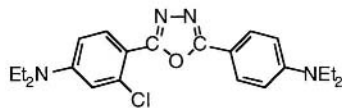
bis(p-ethoxyphenyl)acetaldehyde
di-p-methoxyphenylamine enamine
Rice et al. (1985)

Enamines



p-diethylaminobenzylaldehyde
diphenylhydrazone (DEH)*
Schein et al. (1986)

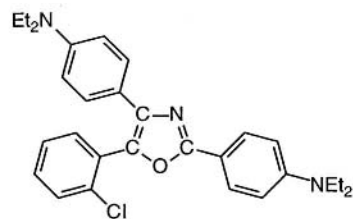
Hydrazones



2,5-bis(4-N,N'-diethylaminophenyl)-
1,3,4-oxadiazole
Schlosser et al. (1978)

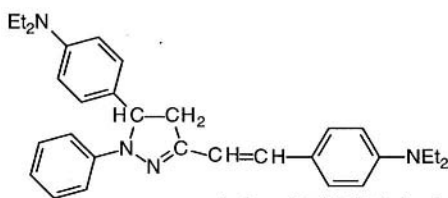
Oxadiazoles

Figure 10.19 The molecular structures, chemical names, and common acronyms of various classes of hole transport molecules.



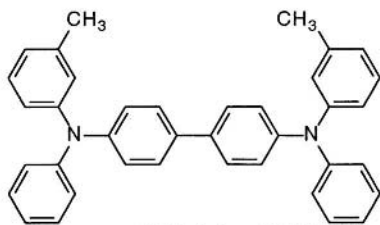
2,5-bis(4-diethylaminophenyl)-4-(2-chlorophenyl)oxazole
Kakuta et al. (1981)

Oxazoles



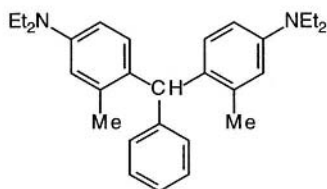
1-phenyl-3-(4'-diethylaminostyryl)-5-(4''-diethylaminostyryl)pyrazolene (DEASP)*
Meitz et al. (1977)

Pyrazolines



N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD)*
Stolka et al. (1984)
Pai et al. (1984)

Triarylaminines



bis(4-N,N-diethylamino-2-methylphenyl)phenylmethane
Borsenberger et al. (1978)

Triarylmethanes

intermolecular orbital overlap (Murayama et al., 1988). Dimer sites are believed to be hole traps in polyfunctional and polymeric charge transport materials such as PVK. Molecules designed according to these principles have been found to have improved transport properties. Examples are the styryl or stilbene classes that have been described by Makino et al. (1988), Sasaki (1988), and Ueda (1988).

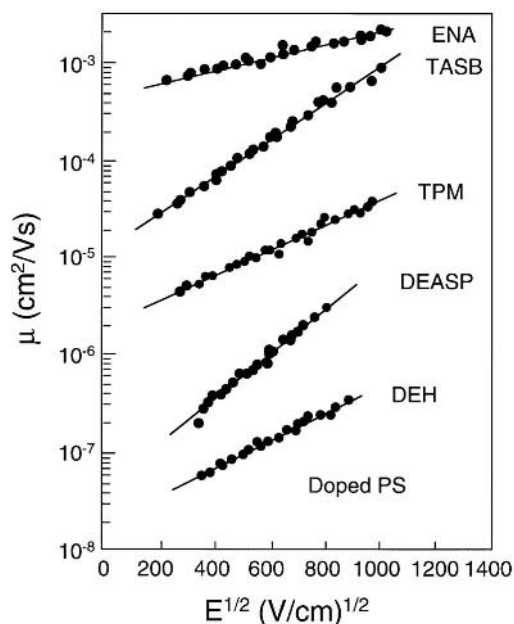


Figure 10.20 The field dependencies of the room temperature hole mobilities for a series of triphenylmethane (TPM), arylamine (TASB), enamine (ENA), pyrazoline (DEASP), and hydrazone (DEH) derivatives doped into poly(styrene) (PS). The donor concentrations were 40%.

Figure 10.20 shows the field dependencies of room temperature mobilities of different donor molecules doped into poly(styrene): *N,N'*-bis(2,2-diphenylvinyl)-*N,N'*-diphenylbenzidine (ENA), bis(ditolylaminostyryl)benzene (TASB), bis(4-*N,N*-diethylamino-2-methylphenyl)(4-phenylphenyl)methane (TPM), 5-(*p*-diethylaminophenyl)-1-phenyl-3-(*p*-diethylaminostyryl)-pyrazoline (DEASP), and *p*-diethylaminobenzaldehyde diphenylhydrazone (DEH). In virtually all doped polymers described in the literature, the mobilities are field dependent, varying approximately as $\mu \propto \exp(\beta E^{1/2})$, where β is a temperature-dependent constant. The mobilities are very low, strongly field and temperature dependent, as well as dependent on the dopant molecule, the dopant concentration, and the polymer host. Figure 10.21 shows the effects of dopant concentration for 1-phenyl-3-((diethylamino)styryl)-5-(*p*-(diethylamino)phenyl)pyrazoline (DEASP) doped polycarbonate. The mobilities are strongly concentration dependent, increasing with increasing concentration. Describing the results by the disorder formalism yields values of σ between 0.07 and 0.16 eV. In most materials, σ , the energy width of the hopping site manifold, is independent of the dopant concentration. Values of the positional disorder parameter Σ are between 1.0 and 5.0, increasing with increasing dilution.

Recent studies have also shown that the presence of large dipole moment functionalities has a deleterious effect on transport. The dipoles can be associated with the donor or acceptor molecules, the polymer repeat unit, or polar addenda. The presence of highly polar groups results in an increase in σ . This has been described by a model of dipolar disorder, due to Borsenberger and Bäessler (1991), and more recently by Dieckmann et al. (1993), Sugiuchi and Nishizawa (1993), Young (1995), Parris (1996), and Hirao and

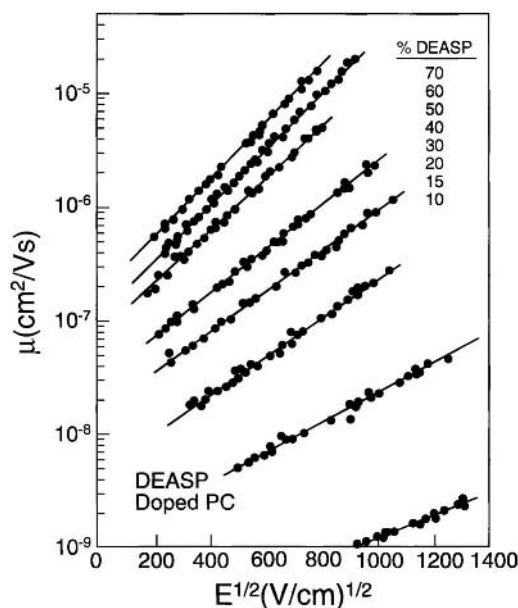


Figure 10.21 The field dependencies of the room temperature hole mobilities of 1-phenyl-3-((diethylamino)styryl)-5-(*p*-(diethylamino)phenyl)pyrazoline (DEASP) doped polycarbonate for different DEASP concentrations.

Nishizawa (1997). For a review of dipolar effects on transport, see Young and Fitzgerald (1995) and Young et al. (1995).

For many years, the polymer was thought to have little influence on the transport properties. Recent evidence, however, shows that the polymer can have a very considerable effect on transport (Sasakawa et al., 1989; Kanemitsu and Einami, 1990; Aratani et al., 1990; Kanemitsu, 1992; Yuh and Pai, 1992; Hirao et al., 1993). Depending on the polymer, the mobilities vary by as much as three orders of magnitude. Figure 10.22 shows the hole mobilities of *N,N'*-bis(2,2-diphenylvinyl)-*N,N'*-diphenylbenzidine (ENA) doped into different polymers: poly(styrene) (P-1), bisphenol-A polycarbonate (P-2), poly(4,4'-isopropylidene bisphenylene-co-4,4'-hexafluoroisopropylidene bisphenylene (50/50) terephthalate-co-azelaate (65/35) (P-3), poly-(4,4'-(2-norborylidene)diphenylene terephthalate-co-azelaate (40/60)) (P-4), a phosgene-based polyester carbonate (P-5), and poly(vinyl butyral) (P-6). In part, these results are due to dipole moments associated with the polymer repeat unit. Apolar polymers, such as poly(styrene), result in low values of σ , while highly polar polymers, such as polycarbonates or polyesters, give high values of σ . Subtle effects such as ground state charge-transfer complex formation between the transport molecule and the polymer may also be important (Scott et al., 1990).

In addition to efficiently transporting charge, the transport layer must also accept charge from the generation layer with high efficiency (Kanemitsu and Imamura, 1987, 1989). Thus a correlation is predicted between the injection efficiency and the oxidation (reduction) potential of the donor (acceptor) molecule of the transport layer with low potentials favoring injection. Correlations between the oxidation potentials of the donor

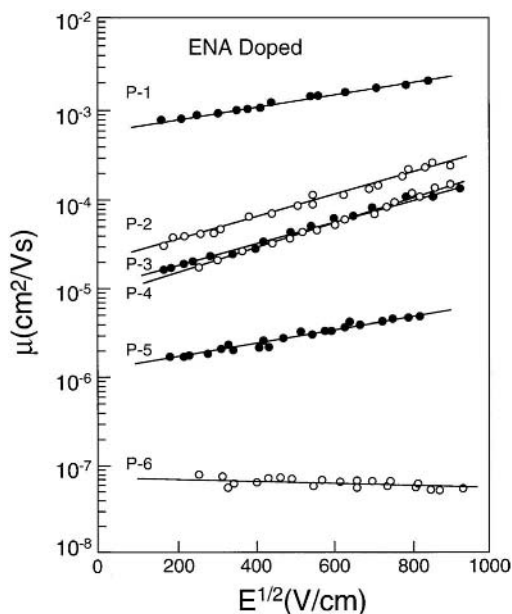


Figure 10.22 The field dependencies of the room temperature hole mobilities of *N,N'*-bis(2,2-diphenylvinyl)-*N,N'*-diphenylbenzidine (ENA) doped into poly(styrene) (P1), bisphenol-A polycarbonate (P2), a fluorinated polyester (P3), a polyester (P4), a fluorinated polyester-copolycarbonate (P5), and poly(vinyl butyral) (P6). The ENA concentration was 40%.

molecules and the injection efficiencies have been reported by Melz et al. (1977), Kakuta et al. (1981), and Umeda et al. (1993). For photoreceptors with generation layers composed of an azo pigment and transport layers containing different enamine derivatives, the sensitivity was the highest for enamine derivatives with the lowest oxidation potentials (Rice et al., 1985). Others have noted that within a given class of compounds, correlations between photoinjection efficiency and oxidation potential are complex and depend on the generation material (Murayama et al., 1988). Kubo et al. (1988) reported that dark decay caused by hole injection from polypyrrole into various transport layers correlated with the oxidation potential of the donor molecule of the transport layer.

Polysilanes $(R_1R_2Si)_n$ (West, 1986; Miller and Michl, 1989) are a class of materials that have high hole mobilities. These have been used as transport layers with generation layers of H_2Pc and $TiOPc$ dispersed in poly(vinyl butyral) (Yokoyama and Yokoyama, 1989). A poly(phenylmethylsilane) transport layer used with a $TiOPc$ generation layer performed satisfactorily in a laser printer. For a variety of reasons, including perhaps synthetic complexity, physical characteristics, and photoinstability, these materials have not been widely utilized as hole transport materials.

Transport active polymers, in which the polymer and the donor molecule are combined, are an alternative to molecularly doped polymers. The hole mobilities of these materials are significantly lower than related molecularly doped polymers, typically by a factor of 10 to 100. The cause, at least in the case of PVK, is believed to be hole trapping at carbazole dimer sites whose signature is excimer emission. Considerations of the importance of molecular rotation in permitting overlap of the molecular orbitals of neighboring

transport molecules (Slowik and Chen, 1983) has led to the synthesis of carbazole-substituted methacrylate and acrylate polymers. It was thought that the carbazole moiety would be far enough removed from the polymer backbone to be relatively free to rotate at temperatures below the polymer glass transition. Some of these polymers did exhibit enhanced hole mobilities relative to PVK (Oshima et al., 1985, 1985a). Polymers that do not show excimer emission have also been prepared (Ito et al., 1985), and some of these show improved hole mobilities relative to PVK (Hu et al., 1988). Polymeric transport materials continue to be investigated (Domes et al., 1989; Frechet et al., 1989; Murti et al., 1991).

In addition to their relevance to transport layers, transport phenomena in generation layers are also important. Most studies have been made of various phthalocyanines. Both vapor-deposited and dispersion layers have been investigated.

As normally prepared, CuPc is p-type, although n-type conductivity has been observed following various heat treatments (Delacote et al., 1964). Hole mobilities have been reported by Sussman (1967), Hamann (1968), Mycielski et al. (1982), Ziolkowska-Pawlak et al. (1983), and Gould (1985). The values were between 10^{-4} and 10^{-2} cm²/Vs. Usov and Benderskii (1970) reported a mobility of 0.40 cm²/Vs for H₂Pc. Nespurek and Lyons (1981) reported the hole range in H₂Pc as 2×10^{-10} cm²/V. Ahmad and Collins (1991) reported a mobility of 6×10^{-6} cm²/Vs for triclinic PbPc. Kontani et al. (1995) measured hole mobilities in vapor-deposited TiOPc. A key result of the work of Kontani et al. is that the mobilities are strongly dependent on the substrate temperature during the vapor-deposition process. The mobilities were between 6.0×10^{-6} and 8.0×10^{-5} cm²/Vs. The differences were attributed to an increase in film crystallinity as the substrate temperature was increased. Hole mobilities of vapor-deposited ClAlPc were measured by Ioannidis et al. (1993, 1994). The mobilities were between 2 and 6×10^{-4} cm²/Vs.

Kitamura and Yoshimura (1992) measured hole mobilities of dispersions of TiOPc in a polyester and a polycarbonate. The mobilities were in the range of 10^{-7} to 10^{-6} cm²/Vs. Enokida et al. (1993) measured hole mobilities of TiOPc dispersions in different polymers. The results were dependent on the specific form of the pigment as well as the polymer. Valerian and Nespurek (1993) measured the hole range of vapor-deposited α -H₂Pc. The values were between 4×10^{-11} and 2×10^{-9} cm²/V. The results indicated that the layers were highly inhomogeneous with the distribution of trapping centers distributed predominately in the vicinity of the substrate. Omote et al. (1995) measured hole mobilities in dispersions composed of x-H₂Pc in poly(vinyl butyral) and poly(styrene). At room temperature, the mobilities were in the range of 10^{-6} to 10^{-5} cm²/Vs.

Electron Transport

The approach taken for the search for suitable acceptor molecules is guided by several principles. First, the molecule must be nontoxic. The mutagenicity of TNF suggests that caution must be used with this and related materials. Second, it must be readily synthesized and purified. Third, the molecule should have a low reduction potential (high electron affinity). Since molecular oxygen, a potential electron trap, is always present in relatively high concentrations, the reduction potential of the acceptor molecule must be lower than that of oxygen. Reduction potentials determined in solution can be correlated with gas phase electron affinities (Loutfy et al., 1984). Fourth, the acceptor molecule must be weakly polar. Finally, the acceptor molecule should be highly soluble so that high-concentration films can be prepared.

The above requirements have made the search for electron transport materials difficult. To achieve the desired reduction potential, it is necessary to attach electron-withdraw-

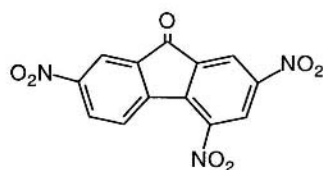
ing substituents, such as nitro or dicyanomethylene functionalities, on a parent aromatic ring such as a fluorene (Kuder et al., 1978). Unfortunately, many of these molecules are highly polar. Further, these frequently show irreversible redox chemistry, with correlated electron trapping. Also, the introduction of electron-withdrawing substituents reduces the solubility so that high-concentration layers often cannot be prepared without crystallization. For the above reasons, the development of electron transport materials has been slow. This is somewhat surprising because among the earliest organic photoreceptors were IBM's PVK:TNF charge-transfer complex and the dye-polymer aggregate developed at Eastman Kodak Company. In both materials, electron transport occurs over considerable distances in the absence of trapping. The mobilities, however, are too low for current applications.

Figure 10.23 shows structures of representative acceptor molecules. Unlike donor molecules, there are no molecular classes by which these molecules can be described. Figure 10.24 shows the field dependencies of the room temperature mobilities of different acceptor molecules doped into poly(styrene): 3,5'-dimethyl-3',5-di-*t*-butyl-diphenyl-quinone (DPQ), N,N'-bis(1,2-dimethylpropyl)-1,4,5,8-naphthalenetetracarboxylic diimide (NTDI), 1,1-dioxo-2-(4-methylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran (PTS), 2-*t*-butyl-9,10-N,N'-dicyanoanthraquinonediimine (DCAQ), and 2-methyl-2-pentyl-1,3-bis(dicyanomethylene)indane (IND). Electron mobilities of molecularly doped polymers are typically some one to two orders of magnitude lower than hole mobilities. The field, temperature, and concentration dependencies, however, are similar. The results of most recent studies have been described by the disorder formalism. The results yield values of σ between 0.09 to 0.16 eV, considerably higher than values for donor doped polymers.

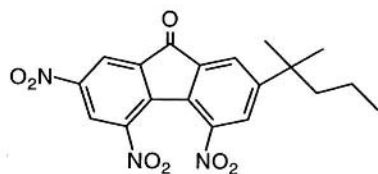
Akyl-substituted nitrated fluorene-9-ones were synthesized with the expectation of improved solubility and the hope for lowered toxicity (Loutfy and Ong, 1984; Loutfy et al., 1984; Ong et al., 1985). These compounds showed improved solubility. Compared to TNF, the mobilities were somewhat improved. Studies have been carried out with dual-layer photoreceptors using transport layers of (4-*n*-butoxycarbonyl-9-fluorenylidene) malonitrile and generation layers of a dispersed squaraine (Murti et al., 1987) and vapor-deposited VOPc (Loutfy et al., 1985b). Electron trapping was found to be important in both materials. The electron mobilities of this molecule in a polyester have been reported by Borsenberger and Bäessler (1991a). An acceptor doped polymer, with this acceptor functionality pendant, has been prepared and used as the transport layer in a photoreceptor with a TiOPc generation layer (Sim et al., 1996). The discharge was highly efficient, although there was a significant residual potential.

More recent activities have centered on the synthesis of new classes of materials. Thus far, however, none of these materials have mobilities comparable to donor doped polymers. When these materials have been used in a dual-layer configuration, the thicknesses of the transport layers are considerably less than in photoreceptors with hole transport layers.

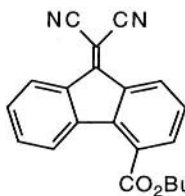
Some of the more recently investigated classes of compounds include 4*H*-dicyanomethylene-thiopyran-dioxides (Scozzafava et al., 1985; Detty et al., 1995; Borsenberger et al., 1995a), N-(nitrofluorenylidene)anilines (Matsui et al., 1993), 6,13-diazanaphtho[2,3-*b*]fluorene-5-arylimino-7,12-diones (Mizuta et al., 1996), 9,10-N,N'-dicyanoanthraquinone-diimines (Borsenberger et al., 1994, 1995), 4,4'-diphenylquinones (Yamaguchi and Yokoyama, 1991), and naphthyl-substituted oxadiazoles (Tokuhisa et al., 1995). The latter is interesting because oxadiazoles are usually considered to be donor molecules.



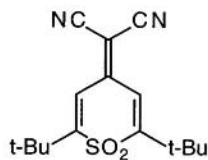
2,4,7-trinitro-9-fluorenone (TNF)
Gill (1972)



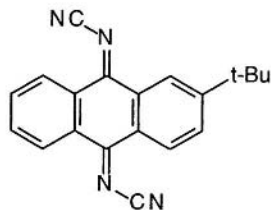
2-(1,1-dimethylbutyl)-4,5,7-trinitro-9-fluorenone
Ong *et al.* (1985)



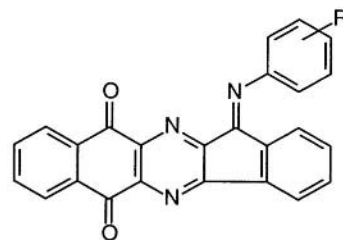
(4-butoxycarbonyl-9-fluorenylidene) malononitrile
Murti *et al.* (1987)



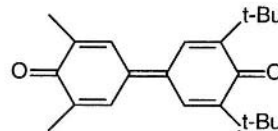
2,6-di-tert-butyl-4-dicyanomethylene-4H-thiopyran-1,1-dioxide
Scozzafava *et al.* (1985)



2-tert-butyl-9,10-N,N'-dicyanoanthraquinonedimine
Borsenberger *et al.* (1994, 1995b)



6,13-diazanaphtho[2,3-b]fluorene-5-arylimino-7,12-diones
Mizuta *et al.* (1996)



3,5-dimethyl-3',5'-di-tert-butyl-4,4'-diphenyl-4,4'-dione
Yamaguchi *et al.* (1990)

Figure 10.23 The molecular structures, chemical names, and common acronyms of typical classes of acceptor molecules.

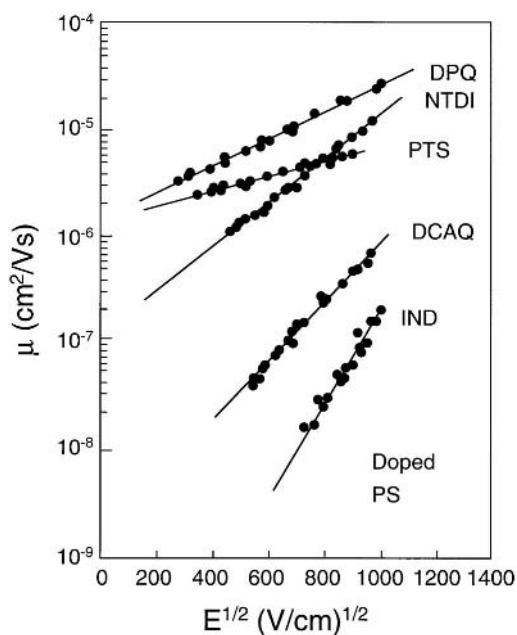


Figure 10.24 The field dependencies of the room temperature electron mobilities of a series of dephenquinone (DPQ), naphthalene diimide (NTDI), sulfone (PTS), dicyanoanthraquinone (DCAQ), and indane (IND) derivatives doped into poly(styrene). The acceptor concentrations were 40%.

Magin and Borsenberger (1993) measured electron mobilities in vapor-deposited films of *N,N'*-bis(2-phenethyl)-perylene-3,4:9,10-bis(dicarboximide). The field dependencies of the mobility showed the $\ln \mu \propto \beta E^{1/2}$ relationships commonly observed in doped polymers. The temperature dependencies, however, could not be described by either an Arrhenius relationship or a $\ln \mu \propto -(T_0/T)^2$ relationship. The width of the hopping site manifold σ was determined as 0.080 eV. Consistency with predictions of the disorder formalism, however, required an additional source of activation. The source of the activation was suggested to be either polaron formation or trapping.

Ioannidis and Dodelet (1997, 1997a, 1997b) measured electron mobilities of vapor-deposited ClAlPc. The mobilities increased with increasing substrate temperature and decreasing deposition rate. This was attributed to an increase in order. The mobilities were significantly degraded by the presence of air. The electron and hole mobilities were of comparable magnitude.

Thus far, positive-charging photoreceptors have been prepared either in the single-layer configuration or in a dual-layer configuration with the generation layer uppermost. For DAD applications, however, there is a need for conventional dual-layer photoreceptors that can be charged positively. Thus there is a need for electron transport materials. Suitable acceptor molecules, however, must have a combination of a low reduction potential, a high solubility, and a low dipole moment, a combination that has thus far proved elusive.

Bipolar Transport

An interesting recent development is that polymers doped with mixtures of donor and acceptor molecules show bipolar transport in which the mobilities of each are unaffected

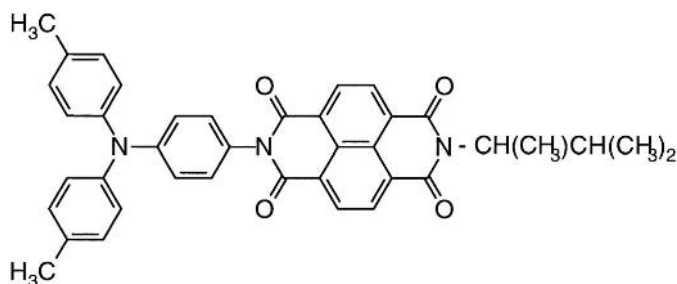


Figure 10.25 A bipolar charge transport molecule.

by the presence of the other. Thus Yamaguchi et al. (1990, 1991) described single-layer photoreceptors containing mixtures of 3,5-dimethyl-3',5'-di-*t*-butyl-4,4'-diphenylquinone and N,N,N',N'-tetrakis(*m*-methylphenyl)-1,3-diaminobenzene in poly(4,4'-cyclohexylenediphenylcarbonate) with TiOPc. Gruenbaum et al. (1996) described electron mobilities of transport layers composed of 4*H*-1,1-dioxo-4-dicyanomethylidene-2-*p*-tolyl-6-phenylthiopyran and tri-*p*-tolylamine in a polyester with a TiOPc generation layer. Lin et al. (1996) described electron and hole mobilities of a vapor-deposited bipolar transport layer composed of N,N'-bis(1,2-dimethylpropyl)-1,4,5,8-naphthalenetetracarboxylic diimide and tri-*p*-tolylamine. A bifunctional molecule N-[*p*-(di-*p*-tolylamino)phenyl]-N'-(1,2-dimethylpropyl)-1,4,5,8-naphthalenetetracarboxylic diimide was described by Kaeding et al. (1996). The structure is shown in Fig. 10.25. In this material, electron and hole mobilities are comparable with similar field and temperature dependencies.

10.4.4 Fatigue

Fatigue is the occurrence of changes in electrical properties with use. Changes in chargeability, dark discharge, sensitivity, and residual potential are examples. These may occur gradually with extended cycling under nominal conditions or rapidly after unintended exposures to environmental changes. Fatigue may necessitate the use of complex process compensation to avoid image quality degradation. Thus a considerable effort has been devoted to achieving fatigue resistance, either by the appropriate choice of materials or by the addition of additives.

Fatigue, manifested as an increase in the residual potential with use, commonly results from range limitations due to trapping (Okuda et al., 1982; Pai and Yanus, 1983; Murti et al., 1991a; Kasap et al., 1992). Trapping at the interface between the generation and transport layers has also been reported (Kanemitsu and Imamura, 1989, 1989a, 1990; Kanemitsu et al., 1990; Kanemitsu and Funda, 1991). Effects of environmental factors such as seasonal changes in humidity have been described by Law (1987).

Radiation-induced fatigue has recently received considerable attention. Unfiltered cool-white fluorescent light has a significant ultraviolet component that can be absorbed by the transport layer and lead to photochemical damage. The IBM photoreceptor using the bisazo pigment Chlorodiane Blue in the generation layer is permanently damaged by exposure to room illumination (McMurty et al., 1984). The transport layer thus includes a dye to absorb the ultraviolet component (Champ and Vollmer, 1987). Recently, the details of the fatigue were elucidated by relating these effects to the photochemistry of the DEH donor molecule (Pacansky et al. 1987, 1991). DEH undergoes the photocycliza-

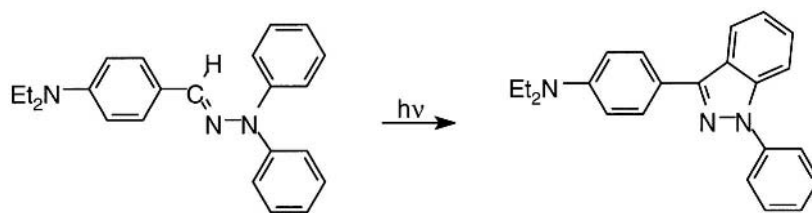


Figure 10.26 The solid-state photocyclization reaction of p-diethylaminobenzaldehyde diphenylhydrazone (DEH), a donor molecule commonly used in transport layers. (After Pacansky et al., 1987. Reprinted from *J. Photochem.* 37:293. Copyright 1987, Elsevier Science Publishers.)

tion, shown in Fig. 10.26, with a very high quantum efficiency. The effects of ultraviolet exposures on hole transport of DEH doped polycarbonate have been described by Stasiak et al. (1995) and Stasiak and Storch (1996, 1996a, 1996b). Mizuta et al. (1993) reported that single-layer photoreceptors containing 9-isopropylcarbazole N,N-diphenylhydrazone as the donor molecule are fatigued on exposure to radiation absorbed by the transport layer. The results were interpreted by a mechanism in which ultraviolet radiation induces isomerization of the anti- to the syn-isomer. The latter has a lower ionization potential and is thus a hole trap. In the single-layer configuration, hole trapping near the free surface results in the creation of a space charge that causes decreased sensitivity. Weiss and Chen (1995) have shown that transport layers containing tri-*p*-tolylamine undergo ultraviolet-induced photochemical reactions that cause fatigue in the form of an increasing residual potential with use. Enokida et al. (1991) reported that ultraviolet-radiation-induced fatigue of a photoreceptor containing a poly(methylphenylsilylene) hole transport layer could be explained in terms of transport layer photodecomposition.

In addition to changes in the transport properties, exposure of some transport layers to ultraviolet radiation leads to increased dark discharge (Kanemitsu and Imamura, 1988; Kanemitsu et al., 1989; Nabeta et al., 1990; Hirao et al., 1994). Although the mechanistic details are unclear, one likely explanation is the photoinduced electron transfer from the donor molecule to an acceptor molecule, creating a radical cation (Limburg et al., 1983). Since donor molecules are designed to have low oxidation potentials, even weak acceptors will suffice. This effect can be enhanced and such films used as electrophotographic masters (Ogawa et al., 1993).

The patent literature has many examples of addenda that can act as radical traps and quenchers of excited states, singlet oxygen, and superoxide to prevent transport layer photooxidation. See, for example, Limburg and Pai (1982) and Limburg and Renfer (1986). Surprisingly, ultraviolet radiation and electron beam curing have been investigated for the preparation of dual-layer photoreceptors (Pacansky et al., 1987a). Preliminary results indicated feasibility for the generation layer, but high dark discharge rates occurred when the transport layer was radiation cured. Radiation curing is a novel approach that avoids the use of the solvents necessary for solution coating technologies.

It is well known that ozone, a by-product of the corona discharge process, is very reactive toward most organic materials (Nashimoto, 1988). It has been shown that a styryl donor molecule undergoes ozonolysis, yielding carbonyl-containing products that are hole traps (Takenouchi et al., 1988). Interestingly, it was found that for this family of donor molecules, photoreceptors containing those with lower ionization potentials showed decreased ozone sensitivity. Other by-products of the corona discharge process are nitrogen oxides (Haridoss et al., 1982; Goldman and Sigmond, 1985; Nashimoto, 1988). These are

potent oxidizing agents. Reactions of transport layers with nitrogen oxides can lead to degraded sensitometry (Weiss, 1990). In addition, acids formed by a combination of these nitrogen oxides with water can lead to image degradation by increasing the conductivity of the photoreceptor surface (Yarmchuk and Keefe, 1989; Weiss et al., 1996).

10.5 FUTURE DIRECTIONS

In the past two decades, organic photoreceptors have played an increasingly important role in xerography. Because of their photoelectronic properties, their low cost, and the ability to prepare these materials in large areas as flexible layers, or on drum substrates, organic materials are now used for a wide range of both copier and printer applications. Based on recent developments, we expect this trend to continue.

We anticipate that increased sensitivity, longer process lifetimes, higher fatigue resistance, and higher mobilities will be primary objectives. In addition, there will be increasing emphasis on materials for DAD applications. Here, enhanced near infrared sensitivity, electron transport layers, and lower dark discharge are primary requirements. Finally, we anticipate increasing emphasis on materials that can better withstand the chemical and physical environment of xerographic engines.

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11

Photoreceptors: Recent Imaging Applications for Amorphous Silicon

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11.1 INTRODUCTION

A decade has passed since Joe Mort wrote what is now Chapter 16, but our understanding of the physics of amorphous silicon (a-Si) is little changed from what he presented there. Silicon, in its various forms, lies at the hearts of TFT liquid crystal displays, integrated circuits, solar power cells, sensor elements, and wide-area photoreceptors for images. These application areas are evolving separately in their different directions at their various rates, and it would be unusual and difficult to address more than one area in a single writing.

This update chapter is confined to wide-area amorphous silicon photoreceptor drums capable of receiving an electrostatic latent image for the purpose of development and transfer to a wide-area receiver—typically paper. For photoreceptor applications, a-Si is used only on rigid drums. There would be great demand for photoreceptor belts, but a-Si, at the thickness required, does not flex enough to be usable on a belt. Amorphous silicon in photoreceptor applications must be hydrogenated as explained in Chapter 16. This update chapter will therefore cover only advances in a-Si:H photoreceptor drums. For easier reading, “hydrogenated” and “:H” will be omitted and this material will be abbreviated as “a-Si” in the text.

Most of the recent advances in a-Si technology are related to its commercialization. Inorganic photoreceptor drums were codeveloped with photocopiers beginning in the 1950s. Low-cost organic photoconductors (OPC) enabled the development of less expensive laser printers and photocopiers beginning in the 1970s. These technologies defined the market for photoreceptors. When a-Si photoreceptor drums began to be manufactured in the 1980s, their commercialization depended upon them being perceived as useful com-

ponents in existing or newly developed photocopiers and laser printers. The overwhelming benefit of a-Si drums is their long life, closely followed by their high process speed. The major barrier to their immediate adoption was their cost of manufacture, although a number of other characteristics of a-Si prevented its easy use within existing machines. The recent advances in a-Si photoreceptor technology have been mostly focused on reducing the cost of a-Si drums and on modifying other characteristics so that they operate more like selenium-based or OPC drums.

When a-Si drums became feasible, they generated a flurry of technical papers from universities and manufacturers. This interest peaked in 1989, but then many companies withdrew from merchant and internal manufacturing. Since 1993 most papers on a-Si photoreceptor drums have come from either Kyocera Corporation in Japan or from the partnership of AEG Elektrofotografie GmbH and Forschungs-und Applikationslabor Plasmatechnik GmbH in Germany. Ikeda et al. (1996) mentions that Kyocera began shipping a-Si drums in 1984 with cumulative output reaching 1 million drums in 1993.

11.2 THE BASIC a-Si PHOTORECEPTOR DRUM

a-Si photoreceptor drums are composed of at least three layers on a metal substrate, as shown in Fig. 11.1. The middle photosensitive layer performs the basic function of the drum. Under it is the carrier blocking layer, which prevents the injection of charge carriers from the metal substrate that would ruin the characteristics of the photosensitive layer. Outermost is the surface protection layer, which protects the photosensitive layer against abrasion and retains the surface charge. The following descriptions of advances will build upon this minimal structure.

In practice the metal substrate is an extruded aluminum tube machined and polished to an extremely smooth finish. Hu (1993) showed that the acceptance of surface potential of an a-Si:H photoreceptor is very sensitive to the microroughness of the substrate surface. However, when an infrared laser will expose the photoreceptor, then it is helpful if the substrate surface is carefully roughened to prevent internal reflections. Of course the substrates must be free of all contaminants before thin film deposition. Although exacting, these requirements are well within the capabilities of many vendors and will not be further discussed.

The main cost arises from the very slow deposition time of the relatively thick photosensitive layer. The plasma CVD process is used essentially as described in Chap-

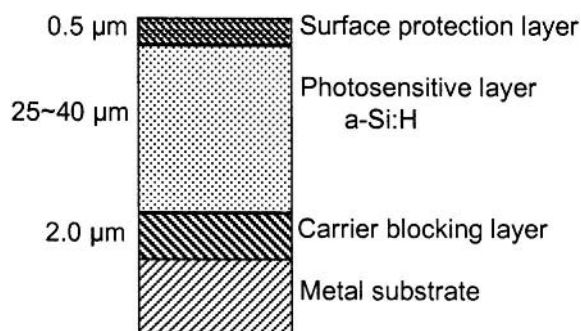


Figure 11.1 Basic layer structure of the a-Si drum.

ter 16. The blocking layer and surface protection layer are deposited inside the same reactor within the same pumpdown as the photosensitive layer.

11.3 IMPROVED CHARGE ACCEPTANCE

During its operation, the surface area of a photoreceptor drum is evenly charged in the dark, and then selected areas are discharged by laser or LED exposure light or by focused visible light from an original image. The latent image then consists of regions of voltage differences on the surface of the drum. The larger this voltage contrast, the easier to develop the image and ultimately, the better the image.

The classic capacitor model shows the factors involved in charging a drum:

$$V = \frac{d}{\epsilon \epsilon_0 S} Q$$

where V , d , ϵ , ϵ_0 , S , and Q stand for the surface voltage, the dielectric layer thickness, the relative dielectric constant, the permittivity of free space, the drum surface area, and the charge amount, respectively.

One of the first applications for a-Si drums was to bring their extraordinary long life and nontoxicity to the high-speed copier industry, which was already using selenium based drums. The dielectric constant of a-Si is 12 to 13 compared to 6 to 9 for a-Se. In a replacement situation, Q and S would be fixed for an existing print engine. Clearly, the layer thickness d must be made thicker than for a-Se. However the *dark decay* rate of a-Si limits the utility of simply increasing d . The background thermal vibrations in the a-Si material are sufficient to excite enough carriers into the conduction band to cause a noticeable drop in surface potential. Of course this is a function of temperature, and the attainable surface voltage will drop by 5 to 10 V per °C of temperature increase. The point is that the number of thermally excited carriers increases with volume, and hence it increases with the increasing thickness of the a-Si dielectric layer.

Ikedo et al. (1992) described how to construct an a-Si drum so as to obtain surface potentials equivalent to amorphous selenium, more than 800 V at 42°C at a charge amount of 0.2 $\mu\text{C}/\text{cm}^2$. Their solution was to add a highly efficient carrier generation layer on top of the photosensitive layer, made of the same material, only deposited more slowly and called a *low-rate* layer. To visualize this layer structure, look ahead to Fig. 11.6.

The low-rate layer has a lower defect density and a smaller percentage of hydrogen. Figure 16.1(c) in Chapter 16 shows only single hydrogen atoms on the dangling bonds (Si-H bonds). More recent IR absorption measurements show that Si-H₂ bonds are also present and that the proportion of Si-H₂ bonds is less in the low-rate material than in the normally deposited s-Si. Other measurements show that the low-rate material has a lower concentration of hydrogen. All this suggests a lower defect density in the low-rate material. The thermal generation of carriers is presumed to happen at defects, so the thermal generation of carriers in the low-rate layer is less. The functional result is that the thin, low-rate, carrier generation layer inhibits dark decay conduction, trapping carriers at the interface, so that the main photosensitive layer can be made thicker to sustain a higher surface charge. Figure 11.2 shows the improvement in charge acceptance.

A thicker photosensitive layer also improves the sensitivity of the drum. From the capacitor model, when voltage is increased by increasing the layer thickness, the charge density Q/S does not increase, meaning less charge per volt. Fewer photogenerated charge

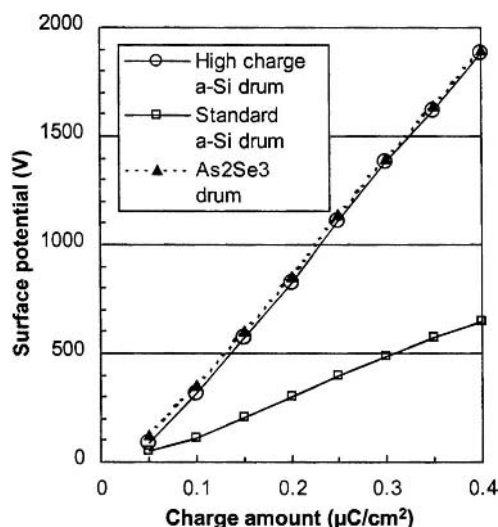


Figure 11.2 Charge acceptance of a-Si drums configured for visible light exposure.

carriers are required, so less exposure energy is required to discharge one volt, hence the higher sensitivity. Visible light is absorbed within the top 1 to 2 μm of the photosensitive layer, so most photogenerated charge carriers originate there.

11.4 BOTH CHARGE POLARITIES

Selenium-based photoreceptor drums were always positively charged because of the physics of selenium. This was an environmental advantage in that a positive charging corona generates much less ozone than a negative charging corona. As a replacement for a-Se, a-Si is also positively charged. This requires that the blocking layer be strongly doped with boron to prevent injection of the substrate metal's electrons into the photosensitive layer. The photosensitive layer is slightly doped with boron in order to achieve maximum photoconductivity, as explained in Section 2 of Chapter 16.

The physics of OPC, as first developed and commercialized, required negative charging. For compatibility with these print engines, a-Si for negative charging was developed. It was initially assumed that doping the blocking layer with phosphorous or another group III element would be necessary. However Ikeda et al. (1998) showed that this was unnecessary. a-Si is intrinsically an n-type semiconductor, and this turned out to be sufficient to prevent injection of carriers from the aluminum substrate. This finding was beneficial to manufacturing because it eliminated the use of dangerous phosphine (PH_3) gas.

The charge acceptance and the photoresponse properties of negatively charged a-Si are similar, in fact almost identical, to those of positively charged a-Si.

11.5 PHOTORESPONSE

Photoresponse is how quickly a charged photoreceptor loses its charge after it is exposed to light and is a most significant limitation on the speed of laser and LED printers. A pixel is exposed on a rotating drum. By the time that pixel reaches the development station,

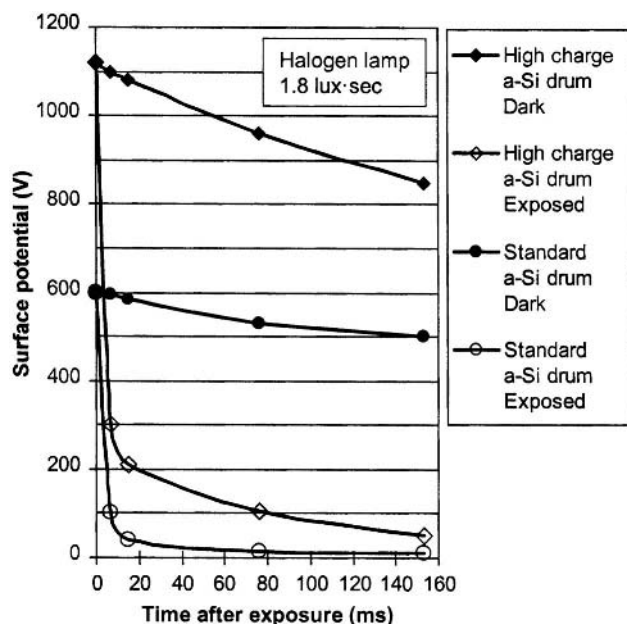


Figure 11.3 Photoresponse of a-Si drums configured for visible light exposure.

its voltage must have dropped enough to be developed. a-Si does this faster than the other photoreceptor technologies. For background, Fig. 11.3 shows the photoresponse to visible light of the high-charge and standard-charge drums previously discussed. Process speeds of less than 10 ms are possible. Dark decay curves are also shown, and within this high-speed time frame, the dark decay is not significant. Note that, for the standard drum, the surface potential quickly discharges to almost zero. From a 600 V charge, the development system sees a 550 V contrast voltage. By comparison, OPC discharges to a significantly higher residual voltage, which reduces the contrast voltage.

Refer to Borsenberger and Weiss (1998) for definitions of *emission-limited* discharge and *space-charge-limited* discharge. The sloping lines on the left of Fig. 11.4 show the emission-limited discharge of a-Si for different layer thicknesses. This sensitivity to exposure intensity exceeds that of selenium-based alloys and almost equals that of OPC. The emission-limited discharge of a-Si is linear, so it can be used for continuous-tone printing. The steeper slope reflects the higher sensitivity of thicker layers at higher surface potentials.

It is the space-charge-limited discharge of a-Si that makes it faster than OPC. Once the charge carriers are generated, they move quickly through a-Si. Adam et al. (1997) show that the charge carrier mobility of a-Si is three orders of magnitude higher than that of OPC. This is easily understandable because silicon is a true semiconductor.

11.6 FATIGUE AND TEMPERATURE EFFECTS

a-Si does not exhibit electrical fatigue. The graphs of the significant electrophotographic properties in Figs. 11.2 through 11.5 would be almost identical if measured after a million prints. This is in great contrast to the limited fatigue life of OPC.

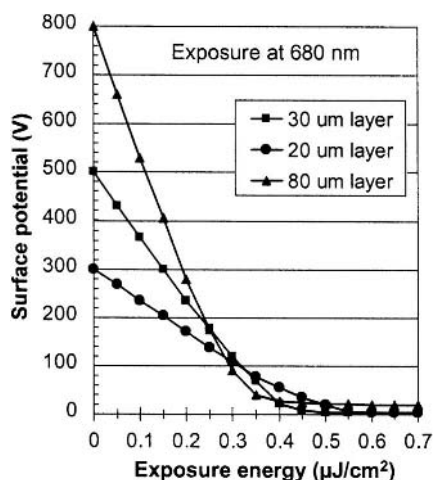


Figure 11.4 Photosensitivity as a function of layer thickness, for a-Si drums configured for visible light exposure.

It is possible to induce light fatigue in a-Si, but the effect is small. For example, Ikeda (1998b) shows a gain in surface potential of only 50 V when a drum is exposed to a fluorescent a few centimeters away, for 24 hours. This phenomenon is called the *Staebler-Wronski effect*. The mechanism is the creation of charge trapping sites. Routine incidental exposure to room light is simply not a problem.

The Staebler-Wronski effect can be reversed by annealing the drum at 200°C for 2 hours. In fact, a-Si drums can even be operated at temperatures in this range. There is no phase separation as with OPC. Temperatures up to 250°C are still below the deposition

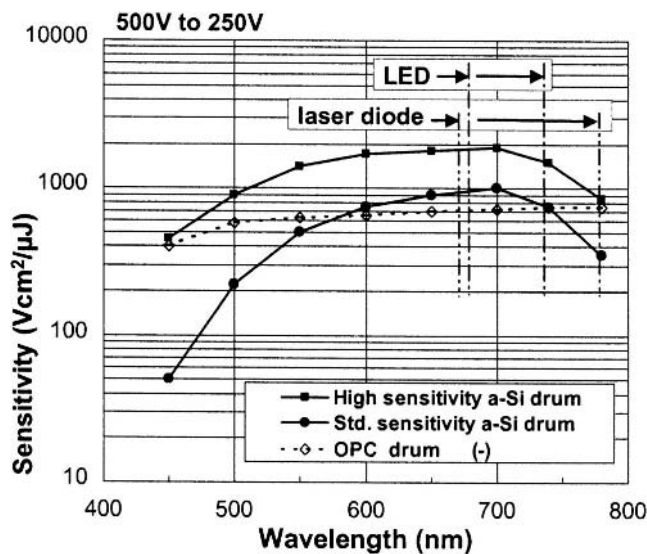


Figure 11.5 Spectral sensitivity of a-Si drums configured for near-infrared exposure.

temperature. This high-temperature capability can be used to dry out liquid toner or to accomplish other printer design objectives. Of course dark decay increases with temperature, but in a predictable manner. Attainable surface voltage declines by 5 to 10 volts/°C for standard thickness photosensitive layers. This sensitivity can be reduced to 1 volt/°C if inexpensive thin layers are used. Operation at 40°C is typical to prevent accumulation of surface moisture, as discussed in Section 8 Surface Protection Layer.

Another effect of temperature is that the aluminum substrate must be thick enough to not deform at the high deposition temperatures. This adds to the cost burden when compared to small, thin-walled OPC drums. But when large OPC drums are made with thick substrate walls for stability, then the cost difference is reduced.

11.7 SPECTRAL RESPONSE

a-Si has high sensitivity across the visible spectrum with a broad peak around 700 nm. At longer wavelengths, it is more sensitive than selenium-based photoreceptors, leading to more accurate, high-speed analog photocopiers. However, laser- and LED-based print engines, including digital copiers, only require sensitivity to their particular exposure device. a-Si has always been particularly well suited for LED print engines, because several low-cost diodes emit at wavelengths to which a-Si is very sensitive. However, the huge desktop laser printer market developed using low-cost 780 nm semiconductor lasers and OPC photoreceptors. The sensitivity of a-Si falls off past 740 nm, which initially discouraged its use. The development of thick-layer, high-sensitivity a-Si then raised its sensitivity at 780 nm to be equivalent to OPC, as shown in Fig. 11.5. The more recent emergence of low-cost 655 nm semiconductor lasers for the DVD market is expected to speed the adoption of standard thickness a-Si drums for future laser print engine designs.

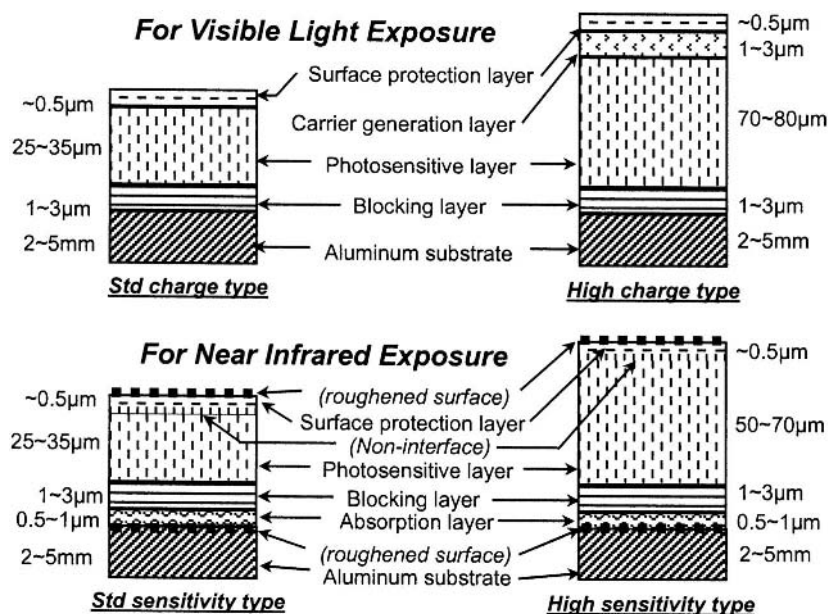


Figure 11.6 Layer structures of four variations of a-Si drums.

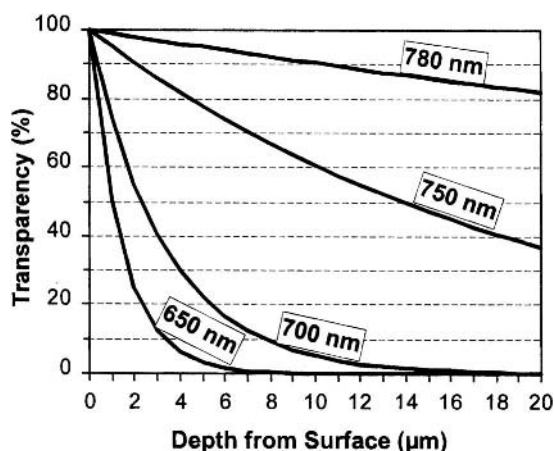


Figure 11.7 Penetration of exposure light into a-Si, as function of wavelength.

If a near-infrared laser is used on a standard a-Si drum, the result will be interference patterns from internal reflections. Interference patterns can be eliminated by incorporating some or all of the following modifications to the drum. First, begin with a roughened substrate surface, which results in a roughened drum surface. Second, use an absorption layer immediately next to the substrate surface, which prevents light from reaching the substrate surface. Third, reduce the discontinuity of the interface between the photosensitive layer and the surface protection layer, so that reflections from it are reduced. The other interface, between the blocking layer and the photosensitive layer, is not distinct enough to cause reflections. Figure 11.6 shows these modifications and includes the previously discussed visible light drums for comparison.

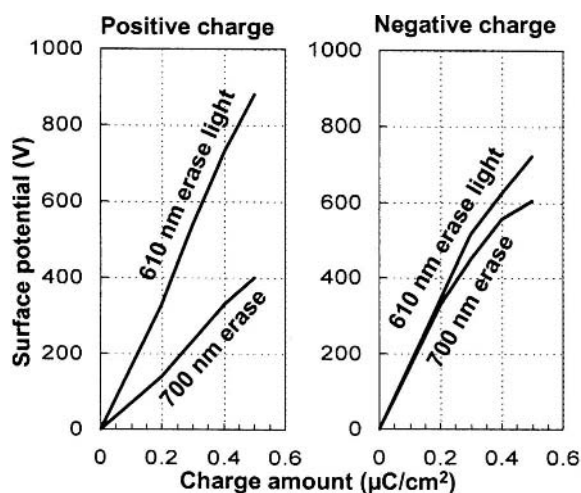


Figure 11.8 Effect of erase light wavelength on charge acceptance, for positive and negative charging.

Earlier it was stated that visible light was absorbed within 1 or 2 μm . Yet near-infrared light reaches the drum surface to cause reflections. Clearly, the depth to which light penetrates a-Si is a function of wavelength. Figure 11.7 illustrates this relationship. The big difference in transparency between 700 and 780 nm corresponds to the falloff of sensitivity in Fig. 11.5.

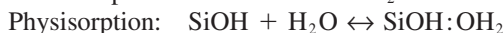
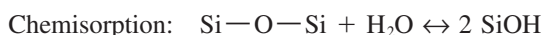
The choice of the wavelength of the erase light also affects the performance of a-Si drums. The purpose of the erase light is to uniformly discharge the entire surface of the photoreceptor so that no image remains. The charge carriers generated by the erase light can become trapped in the photosensitive layer and then emerge during charging to reduce the surface potential. The amount of this trapping varies with the penetration of the erase light, so it is more troublesome at longer wavelengths, seriously limiting the acceptance potential of drums for near-infrared applications. This is called the erase light memory effect. Figure 11.8 shows it and also shows that it is not as noticeable on negatively charged drums.

11.8 SURFACE PROTECTION LAYER

All current manufacturers of a-Si drums utilize an outer layer a-SiC:H. SiN is no longer used. As mentioned in Chapter 16, a layer is required to prevent the injection of charge carriers from the surface. a-SiC performs this function, and by depositing it very carefully, the field effect mechanism of lateral image spread is minimized.

a-SiC makes an extremely hard, abrasion-resistant surface. A 100 mm diameter drum will last over 4 million pages, and a 200 mm drum will double that to 8 million pages. SiC is impervious to the organic solvents in liquid toners and to the NO_x byproducts of corona charging.

Another type of lateral spreading of the latent electrostatic image can occur if a conducting film accumulates on the surface of the drum. Ozone generated by the corona oxidizes the silicon on the a-SiC surface into a hydrophilic oxide, which then absorbs water to form a conducting layer. Stahr et al. (1997) describe the process by



First generation a-Si drums optimized the carbon content of the a-SiC:H layer to minimize dark conductivity and maximize a-SiC hardness. Water absorption was prevented by keeping the drum surface heated to approximately 40°C.

Ikeda et al. (1996) describe the optimization of the carbon content for sharp printing at 25°C. The idea is to eliminate Si atoms from the SiC on the surface of the drum. Carbon concentrations above 96% were found to eliminate image blurring, compared to the 85% of the first-generation a-SiC:H coatings. This *C-rich* layer is applied on top of the usual SiC layer. The deposition rate drops as the carbon content of the surface layer increases, from approximately 0.3 $\mu\text{m}/\text{h}$ at 85% to approximately 0.1 $\mu\text{m}/\text{h}$ at 97%. This production inefficiency was resolved by switching the 13.56 MHz RF power on and off, at 1 kHz and at a duty ratio of 1:1. This takes advantage of the fact that the energy efficiency of the C-rich layer deposition is higher while the RF power is being switched on, compared to continuous deposition with steady RF power.

Some polishing of any photoreceptor drum surface naturally occurs from the paper and cleaning blade. To build a heaterless print engine, it is not sufficient simply to use a

C-rich layer. The polishing effect must also be increased by modifying the toner and cleaning subsystem to be more abrasive.

11.9 OPTIMIZATION FOR PRINT ENGINES

Achieving a fine resolution requires a thin photosensitive layer. When a single dot is exposed, the generated charge carriers repel each other as they move to the surface. This causes the image of the dot to grow. The thicker the layer, the more time for lateral movement. However a thick layer is required for a high surface charge. Optimization of the layer thickness requires consideration of both these conflicting requirements.

Sasahara et al. (1998) describe a series of experiments to optimize the interface between the photosensitive layer and the surface protective layer. The CH_4/SiH_4 gas ratio, deposition time, and B_2H_6 dopant gas ratio were varied, and a photosensitive layer increase from 20 μm to 40 μm was achieved while maintaining a sharp dot size of 70 μm using dry toner. The results of this effort are shown in Fig. 11.9, where boundary curves show the simultaneous maximums of resolution and layer thickness. The tradeoff against surface potential is shown in Fig. 11.10.

The resolution, or minimum dot size, depends on the design of the print engine. Print resolution can be dramatically increased by using liquid toner, as shown in Fig. 11.9. Much smaller toner particles can be used, and the pigment content of liquid toner particles can be higher. It is feasible to use liquid toner with a-Si photoreceptors because the a-Si:H and a-SiC:H materials do not degrade in the toner solvent, whereas OPC does. With the more saturated color, reduced toner pileup, and increased resolution of liquid toner, it is possible to design color print-on-demand systems that have the image quality of offset presses.

11.10 MANUFACTURING a-Si PHOTORECEPTOR DRUMS

a-Si drums are manufactured by the plasma CVD process, essentially as shown in Figs. 4 and 5 of Chapter 16. Silane gas (SiH_4) is always the source of the silicon with methane

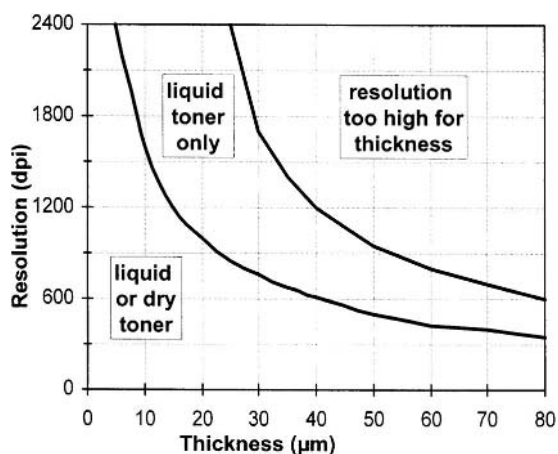


Figure 11.9 Achievable resolution and layer thickness combinations, by type of toner.

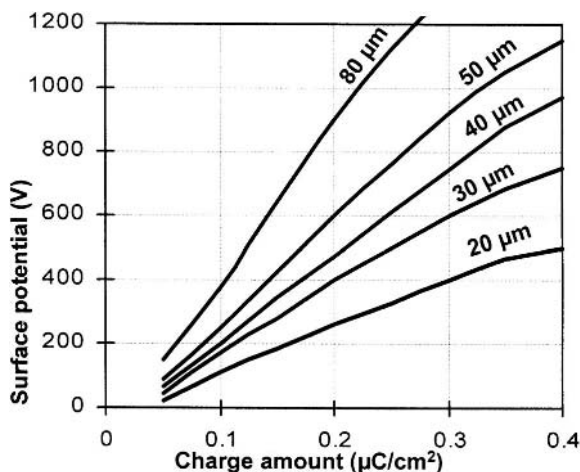


Figure 11.10 Charge acceptance of a-Si drums as a function of layer thickness.

(CH₄) added at the end as a source of carbon for the a-SiC:H surface layer. The drum substrate is heated to the range of 250 to 300°C.

The drum substrate typically is grounded and capacitively coupled to the counter-electrode, with plasma generated between the drum and the counterelectrode at radio frequencies. 13.56 MHz is mentioned by Ikeda et al. (1992), Lutz et al. (1996), Stahr et al. (1997), and Sasahara et al. (1998). 27.12 MHz is also mentioned by Lutz et al. (1996) and Stahr et al. (1997).

Increasing the speed of the a-Si deposition rate was the subject of research by several teams. Röhlecke et al. (1997) reported deposition rates of up to 18 $\mu\text{m}/\text{h}$ by using helium to dilute the SiH₄. Takahashi et al. (1989) reported deposition rates of approximately 17 $\mu\text{m}/\text{h}$ by using argon to dilute the SiH₄. Lutz et al. (1996) reported “With the optimizing of helium dilution, TEB doping and increasing of RF frequency the properties of photoreceptor are quite respectable with deposition rates in the range from 10 up to 15 $\mu\text{m}/\text{h}$.” On the other hand, decreasing the deposition rate to 2 $\mu\text{m}/\text{h}$ with helium dilution (Ikeda et al., 1992) or to 2.5 $\mu\text{m}/\text{h}$ with H₂ (Sasahara et al., 1998) achieves a high-sensitivity charge generation layer.

When boron impurity doping is necessary, diborane (B₂H₆) is typically used, although Lutz et al. (1996) report that triethylboron (TEB) is effective and safer. Phosphine (PH₃) is typically used when phosphorous doping is required (Ikeda et al., 1998).

11.11 a-Si DRUM COSTS

a-Si is more costly than OPC because of the slow deposition rate. Manufacturers do not disclose production costs, but Ikeda (1998b) showed relative costs of a Kyocera a-Si drum from 1992 to 1998. Costs declined about 80% over these 6 years.

The longer life of an a-Si drum should mean a lower total cost of ownership, which, divided by page volume, should yield a lower cost per page. Lyra Research (1999) added up street prices of laser printers, consumables, and maintenance, comparing the printer using a-Si in each category against competitors using OPC. For the 16–18 page per minute category over 5 years, the cost per page for a-Si was 1.2 cents compared to 1.9 and 2.1

cents for OPC. For the 24–28 page per minute category over 5 years, the cost per page was 1.2 cents compared to 1.8 cents for the three OPC competitors, thus proving that use of a nonconsumable a-Si drum reduces the total costs by 33% at these print volumes.

11.12 SUMMARY

The benefits of a-Si photoreceptor drums are

- Long life
- Fast photoresponse
- No electrical fatigue
- Material safety

Available variations include

- Visible light or near-infrared exposure
- Positive or negative charging
- High or standard charge acceptance
- High or standard sensitivity

Their natural applications are high-speed or high-volume laser or LED print engines and office laser or LED printers where cost per page or reduction of consumables are important.

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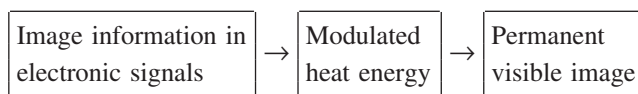
Thermal Imaging Materials

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12.1 INTRODUCTION

Thermal printing is a direct printing process in which image information in electronic signals is converted to image modulated heat energy, which produces a printed image by either chemical or physical means, or by a combination of both.



Unlike photography, which has been perfected over the years while maintaining the underlying silver halide chemistry, thermal imaging has evolved through a variety of chemical and physical processes and encompasses different printing as well as image forming mechanisms.

Thermal printing processes are characterized in terms of the chemical and physical mechanisms that form the image; direct printing and transfer printing. In direct printing, the image is formed directly in the print media. Transfer printing employs a donor ribbon that contains the colorant, which is transferred to the print medium during printing. The two thermal printing processes are generally referred to as “direct thermal printing” and “thermal transfer printing,” and this terminology will be used throughout this chapter.

The objective of this chapter is to familiarize the reader with the chemical and physical processes involved in forming the image and the media required for printing. A review of thermal media necessarily needs to consider the printer in which they are used. Media and printer constitute a complex imaging system that is carefully matched. The material presented here is a compilation of data and information published in the scientific, technical, and patent literature.

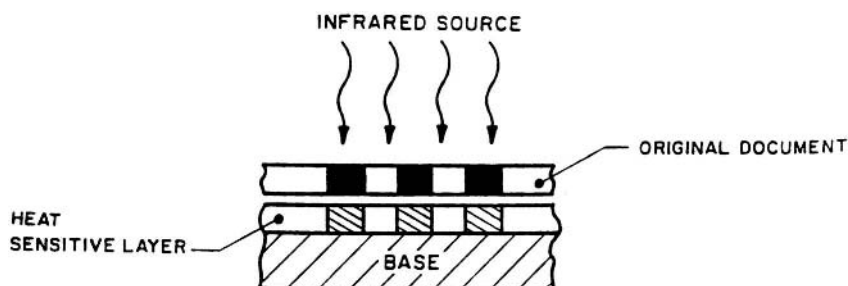


Figure 12.1 ThermoFax paper of the 1950s by 3M. (From Diamond, 1989.)

12.2 EARLY THERMAL PRINTING PROCESSES

Benjamin Franklin was probably the first person to use thermal energy to make an image. In 1759 he placed a number of square pieces of various color cloths on snow in bright sunshine. After a few hours he observed that the cloths had sunk into the snow to varying degrees, with darker cloths having sunk the deepest (Burlingame, 1967).

It took 200 years before the process of light-to-heat conversion, observed by Benjamin Franklin, was commercially utilized for printing. In the 1950s, 3M introduced ThermoFax, a document copying process the inventor had named Thermography (Harriman, 1978), the printing through a chemical reaction induced by heat. Hard copies are generated by an infrared source that causes differential heating in the original placed on top of a heat sensitive paper (Fig. 12.1). As a result, the thermal energy pattern is converted to a visible image in a heat sensitive layer, containing organometallic salts and reducing agents dispersed in a binder matrix. Heat causes reduction of the light colored salts to their dark, metallic state (Miller, 1956).

Earlier thermographic processes employed physical changes to create a visible image. Electrocardiograph chart printers, introduced in the 1930s (Fig. 12.2), used a heated metal stylus to create a line trace when moved over a coating of a white, waxy layer applied over a dark paper or interlayer. The white layer becomes transparent when heated, exposing the dark color underneath. The patent literature is replete with such blushed or obscuring layers that can be made transparent by heat fusing (Gold, 1964). These papers were pressure sensitive, gave poor definition, and were replaced by chemical thermographic papers. Upon heating chemical type papers above the conversion temperature, an irreversible chemical reaction takes place, and a colored component is produced (Jacobsen et al. 1976).

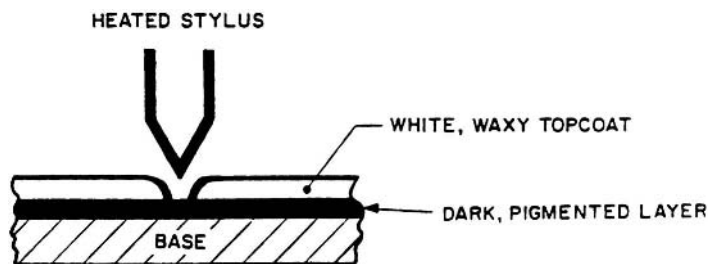


Figure 12.2 Electrocardiograph chart paper of the 1930s. (From Diamond, 1989.)

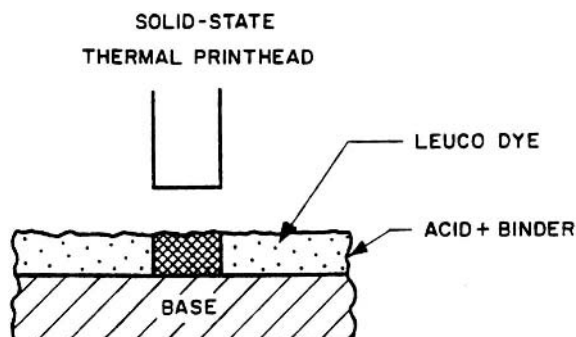


Figure 12.3 Thermal printer with electronically addressable printhead and direct thermal paper introduced by NCR in the 1960s. (From Diamond, 1989.)

In the 1960s, NCR introduced direct thermal print papers with a heat sensitive coating consisting of a “colorless” dye precursor and phenolic acid in a binder matrix (Talvalkar, 1969). When heated, the two colorless components react to form the colored leuco dye. The printer used a solid-state, electronically addressable printhead (Schroeder, 1964). Printer and media configuration are shown in Fig. 12.3. These initial coatings had low thermal sensitivity, and the rough paper surface adversely affected print quality. Over the years, the process has been steadily improved, and today leuco dye chemistry remains the technology of choice for direct thermal printing.

The printhead developed by Schroeder was also incorporated in a thermal transfer printer, called a thermal teleprinter, by Joyce of NCR and Homa of the U.S. Army (Joyce and Homa, 1967). The printer used a donor ribbon coated with a colored material that became tacky when heated, and the image could be transferred several times to plain paper under pressure (Chang, 1995). These NCR developments marked the beginning of thermal printing as we know it today.

12.3 THE THERMAL PRINTER

12.3.1 Thermal Printheads

The thermal printhead is the core of the thermal printing system. It consists of a fixed array of microscopic heating elements. When electrical energy is applied to the resistor elements, heat is generated in the area under the elements. The thermal printhead is in continuous contact with the thermosensitive recording material, moving against it under substantial pressure, while being subjected to the heating and cooling cycle thousands of times per minute. The most common thermal heads employed today are the thick film type and the thin film type. Thick film products were introduced by Hewlett Packard, NCR, and other major manufacturers in the early 1970s, followed by thin film heads later in the decade.

Figure 12.4 shows the structural differences between the two types of printheads. The fabrication process entails depositing successive layers under carefully controlled conditions. Thin film resistor layers are coated using vacuum deposition or sputtering for the resistor material, such as Ta_2N , resulting in extremely thin films measuring only 0.05–0.5 microns. Photolithography and microetching are used to form the individual resistive

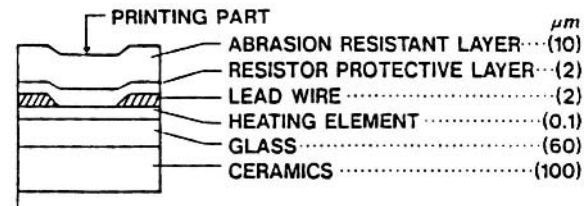
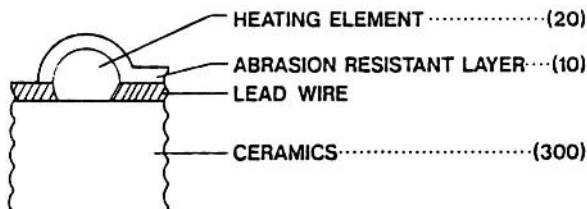
THIN FILM TYPE**THICK FILM TYPE**

Figure 12.4 Structural differences between thick film and thin film printheads. (From Sodeyama, 1986.)

elements and to provide isolation between adjacent print elements. The thick film type resistors are screen coated with a paste of ruthenium oxide and sintered at high temperature, with film thicknesses ranging from 20 to 40 microns. Each resistor is a separate area. One side of the circuit is a common conductor touching all resistors, and the other side is made of individual conductors touching individual resistor elements.

The next issue is the location of the line of individual resistors, on the flat side of the head or close to or on the edge of the head. With resistors located on the flat side of the head, the print medium has to pass over a round platen. This led, in the early 1990s, to the introduction of edge or near edge type printheads that can use round or flat platens. Flat platens allow printing on rigid media and the design of smaller and more compact printers.

The printhead is made up of the individual resistor elements, numbering from a few to several thousands. The size of the heating elements varies from about 100 to 350 microns with spacing ranging from about 2.5 elements/mm for low-density up to 24 elements/mm (600 dpi) for high-density print heads. The element density is the most important factor determining the resolution of the printed image. Fig. 12.5 shows thermal head types in terms of the arrangement of the heating elements. The matrix type arrangement, popular initially, has largely been replaced with lower cost vertical serial printers, with the head moving across the print medium. Horizontal line heads are made in the width they will print, and only the paper moves, while the head remains in a fixed position. As a result, the printing unit is more reliable and easier to maintain.

Printing with resistive thermal heads is inherently a wasteful process. Much energy is lost in heating parts of the thermal head that are not used for printing. Designing heads with better thermal insulation has limitations, because individual heater elements have to cool down between each printing cycle to prevent printing without signal. The cooling time, much longer than the heating response, is the limiting factor on pulse repetition rate. Higher speeds can be achieved with "historical" correction. Because the initial temperature of each heating element varies with its heat history, electronic compensation methods are

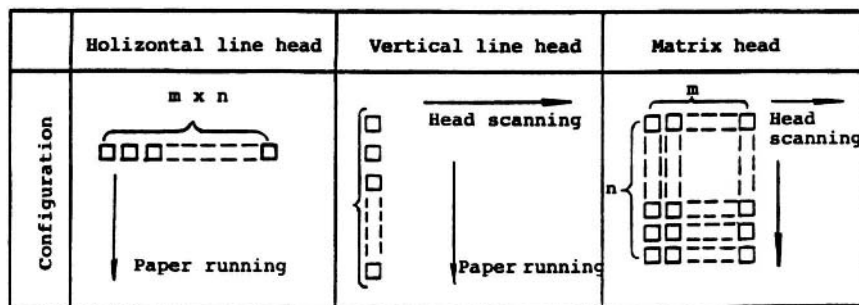


Figure 12.5 Dot element arrangement in thermal printheads: horizontal, vertical, and matrix, showing printhead scanning versus paper travel.

used to control the energy pulse duration based on the pulse history of that element. A similar technique may be needed to correct for the influence of adjacent data in the array.

Poorer thermal insulation between dots and greater thermal gradients within dot elements are found in thick film elements, resulting in greater dot bleed effects. The advantages of thick film heads are lower cost, higher heat transfer efficiency, and better abrasion resistance. This makes them suitable for operation in harsh industrial applications and cost sensitive designs such as fax machines and point of sales printers. The higher energy dissipation allows the use of low-sensitivity media.

In thin film heads, the low mass dot elements and good thermal insulation across the print head axis minimize dot bleed effects, yield inherently sharp and crisp individual dot images, and result in much shorter response time, the critical determinant of print speed. Thin film heads are capable of higher resolution [which has reached 600 dpi (Namiki, 1997)] and control of thermal uniformity and repeatability within one percent of temperature. This makes them better suited for grey scale and continuous tone printing.

12.3.2 The Thermal Printing Process

One of the outstanding features of the thermal printing process is its reliability. There are few moving parts that can break down. Thermal head life is usually measured in terms of thermal shock and kilometers of substrate travelled. In case of thermal shock, each element is subjected to a thermal rise from 25°C up to 425°C over approximately two ms (Srivastava, 1989). This is a very severe temperature change over a short time frame. Thick film heads are rated for 70–100 million and thin film heads for 30–50 million thermal pulses. After that, resistance of the element may change, which can result in deterioration of image quality. Printing a full page of text requires each element to be cycled approximately 66 times. In actual applications, thermal failure is extremely rare and is seldom catastrophic. From an abrasion standpoint, a thick film printhead is capable of imaging 75 to 100 km of paper under normal operating environments. This translates to about 225,000 to 300,000 prints or approximately 240 prints per day every working day for 5 years.

Thermal printing provides several unequalled combinations of print quality, speed, simplicity, reliability, and low cost. In bar codes and other labeling applications, no other technology can match the image sharpness of thermal printing anywhere near the price. The simplicity and reliability of the thermal printing process is a major reason it has found widespread applications where this is paramount, in fax machines that need to be operational on demand, unattended for 24 hours and 7 days a week, and in point of sales receipt and airline ticket printing and similar situations where failure would be highly disruptive.

12.4 DIRECT THERMAL PRINTING

Thermal printing on heat sensitive paper, or direct thermal printing, is the simplest printing technology today. The thermal printhead rests directly on the print paper. Electronic signals are converted to electric pulses and, through a driver circuit, selectively transferred to the heating elements of the printhead. The print paper carries a heat sensitive layer containing colorless components that react and form a colored dye at elevated temperatures. No waste is generated in the process. Because most of the technology is in the paper, rather than the printer, it is possible to build very low cost, compact, reliable printers that consist of little more than the thermal print head and rollers to feed the paper. Most of the world is now quite familiar with thermal printing because the technology is widely used in facsimile machines.

12.4.1 Direct Thermal Printing Systems

Leuco dye chemistry, developed and commercialized by NCR in the 1960s, has much improved over the years and is still the dominant direct thermal printing technology today. Other methods were largely replaced by leuco dye systems with superior stability, response, and contrast retention, or confined to specialized niche markets.

Diazo dye chemistry has been adapted to direct thermal printing. Diazo dyes are formed through the reaction of a diazonium salt compound and coupler in the presence of a sensitizer and base. Because of the high cost of the paper and large size of the printer, diazo based papers have not become widely accepted for facsimile printing, but they have found applications in medical diagnostic and scientific recording, and more recently for color printing.

12.4.2 Leuco Dye Direct Thermal Print Papers

Leuco dye based direct thermal papers are the current workhorse in commercial use. The heat sensitive coating consists of a number of active ingredients (Fig. 12.6). The color forming components are colorless leuco dye precursors of the triphenylmethane and fluorane type containing lactone rings and phenolic acid developers. Another critical ingredient in the color forming reaction is the sensitizer, a solid material that typically melts at a low temperature ($<100^{\circ}\text{C}$). It acts as a solvent for the dye precursor and developer, forming a eutectic mixture during printing. Color develops by the phenolic acid contributing a proton that attacks the lactone ring of the dye precursor. This brings about a new compound in which a quinoidal resonance in the dye cation is responsible for the appearance of color. Depending on the nature of the leuco dye, various colors can be obtained, but in practice black is predominant. For bar code printing, leuco dyes that absorb in the near IR and can be read with LED and LD light sources have been developed (Higaki, 1990).

The color forming process is reversible, and antioxidants added to the coating, which act as stabilizers, move the equilibrium point of the color reaction toward the colored species (Goodwin, 1993). Other stabilizers include Novolak type epoxy compounds that react with the leuco dye (Watanabe et al., 1993), nonphenolic developer compounds containing sulfonylurea functional groups (Takahashi et al., 1994), and UV absorbing polyurethane/polyurea fillers (Mandoh et al., 1993). The stability of the printed image is affected by PVC plasticizers, marking pens, hand lotions, and a variety of chemicals. Microencapsulation of the dye precursor and salicylic acid developers increase resistance of the image to chemical attack (Miyamoto, 1991).

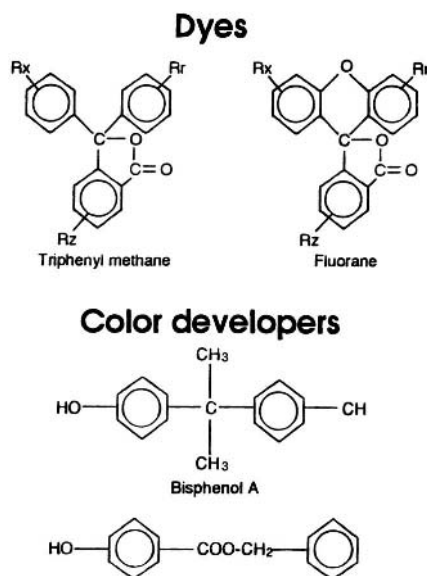


Figure 12.6 Dye precursors and phenolic acid developers for leuco dye direct thermal printing. (Courtesy of Diamond Research Corporation, Ojai, California.)

While the chemicals participating in the color reaction are vital, other components are critical to the function and performance of thermal papers. Coating binders commonly used are high molecular weight water soluble or dispersible polymers, such as polyvinyl alcohol, polyvinyl acetate, and modified cellulose and starch derivatives. The binder should exhibit high pigment tolerance and adhere firmly to the paper. It must resist attack from oil, fat, and alcohol and should not resolubilize easily when wetted with water. Pigments and lubricants, such as zinc stearate, act as release and slip agents that prevent sticking of the paper to the printhead. Waxes added to the coating increase thermal sensitivity and cause the image to flow together so that more uniform print characters are formed. Antistatic agents help dissipate electrical charges that can be created as the paper feeds through the printer.

In addition to the active, color forming layer, other coating types are applied to direct thermal media that change its functionality. The base coat, applied directly on the base sheet, contains clay and binders and produces a level surface on which the active layer is coated. This facilitates good contact between paper and thermal head, assuring uniform image formation. It increases opacity and brightness of the sheet and acts as absorber for excess chemicals that may contaminate the printhead. Effective heat energy transfer to the color forming layer can be increased by introducing voids or air capsules into the base layer. This increases the thermal insulating properties, minimizes heat loss into the paper, and thereby increases thermal sensitivity (Lewis et al., 1992; Motosugi et al., 1992).

A third coating type used in direct thermal papers is the top coat. The top coating, primarily used for tags and labels, contains binders, clays, and lubricants, can impart pencil writability and erasability (Hara, 1991), and acts as a seal and protective coat for the heat sensitive layer. The final coating used in thermal papers is the back wet or the back coat. Its primary function is curl control and the imparting of antistatic properties. Only rarely are all of these coatings used on one sheet, but different coatings are combined to meet

the requirements for specific applications. Thermal papers for pressure sensitive labels receive an adhesive back coating that is covered with a releasable liner (Arbree et al., 1986). More recently, special thermal printers were introduced that print on liner free thermal media. These self-wound, linerless media have the silicone release coating applied over the active thermal or top coating.

The performance of thermal papers has improved considerably over the years. Maximum density is affected not only by the composition and level but also by the particle size of the active ingredients (Usami, 1990). Increased sensitivity has resulted in higher printing speeds and reduced power consumption and load on the thermal head. Examples of papers exhibiting increasing thermal sensitivity are shown in Fig. 12.7.

Early calculator chart papers of the 1970s required heating levels that approached the combustion point of the paper. In today's facsimile sheets, heat from friction, generated by a fingernail scored across the surface, is sufficient to develop the color. Many parameters had to be optimized to bring about this improvement. High smoothness of the paper base, low eutectic temperature and viscosity combined with high dissolving power of the sensitizer, fine particle size of dye precursor and developer, as well as minimizing heat loss to the paper, all act to increase sensitivity. However, there are trade-offs. The increased sensitivity reduces shelf life and renders the product less environmentally stable. The high smoothness of the paper gives it an artificial appearance, quite unlike bond type office papers, a major reason direct thermal papers have not been accepted for correspondence quality printing.

The technology is capable of continuous tone reproduction with either density or area based gradation printing. Intimate contact between medium and thermal head is crucial. Smooth synthetic substrates such as polyester films and synthetic papers and paper laminates, which do not absorb moisture, rather than paper, are used as support. A dynamic tonal range of 64 grey levels with optical densities of up to 1.8 can be obtained.

12.4.3 Transparent Direct Thermal Print Media

Transparent thermal media are faced with the fact that leuco dye coatings, with dye precursor and developer dispersed in powder form in the binder matrix, represent a two-phase

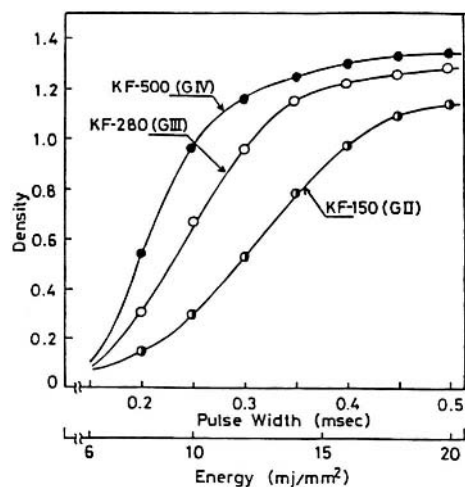


Figure 12.7 Dynamic sensitivity of typical direct thermal papers, sensitivity improved 15–30% each from GII to GIII and GIV. (From Higaki, 1990.)

system with different refractive indices. The coating layer also contains entrapped air, and the resulting light scattering renders the coating opaque.

This was overcome by first dissolving the developer in an organic solvent and emulsifying it in an aqueous solution of a water soluble polymer. The dye precursor, dissolved in oil and encapsulated in a heat sensitive microcapsule to prevent premature color development, is then dispersed in the pseudocontinuous developer phase. By making the refractive indices of the various components nearly equal, the coating can be made transparent (Usami et al., 1989). Maximum optical densities above 2.0 can be achieved, making the process suitable for medical recording (Ohga et al., 1991).

12.4.4 Diazo Dye Direct Thermal Print Media

The reaction mechanism for diazo dye thermal printing is similar to printing with leuco dye chemistry. Two colorless components, a diazonium salt compound and a coupler, react when heated in the presence of a sensitizer and an organic base, to form a colored diazo dye. To prevent color formation at room temperature, the diazonium salt is encapsulated in a heat sensitive microcapsule. The diazonium salt in the unprinted areas can be decomposed through ultraviolet radiation after printing. The dye formation and decomposition reactions are shown in Fig. 12.8.

Decomposition of the unreacted diazonium salt after printing results in a paper that is no longer heat sensitive and adds options for color printing to the process, not available with leuco dye chemistry.

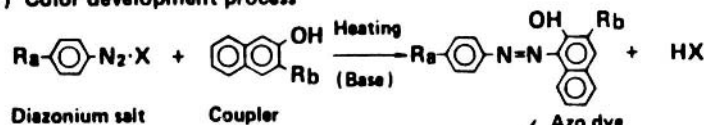
12.4.5 Direct Thermal Color Print Media

Two different approaches have been developed for two-color printing with leuco dye chemistry; color addition and decolorization. Both use two separate color forming layers with different thermal sensitivities, an upper layer with color development taking place at lower temperature and a lower layer with color formed at higher temperature (Watanabe et al., 1993).

In both systems the upper color forming layer is first printed at a lower temperature. In the additive system a second printing at higher temperature produces color in both layers, with the two overlaid colors yielding a third color, i.e., red and green resulting in

UV-Fixable Thermal Recording Paper

(1) Color development process



(2) Fixing process

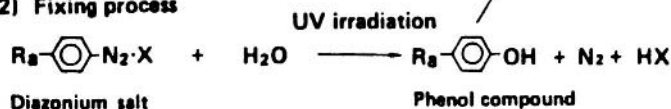


Figure 12.8 Components of UV-fixable, diazo dye direct thermal imaging systems. (From Sato et al., 1985. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

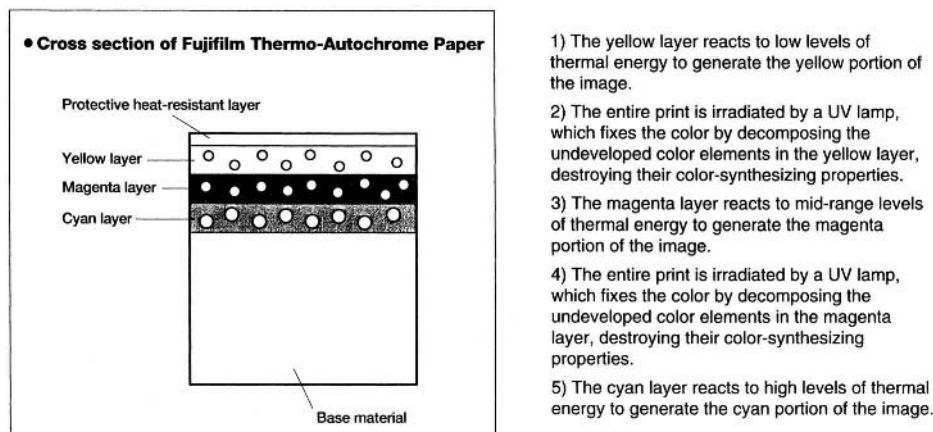


Figure 12.9 Printing and fixing sequence of Fujifilm's Thermo-Autochrome Color Printing System. (Courtesy of Fuji Photo Film Co., Ltd.)

black. A different approach is used for decolorization media where an erasing layer is placed between the two color forming layers. The second printing at the higher temperature develops color in both layers, with the erasing layer at the same time destroying the dye formed in the upper layer, exposing the color in the layer underneath.

Diazo dye chemistry offers another option for color printing through the possibility of decomposing the diazonium compound with UV exposure. For two-color printing the thermosensitive layer contains a mixture of diazonium salts capable of forming green or red diazo dyes. A first thermal printing causes development of both colors, resulting in a black image. The green diazonium salt in the unprinted areas is then selectively decomposed through UV exposure of a certain wavelength. In a second printing step, the red colored image is recorded (Usami, 1990). The same result can be obtained with selected mixtures of cyan, magenta and yellow diazonium salts (Koyano et al., 1997).

Using a combination of diazo and leuco dye chemistry, Fuji Photo & Film Co. has developed a three-color, continuous tone direct thermal printing process. The system, called ThermoAutochrome, was introduced to the market in 1994. Figure 12.9 is a simplified cross section of the print paper structure. The yellow and magenta color forming layers contain diazonium salts and couplers and the bottom cyan layer a conventional leuco dye system. The diazonium salts and leuco dye precursor are encapsulated in microcapsules (Igarashi et al., 1994). Figure 12.10 shows the dynamic color forming response of each layer with reflective optical density plotted against recording energy. The three color layers are printed sequentially at increasing temperatures, and after each printing, the diazonium salt compounds in the yellow and magenta layers are selectively decomposed through UV exposure at wavelengths of 425 nm and 365 nm, respectively. Only the unprinted areas of the cyan layer are not "fixed" and remain heat sensitive after printing.

Encapsulation combined with UV fixing renders the image quite stable, but background density is likely to increase with exposure to light. While image stability of earlier products has been improved, additional work needs to be done (Sakai et al., 1999). A microscopic cross section of the ThermoAutochrome paper is shown in Fig. 12.11. The support is a microporous polyester coated with a TiO_2 filled polyethylene layer on the face side and a clear polyethylene layer on the back. The three color layers are protected by a heat resistant overcoat.

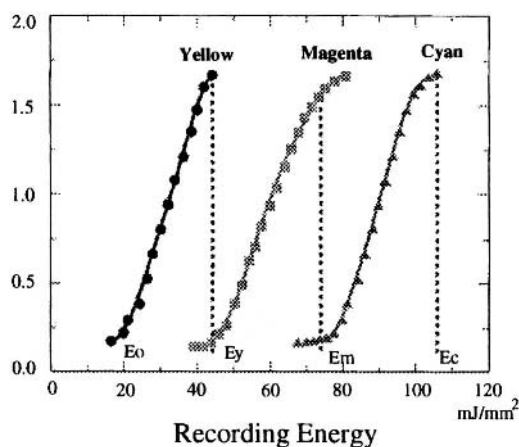


Figure 12.10 Thermal recording characteristics of ThermoAutochrome Color Printing System. Optical density as a function of recording energy. (From Sato et al., 1994. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

The system is aimed at the photographic, video printing, scientific, and medical recording markets. Printers are offered in resolutions of 150 dpi with 128 grey levels and 300 dpi and 254 grey levels. Quality is claimed to be comparable to thermal dye transfer printing, to which it offers an alternative that requires only a single consumable and does not generate waste.

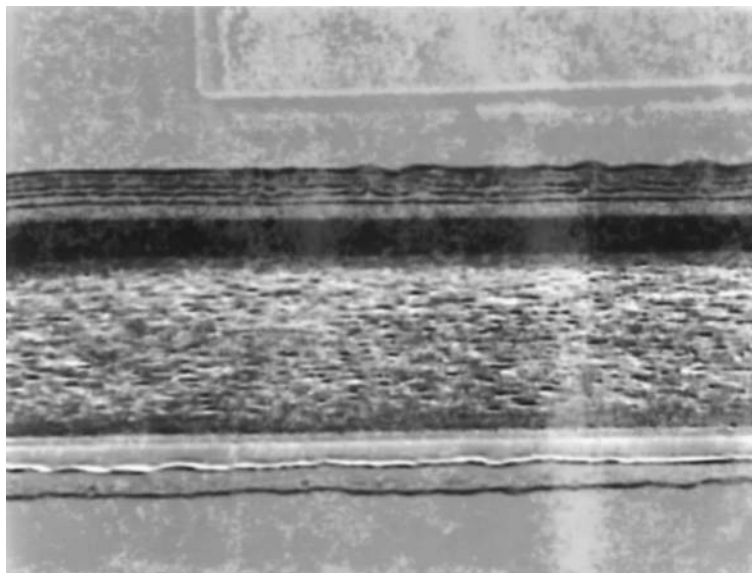


Figure 12.11 Microscopic cross section of Thermo-Autochrome Print Paper. From top: heat resistant layer; yellow, magenta and cyan color forming layers; pigmented polyethylene layer; micro-voided polyester support; clear polyethylene layer; back coat. Total caliper 241 microns. (Courtesy of Felix Schoeller Technical Papers, Inc., Pulaski, New York.)

12.4.6 Future Outlook for Direct Thermal Printing

The ThermoAutochrome System is an impressive example of the technical potential of direct thermal printing and it shows that a technology considered mature can still produce new and unexpected results. For the largest application of direct thermal printing, facsimile, prospects do not look bright. The main reasons are (1) the overall decrease in fax traffic as users switch to e-mail or PC-based fax software and (2) the preference for plain paper fax machines which have become more competitively priced. For industrial, medical, retail, and point-of-sales printing, where media sensitivity is not acute and simplicity, reliable performance, and cost are primary concerns, direct thermal printing is well positioned. Another sector is the dominant output method on ships and aircraft for printing information from satellites, radar, and sonar.

12.5 THERMAL TRANSFER PRINTING

Thermal transfer printing uses modulated thermal energy to transfer a colorant from a donor ribbon to a receiver substrate. The process is the closest nonimpact analog to impact printing with dot matrix printers or typewriters. The ribbon, coated with the colorant material, releases and transfers the colorant to a receiver when heat is applied. Transfer can occur by two different physical processes, depending on the formulation of the ink layer. The image formation mechanisms for the two processes are sufficiently different, and they are treated as separate printing systems in the technical and commercial literature. There is no generally accepted terminology for these two printing processes, and in this chapter the terms thermal mass transfer and thermal dye transfer printing will be used, as they best describe the physical processes involved in forming the image.

Thermal energy sources are most commonly thermal printheads, similar or identical to those used for direct thermal printing, but systems using focused laser beams have recently been introduced. The first thermal transfer printer, developed by NCR for the U.S. Army in the 1960s, was not suitable for commercial use. Thermal transfer products, developed by several Japanese companies, were introduced to the U.S. market in the early 1980s. By 1982, Fuji Kagakushi Kogyo marketed a wide range of color thermal transfer ribbons, and in 1985, 19 thermal transfer printer manufacturers offered a total of 37 printers, 26 of which were color printers. The first laser induced thermal dye transfer product from Kodak made its debut in 1991. An important thermal transfer product was IBM's Quietwriter, which used a resistive, self-heating ribbon instead of a thermal head. The product, introduced in 1984, was withdrawn from the market in 1991 because of unacceptably high consumables cost.

12.6 THERMAL MASS TRANSFER PRINTING

Figure 12.12 is a schematic of a thermal mass transfer printer. The printhead rests directly on the donor ribbon, which is held in close contact with the receiver substrate against a platen. Ribbon and receiver media are passed under the printhead simultaneously. In most printers, the paper and ribbon travel through the print mechanism at the same rate, so the cost per print is constant, independent of the area of ink coverage. This is particularly acute for color printing, which requires three or four separate color panels to produce one print. Some monochrome printers for label applications implement ribbon saving, stopping the motion of the ribbon when blank areas of the print are passing through, and taking the pressure off the head to avoid friction between donor ribbon and receiver.

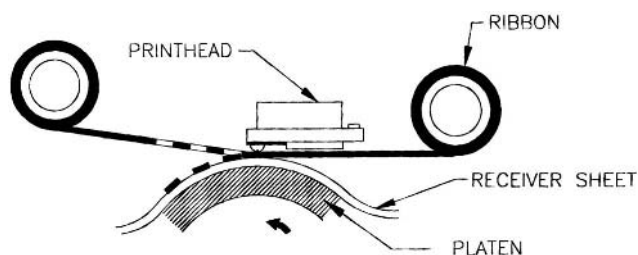


Figure 12.12 Schematic of thermal mass transfer printer. (Courtesy of Atlantek Inc., Wakefield, Rhode Island.)

For color printing, the different color layers on the donor ribbon are coated either in parallel stripes or in sequential patches. The parallel coating of ink is used for serial printers, and the colors are transferred in the printer in units of the various colors before the paper is moved to the next line. For horizontal line printers, the colors are coated in sequential patches on the ribbon. The first color is printed line by line on the whole page; the paper is then returned and the next color printed until all colors have been applied to the image.

The ink layer, coated on a support material, is formulated so that the colorant adheres firmly at room temperature but is transferred to the receiver when thermal energy is applied to the donor. The ink consists of a complex mixture of coloring pigment and binder, which melts at a certain temperature. When the ink layer reaches the melting point, the ink is transferred in a coherent mass to the receiver, hence the term mass transfer. Initially, transfer takes place through a combination of pressure and surface tack to the receiver. Once the entire thickness of the ink layer exceeds the melting point, transfer to a paper surface is aided by the capillary action of the paper fibers. Since the heating elements contact the side of the donor ribbon opposite the ink layer, heat transfer is less efficient compared to direct thermal printing, where the heat sensitive layer is in direct contact with the thermal head.

12.6.1 Thermal Mass Transfer Donor Ribbons

The two main components of the thermal transfer ribbon are the base film and the ink layer. In actual practice, thermal transfer print ribbons consist of several layers coated on a 2.5–6 micron thick polyester film, although condenser tissue paper and cellophane films have been considered (Anczurowski et al., 1987). The ink layer is usually applied over a release layer to assure complete transfer of the ink during printing. The side opposite the ink layer is coated with a heat resistant back layer, which provides release of the ribbon from the printhead and reduces head wear. The back layer may incorporate antistatic or conductive properties. Over/under ink coatings are used to impart special features such as antigloss, correctable print, or security.

The most common material used as binder is wax, and the process is frequently referred to as thermal wax transfer printing. Wax comes in a variety of mixtures of vegetable and mineral waxes from carnauba to paraffin. Resin and wax/resin mixtures are also popular. They are more expensive but provide a harder surface that is resistant to abrasion and scratching. In general, there is an inverse relationship between durability and cost and durability and energy required for printing. Wax is easy to scratch but melts readily for printing. Resin is tough but requires higher printing temperatures and is more expensive, with wax/resin ribbons falling somewhere in between. Wax is printed on a variety

Table 12.1 Thermal Mass Transfer Ink Compositions

	Standard (%)	Midrange (%)	Premium (%)
Wax	65–85	50–70	5–20
Pigments	5–20	5–20	5–20
Resin	5–15	10–25	50–80

Source: From Giga Information Group, Norwell, MA (1995).

of substrates, while resin ribbons are most suitable for printing on synthetic substrates. Reactive ribbons are a variant of resin ribbons, where the resin contains reactive groups attached to the polymer chain that cross-link during printing. The cross-linked polymer no longer melts and is insoluble in most solvents. Wax ribbons contain some resin to provide adhesion to the substrate and resin ribbons some wax to improve slip. Typical formulations are shown in Table 12.1.

Wax ribbons are also called standard ribbons and midrange ribbons wax/resin ribbons. Premium ribbons have a variety of names including 3rd generation, pure resin, and solvent resin.

For a complete transfer of the ink during printing, the ink should have a defined melting point with a sharp drop in viscosity. Melting points are not relevant for resins that go through a glass transition with a more or less broadly defined peak. Differential scanning calorimetry (DSC), in which the amount of power needed to cause a fixed rate of increase in temperature is plotted against temperature, is a convenient way of defining the thermal response of resinous materials. The DSC of a standard wax ribbon is shown in Fig. 12.13. It has a fairly well defined peak, a desirable feature for bimodal printing, as all the ink is transferred almost at once. For variable dot transfer a much broader peak is preferred, so that the amount of ink transferred can be controlled by varying the amount of energy supplied.

The other main component of the ink layer is the coloring component. Organic

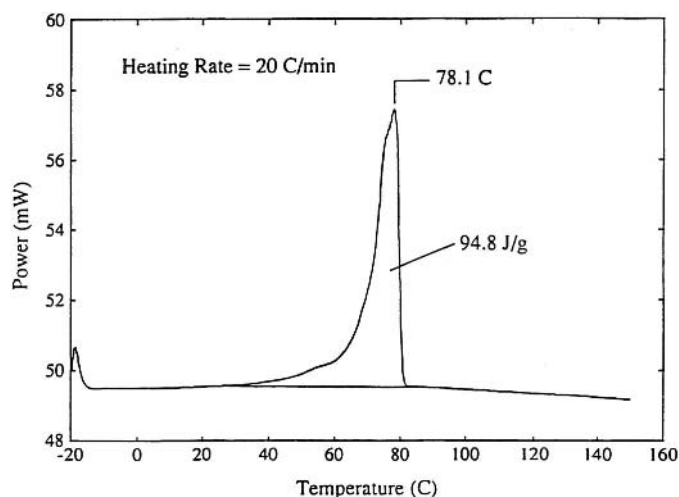
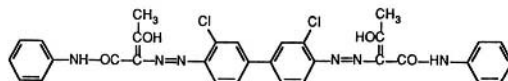
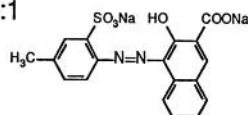


Figure 12.13 DSC of thermal wax transfer ink formulation. (From Giga Information Group, 1995. Contact Sara Martin, Giga Information Group, One Longwater Circle, Norwell, MA 02061, 1-800-874-9980 or 617-982-9500, fax 617-878-6650.)

C. I. Pigment Yellow 12



C. I. Pigment Red 57:1



C. I. Pigment Blue 15

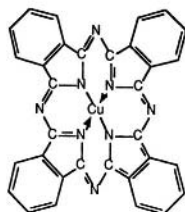


Figure 12.14 Coloring pigments for thermal wax transfer inks. (From Seto et al., 1988. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

pigment dyes are used for colored inks, and examples of pigments used are given in Fig. 12.14. Magnetic inks that contain magnetic components, such as iron oxide, are an important element in thermal transfer printing for MICR encoding (Talvalkar, 1992). Pigment dyes are considerably more environmentally stable than leuco dyes used for direct thermal printing, and black prints with carbon pigment are as stable as the paper support. One drawback is that smear, especially for wax based ribbons, remains a problem particularly at elevated temperatures.

To reduce ribbon costs, multipass thermal ribbons are offered that carry a number of ink layers separated by release layers. They are formulated so that one layer of ink will transfer to the receiver every time a dot is printed. The ribbons, mounted on reversible cartridges, are turned around for the next printing cycle and are conservatively rated at six printing cycles. Another approach uses a heavier ink layer and advances the ribbon at a slower speed than the print medium. The image printed is about four times longer than the ribbon and only a portion of the ink is transferred at each printing step (Giga, 1995).

A multiprinting thermal transfer ribbon, described by Maehashi et al. (1990), employs a single layer that consists of two nonmiscible components: a “supercooling” material and a thermoplastic ink. The two materials have different melting points and solidifying temperatures. At the multiprinting state, the supercooling material is still liquid, while the ink has solidified. Ink is transferred in incremental steps, with separation occurring in the liquid phase. This stage lasts long enough to allow sufficient peel time for most printers.

12.6.2 Thermal Mass Transfer Receiver Papers

In principle, printing should be possible on any medium to which the ink will adhere. In practice, the efficiency of the transfer depends on a combination of heat transfer conditions and the actual surface area contact in the printing nip. When printing is done on the same printer, the physical and mechanical properties of the medium predominantly influence the quality of the transferred image. Incomplete contact between donor and receiver in the printing nip results in print defects through dot fragmentation, density variations, and places with

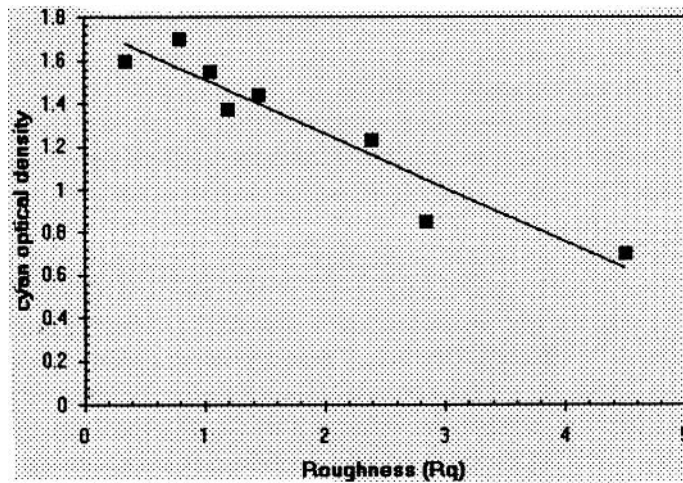


Figure 12.15 Cyan optical density as a function of surface roughness. (From Katsen et al., 1995. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

no transfer at all. The surface topography of the paper is a major contributing factor (Katsen et al., 1995). In Fig. 12.15 surface roughness is plotted against optical print density, with smooth papers resulting in greatly increased optical density. Other factors are nip pressure, with higher pressure increasing contact area, and paper compressibility, which correlates with optical density (Fig. 12.16). High compressibility of the paper has the added benefit of compensating for nonuniformities in the pressure profile of the printing nip.

For effective transfer, it is important that the surface energy of the receiver be high enough to provide good wetting by the ink (>35 dyn/cm). Transfer of the ink begins at its

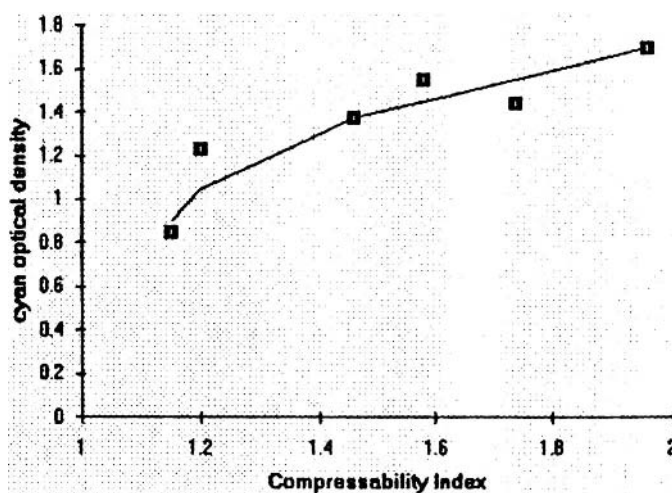


Figure 12.16 Cyan optical density as a function of media compressibility. (From Katsen, 1995. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

glass transition temperature and peaks at its melting point. For optimum transfer, the cohesive force of the ink, the release of the ink from the carrier ribbon, and the surface tension between molten ink and medium surface need to be carefully balanced (Akutsu et al., 1992). This is no different from normal impact printing. In thermal transfer printing, the process is complicated by the rapid change in viscosity of the ink during cooling. Timing and geometry of separating the donor ribbon from the receiver is critical for obtaining good print quality. Sensitometric characterization of thermal mass transfer ribbons has been described by Swift et al. (1992) and methods for the evaluation of receivers by Spivak et al. (1992).

Many coated and machine finished papers are suitable for thermal mass transfer printing, but the requirement for a smooth paper is a drawback for office printing applications. The usual bond type office papers are not well suited, and users prefer the flexibility, familiarity, and “feel” of so-called plain paper. Improvements are achieved by optimizing printing pressure, timing, temperature, and print head design (OEP, 1992), but higher quality laser papers are still required. According to a study from Matsushita (Yoshikawa et al., 1993), high-quality printing is possible on any type of paper by first printing on an intermediate transfer roller and then by transfer to paper. Tektronix and its Japanese partners have taken a different approach and added an extra panel of a clear adhesivelike layer called ColorCoat to the three-color ribbon. Prior to printing the image, the ColorCoat is laid down on the paper in the areas where the image will be printed (Brandt et al., 1996). While this does not result in complete paper independence, printing is possible on a wider range of office papers, including copy papers.

12.6.3 Transparent Thermal Mass Transfer Media

Thermal mass transfer printing is well suited for printing of overhead transparencies. The base material is clear polyester film, which best meets the requirements for transparency, toughness, and heat resistance. Heat generated by the overhead projector can result in curl and cockle of the film. To prevent this, the film is subjected to a shrinking process, so that no subsequent shrinkage will occur.

Antistatic coatings applied to the back side provide low friction for processing through the printer. A surface coating is applied to assure adhesion of the ink (Kulkarni et al., 1995; Zawada, 1995). The coatings produce a slight haziness that does not visibly affect the projected image. Thermal mass transfer printing is one of the best choices for printing of overhead transparencies (Giga, 1993).

12.6.4 Variable Dot Thermal Mass Transfer Printing

Thermal mass transfer printing is a binary process, and resolution is limited by the spacing of the heating elements, at this time 300 dpi or 12 dot/mm for most thermal color devices. This is insufficient for high-quality pictorial printing. Variable dot size printing would considerably improve image quality. Changes in heater element and printer design to produce variable dot size have been suggested (Tsumura et al., 1988; Saito et al., 1993; Inui et al., 1993; Sonoda et al., 1993). Panasonic introduced a printer in 1990 that employed resistor elements with a “waist” in the middle, thereby increasing current density and producing a controllable dot size modulation capability (Degerstrom, 1990).

To produce controlled dot sizes, Fuji Photo Film Co. has combined the halftone modulating method named LOUVER with a thin layer thermal transfer ribbon in the design of their color proofer FIRST PROOF™. According to the company prints with high fidelity of conventional chemical proofs can be produced (Nakamura et al., 1997; Sawano et al., 1997).

One ink ribbon structure for variable dot size printing contains a porous filler in

addition to colorant and binder. The porous material releases ink during printing in proportion to the energy applied (Kutami et al., 1990). Ink ribbons must transmit energy more efficiently, which is achieved in part by reducing the thickness of the ribbon. Ink coating weights are lower, but with higher concentration of pigment. The release layer properties are critical for uniform dot transfer. Recent product introductions by Fujicopian, Casio, and others employ a special printhead and ribbon. The Casio Printjoy, introduced to the U.S. in the fall of 1994, prints at 200×346 dpi and is capable of six bits of color. Geometry and spacing of heating elements are different from those of thermal dye transfer printheads. Resistors are square and exactly half the dot pitch in width, so that the gaps between resistors are as wide as the resistors (Giga, 1995).

Best results are obtained with a micropore receiver paper. A cross section of the paper is shown in Fig. 12.17. The support is a multilayer, biaxially oriented, voided polyolefine paper coated with a spongy mixture of two or more polymers not miscible with each other (Ichii et al., 1989). During printing, the molten ink is absorbed into the pores of the spongy polymer layer in amounts proportional to the energy supplied (Tanaka, 1993). Print quality does not quite reach the level of continuous tone thermal dye transfer prints but is much improved over binary thermal mass transfer. The lower printer and consumables costs make variable dot thermal printing a cost-effective alternative to thermal dye transfer printing in many applications. One drawback is that specialty receiver media are required. Alternative receivers include transparent and white films. They require more energy to print and give less uniform dots. Paper is entirely unsuitable, even when coated.

12.6.5 Resistive Ribbon Printing

An important thermal transfer product was IBM's Quietwriter, introduced as a monochrome serial printer in 1984. It was based on a unique self-heating, resistive ribbon technology. Instead of a print head, the Quietwriter ribbon has a built-in resistive layer that

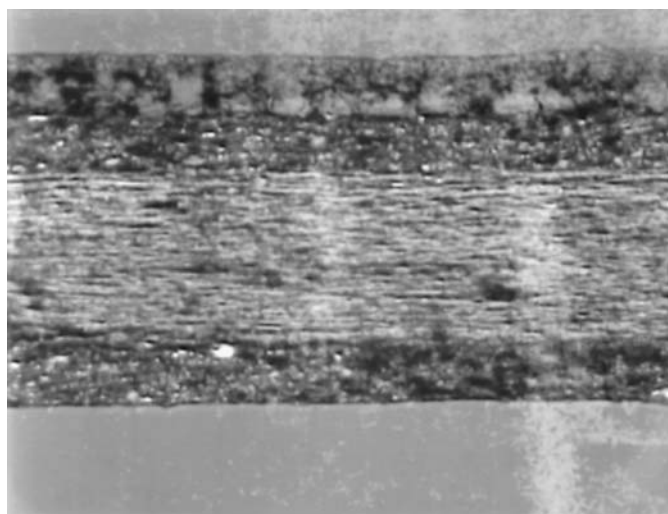


Figure 12.17 Microscopic cross section of thermal mass transfer receiver for variable dot size printing. From top: micropore receiver layer; three-layer, synthetic paper support (center layer is voided). Total caliper 163 microns. (Courtesy of Schoeller Technical Papers Inc., Pulaski, New York.)

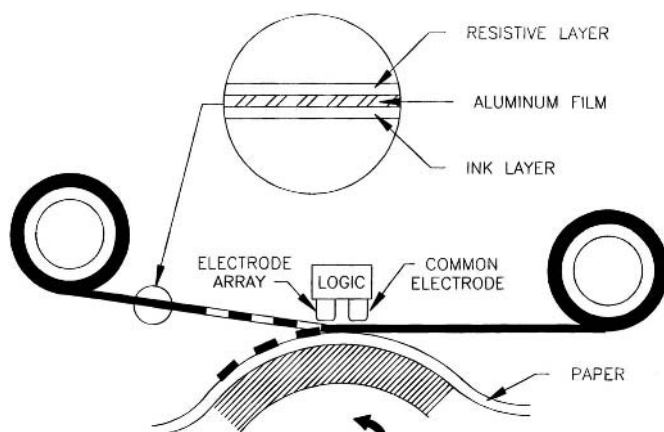


Figure 12.18 Schematic of resistive ribbon printer. (Courtesy of Atlantek Inc., Wakefield, Rhode Island.)

heats up when current is passed through it. Printer and ribbon configuration are illustrated in Fig. 12.18. The ribbon is a three-layer structure with a supporting substrate of an electrically conductive, carbon filled polycarbonate film that serves as the resistive element. The resistive support is coated with a thin layer of aluminum and an ink layer. A polyamide thermoplastic resin, loaded with carbon black, is a preferred ink composition (Crooks et al., 1986, 1989). During printing, electric current flows from the stylus array of the print electrodes through the resistive layer to the aluminum layer, causing localized heat to be generated in the resistor. When the ink is heated, it transfers from the ribbon to the paper. The mechanism is the same as for thermal mass transfer printing with a thermal head.

The advantages of a self-heating ribbon over a thermal printhead are many. There is no thermal cycle time, as with a thermal head, that limits print speed. Inks with a higher melting point, that do not smear, can be employed. The inks can be transferred at higher pressure, a feature that improves image resolution and makes the process virtually independent of the type of paper used (Diamond, 1989). It is possible to produce high resolution electrode arrays of 40 dot/mm or 1000 dpi (Lane et al., 1992).

The technology is applicable to thermal dye transfer printing, as studies by Miyawaki et al. (1990) and Taguchi et al. (1988, 1990) suggest. An eightfold increase in printing speed and 50% lower energy requirements were observed.

The Quietwriter had the best print quality of any thermal mass transfer product on the market, even on plain paper. Unfortunately, the machine also had an unsurpassed supplies cost of twenty cents per page. After launching two more generations of the Quietwriter, IBM withdrew the machine from the market in 1991.

12.6.6 Future Outlook for Thermal Mass Transfer Printing

Thermal mass transfer printing met with its greatest failure in the office color printing market. The high price of the thermal printers and consumables was a key factor while the market was being flooded with low cost color ink jet printers. Thermal mass transfer printing has been successful in other markets, becoming the dominant process for label printing, mainly of variable information and bar codes. The market has seen strong growth of print-

and-apply labeling on demand and new industrial marketing applications continue to evolve (Townsend, 1996). Major progress has been made in industrial grade printheads for bar code printing and miniature printheads for portable printers. For these applications, no other technology can match the performance, reliability, and cost advantages. For wide format signage, thermal transfer printing with resin-based ribbons can offer a number of advantages especially for outdoor exposure, such as durability, UV resistance, and weatherability.

Progress is being made with the introduction of variable dot thermal mass transfer printers (Terao et al., 2000) and microporous receiver papers (Maeda et al., 2000). Improved image quality is extending applications to ID card printing that enable photographs to be incorporated. Both thermal printing processes are expected to dominate this market (Giga 1998).

12.7 THERMAL DYE TRANSFER PRINTING

Thermal dye transfer printing, also known as dye diffusion thermal transfer, is usually called dye sublimation printing in the computer press. This confusion arose because early researchers believed that the process was related to sublimation dyeing of textiles, which was reasonable at the time (Honda, 1985). Since then, others have recognized that the process is one of diffusion, but the term dye sublimation printing persists (Hann et al., 1990; Hodge et al., 1991; Ozimek et al., 2000).

The process is capable of producing near photographic quality images, and the first thermal dye transfer printer, described in a presentation by Sony in 1982, was the Mavigraph color printer for use with the Mavica video camera. In 1985 Hitachi introduced a thermal dye transfer color printer with 64 grey levels per color. The Sony Mavigraph printer became commercially available in 1986, and in 1987 thermal dye transfer printers were introduced by Eastman Kodak, Hitachi, Sharp, ICI, and Dai Nippon Printing.

The imaging system configuration is similar to that of thermal mass transfer printers (Fig. 12.12). Heat is generated by energizing the thermal head in response to electronic image data while driving the donor ribbon and receiver paper underneath. Thermal dye transfer printers employ closely spaced heating elements on a thin film circuit. Each element is usually divided into two parallel sections in order to minimize visible structure in the final print. Thermal dye transfer printing requires more energy than thermal mass transfer or variable dot size mass transfer printing. A power supply that can deliver 2–4 J/cm² is required. Temperatures at the surface of each element can rise to 350°C on the surface of the thermal head and to 260°C at the interface between ribbon and receiver.

While the printer configuration for thermal mass and dye transfer printers is similar, and several manufacturers offer dual-purpose printers that can print on either medium the actual transfer mechanism is quite different. During thermal mass transfer printing, the entire ink layer, including binder, colorants, and additives, is transferred to the receiver during the printing process. As a result, thermal mass transfer printing is inherently a binary process.

During thermal dye transfer printing, only the coloring dye transfers, with the binder remaining attached to the donor ribbon. The transfer mechanism is based on the diffusion of the dye from the donor ribbon into a receiving layer on the receiver surface. The quantity of dye that is transferred, and thus the intensity of color at each image point, depends on the length and intensity of the heating pulse applied to the heating element, so that the process is intrinsically a form of continuous tone printing. The colors are coated on the ribbon as sequential panels. In the printing process, the ribbon moves forward continuously while the receiver is recycled underneath it. The entire image is written in yellow, magenta, and finally cyan, with black as an additional option. A truly continuous tone color image is built by overprinting of the three subtractive colors.

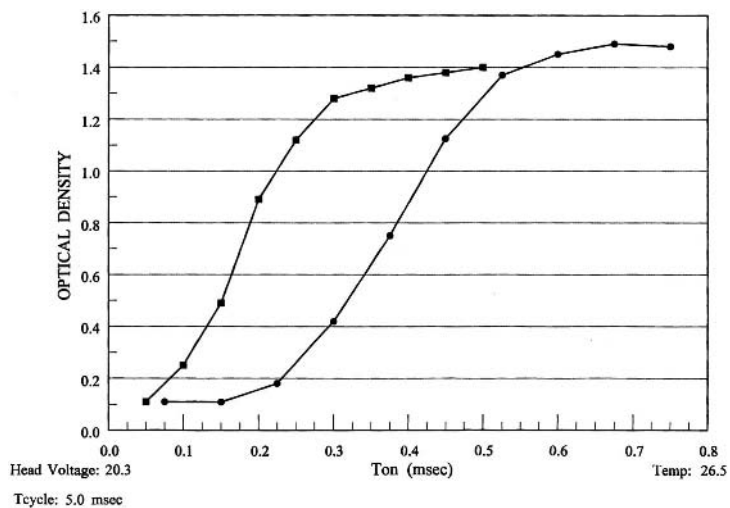


Figure 12.19 Thermal recording characteristics of bimodal thermal mass transfer (—■—) vs. continuous tone dye transfer printing (—●—). (Courtesy of Atlantek Inc., Wakefield, Rhode Island.)

Thermal dye transfer printing exhibits a wide dynamic range, similar to photography. Figure 12.19 illustrates the difference between the dynamic response of bimodal mass transfer and continuous tone dye transfer printing. Dot density variation is primarily a function of media chemistry and accuracy of the thermal control. The strategy is to operate in the “linear” region of the dynamic response. Print quality depends on media color gamut, media motion control, and accurate multiple pass dot registration (Hori et al., 1992). Dye thermal heads are designed to produce up to 256 different levels of color per dot, and by printing the three subtractive primary colors they can generate 16.7 million colors. The results are pictures that are all but indistinguishable from photographic prints to the untrained eye.

Figure 12.20 summarizes results of color research at RIT Research Corp., a spinoff of the Rochester Institute of Technology. The regions marked A and B are adequate in either spatial or color resolution to give the illusion of photographic realism. Area C is somewhat marginal but is adequate for spot color graphics and presentations. Area D is generally unacceptable. The wide boundary between C and D reflects differences in human perception. Moving upward and rightward in this chart represents an improvement in print quality. Much of the chart is empty of products, which have clustered around the top and bottom edges, that is, either at 8 bit/pixel (continuous tone) or 1 bit/pixel (monochrome or bimodal color). Thermal dye printing and ThermoAutochrome are at the top, and have increased to their present level of 8 bits of color and 300 dpi. Variable dot thermal mass transfer printing has been demonstrated at 6 or 7 bits, that is 64 or 128 tone levels, respectively, without giving up spatial resolution and bringing it closer to thermal dye transfer printing. Bimodal thermal mass transfer printers are at the bottom of the chart and, at 300 dpi, fall between areas D and C.

12.7.1 Thermal Dye Transfer Donor Ribbons

Donor ribbon and receiver for thermal dye transfer printing constitute a closely matched pair for optimum print quality. A ribbon/receiver configuration, depicted in Fig. 12.21, shows that the donor ribbon and receiver are multilayer coated structures. The donor rib-

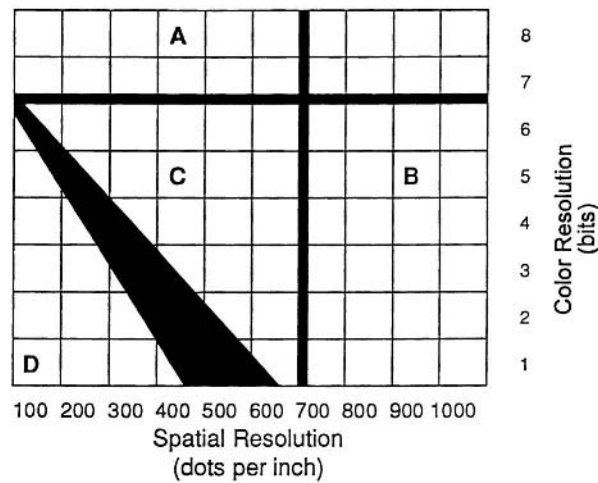


Figure 12.20 Spatial versus color resolution. The regions A and B are adequate in either spatial or color resolution to give the illusion of photographic realism. Area C is marginal but acceptable for presentations and spot color graphics. Area D is unacceptable. The wide boundary between areas C and D reflects differences in human perception. (From Giga Information Group, 1995. Contact Sara Martin, Giga Information Group, One Longwater Circle, Norwell, MA 02061, 1-800-874-9980 or 617-982-9500, fax 617-878-6650.)

bon is based on a biaxially oriented polyester film, typically 3.5–6 microns thick. On the side nearest the thermal head is a cross-linked slip coat, which assures that the ribbon does not stick and moves freely under the head during printing, even though the temperature at the surface of the head rises to 350°C or higher. As the base film is molten at this temperature, it cannot be relied upon to provide structural integrity, so that the slip coat must provide mechanical support during this part of the printing cycle (Sarkar et al., 1991; Hann et al., 1993; Hann, 1994; Tunney et al., 1997). On the other side of the base film is a priming coat, also called a subcoat or a barrier layer, to provide bonding between base film and dye layer deposited on top of it. Another requirement of the subcoat is low affinity/impermeability for the dye to provide a barrier for backward migration during printing (Henzel, 1991).

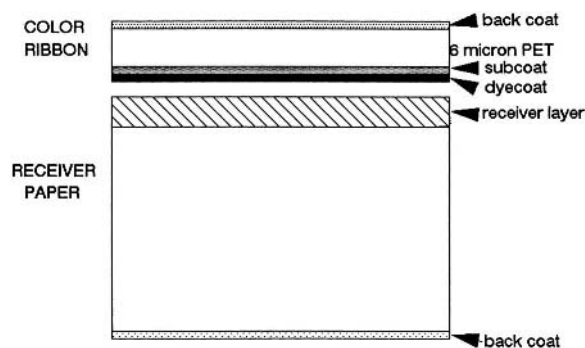


Figure 12.21 Thermal dye transfer donor/receiver schematic. (From Hann, 1994. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

The active dye coat itself consists of a solid solution of dye in a binder polymer, such as cellulose derivatives (Vanier et al., 1987). The dye binder polymer acts as a solvent for the dye (no recrystallization) and must be heat stable, must not stick to the receiver, and must exhibit thermoplasticity. The dye and binder polymer are carefully designed mixtures in order to obtain the desired color, transfer, and stability properties (Katayama et al., 1991; Clifton et al., 1997).

The distinction between sublimation and diffusion is not just academic; it has an impact on the range of dyes that are suitable for thermal dye transfer printing. The early dyes were chosen from a small number of commercially available sublimable textile transfer dyes. The discovery that the process was primarily one of dye diffusion qualified a wider array of dyes as potential candidates for thermal dye transfer printing (Hann et al., 1991). However, in order to fulfill all the requirements, special dyes had to be designed (Bradbury, 1992; Etzbach et al., 1994; Vanmaele, 1994, 1995). Hundreds of patents have been granted describing thermal dye transfer dyes, but commercially used dyes have not been disclosed. A few suitable dyes are shown in Fig. 12.22. Necessary performance requirements are bright color (narrow absorption band), strong color (high extinction coefficient), and the capability of being easily transferred (Tomita et al., 1995), permanently fixed, light fast, and nontoxic. Some of these are at first sight mutually exclusive. It seems unreasonable to expect a dye to be easily transferable and permanently fixed, and in practice a compromise has to be made.

Multiuse ribbons have been disclosed by Ricoh (Mochizuki et al., 1989; Uemura et al., 1993) and Matsushita Electric (Taguchi et al., 1990a). The Ricoh ribbon goes by the acronym MUST, for multiuse sublimation transfer. The essential feature is that the dye is contained in a two-layer structure with different dye concentrations and glass transition temperatures. It is claimed that ten times the utilization can be reached without loss of print density. Matsushita's approach is to advance the donor at a slower speed than the receiver. To permit slippage of donor and receiver during printing it is essential that the modulus of elasticity of the donor ribbon does not change appreciably at the printing

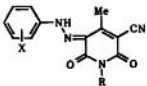
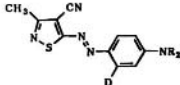
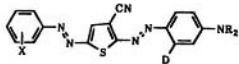
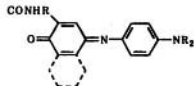
<u>Color</u>	<u>Class</u>	<u>Structure</u>	<u>Company</u>
Yellow	Azo pyridone		ICI/DNP/Kodak
Magenta	Azo		ICI/Kodak
Cyan	Azo		ICI
	Indoaniline		Kodak/Mitsubishi

Figure 12.22 Thermal dye transfer dyes. (From Calder, 1991. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

temperatures. Aromatic polyamide films proved superior in this respect to PET films. No appreciable loss of print density was noticed at a 1:12 speed ratio between donor and receiver, so that a utilization factor of ten seems attainable.

12.7.2 Thermal Dye Transfer Receivers

The receiver sheet consists of a supporting substrate with a functional layer coated on one side and a backing layer on the other. A number of substrates may be used. The preferred support material for reflection prints are rather complicated paper film laminates. Microscopic cross sections of two such laminates, disclosed in US patents from Dai Nippon Inatsu K. K. (Yoshikazu et al., 1988) and Kodak (Campbell, 1994, 1994a), are shown in Figs. 12.23 and 12.24, respectively. Both contain a paper core with a multilayer, voided, synthetic paper laminated to the face or printing side. The back side layer may be either a laminated synthetic paper (12.23) or an extruded polyethylene film (12.24). The lower thermal conductivity of these laminates, compared to other substrates, results in increased thermal sensitivity and optical print density as illustrated in Fig. 12.25. The good conformability and compliance of the voided component of the laminate also reduce printing artifacts caused by nonuniformities in the printing nip. An intermediate layer containing microcapsules, placed between substrate and receiving layer, produces similar effects (Ueno et al., 1993). Radiation curing of foamed coatings to produce microporous layers has been described by Mehnert et al. (1997) as an alternative to voided synthetic paper structures.

For transparencies, clear polyester film is a suitable support. As twice as much dye needs to be transferred to obtain a given density in transmission compared to reflection, there are special requirements for software, print drivers, and ribbon design, and double printing is an option. For printing of identification cards, driver's licenses, etc., that require a durable support, white opaque polyester is the material of choice. A recent introduction

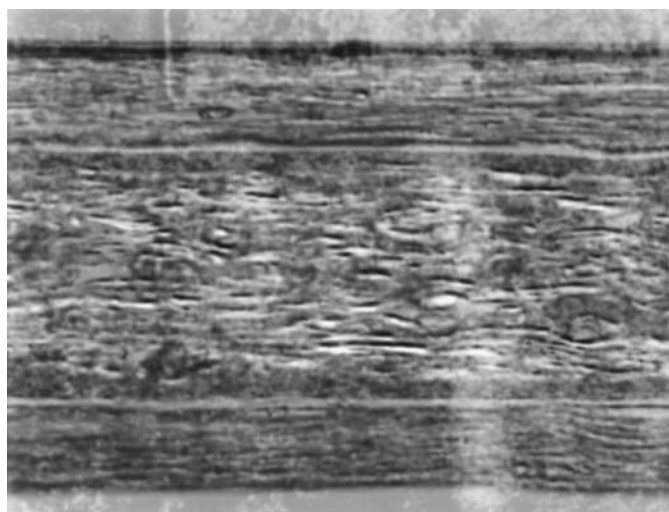


Figure 12.23 Microscopic cross section of thermal dye transfer receiver. From top: Receiver layer; synthetic paper; two-side coated paper; synthetic paper; back coat. Total caliper 192 microns. (Courtesy of Felix Schoeller Technical Papers Inc., Pulaski, New York.)

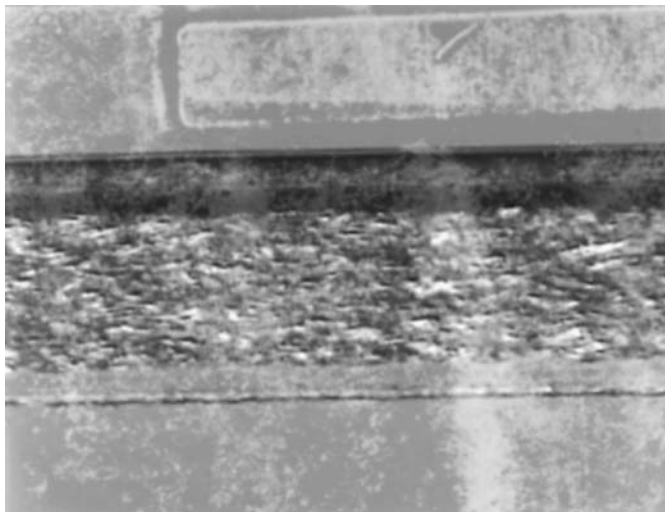


Figure 12.24 Microscopic cross section of thermal dye transfer receiver. From top: receiving layer; synthetic paper; pigmented polyethylene layer; paper; clear polyethylene layer; back coat. Total caliper 210 microns. (Courtesy of Felix Schoeller Technical Papers Inc., Pulaski, New York.)

from ICI Imagedata, for producing passport photos, has security features built into the receiver print medium.

The receiver layer must be receptive to the dye image (Shinozaki et al., 1993) and provide release from the donor after printing; it is typically made by coating a soluble polymer onto a suitable substrate. For thermal transfer dyes, derived from dyes used for dyeing polyester fibers, polyester resin serves as the receiver layer. Other suitable polymers include polycarbonates, polyurethanes, polyvinylchloride, and various copolymers. Thermal sensitivity and optical print density can be increased by modifying the viscoelasticity

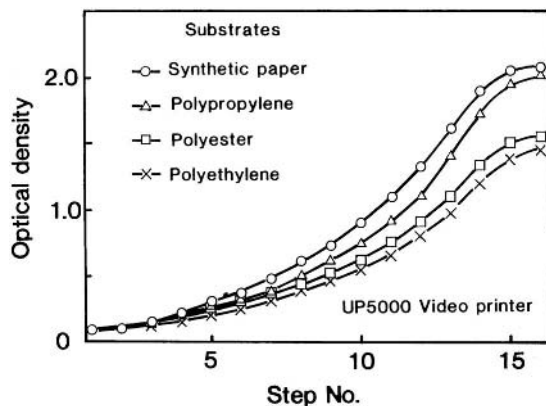


Figure 12.25 Printing characteristics of various thermal dye transfer receiver substrates. Optical density as a function of recording energy. (From Kato et al., 1990. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

of the receiver resin through cross-linking, polymer blends, or polymer alloys and lightfastness can be affected by polymer-dye interactions (Kato et al., 1990a; Clifton et al., 2000). To prevent blocking or sticking between donor and receiver during printing, a silicone or similar release agent is either incorporated into the receiver layer or applied as an overcoat. The receiver layer can be coated directly on the substrate, or over a sublayer or undercoat. Incorporation of antistatic properties into the subcoat allows the dissipation of static charges, without impairing the release properties of the receiver (Hann et al., 1991a). The reverse side of the receiver has an antislip coating to aid feed through the printer.

The need for a highly specialized receiver is a drawback for wider applications of thermal dye transfer printing. An offset printing method, described by Matsushita, overcomes this problem by first printing the image onto an intermediate receiver layer, followed by heat lamination of the printed intermediate receiver to the final substrate (Fukui et al., 1993; Taguchi et al., 1992). Related processes, printing on an intermediate transfer recording medium followed by heat lamination to the final receiver, have been described (Oshima, 1998; Shiral, 1999). A heat seal and protective layer are part of the transfer assembly. These processes are particularly suited for transfer to polymer films and cards.

12.7.3 Thermal Dye Transfer Image Stability

Thermal dye transfer images, while almost indistinguishable from photographic prints, unfortunately fall short of the mark in the area of image stability. Compared to conventional photography, thermal dye transfer prints have inferior light stability and resistance to damage from fingerprints. They are aggressively attacked by plasticized polyvinylchloride sheets and easily retransfer to folders commonly found in office and home environments (Newmiller, 1991). With the dye transferred and absorbed into the receiver layer in a very short period of time during printing, it is not unexpected that retransfer can occur to another dye receptive material.

Reactive donor/ribbon combinations, in which components in the receiver layer react with the transferred dye to form a nondiffusing compound, have been described by Konica and Sony. Konica employs azo compounds capable of forming metallized dyes with a metal ion source in the receiver (Miura et al., 1993). Sony disclosed cationic dyes that form ionic bonds with a clay mineral incorporated in the receiver layer (Ito et al., 1993).

Kodak (Harrison et al., 1994) and Dai Nippon Printing (Oshima et al., 1995; Saito, 1999; Egashira, 2000) have applied a protective layer over the final print, which is integrated into the color ribbon as a fourth patch and laminated with the thermal head. ICI Imagedata has incorporated a protective layer and security features into a passport photo printer. Retransfer and resistance to fingerprints was greatly improved, but light stability improvement depends on the dye systems used (Bradbury, 2000). The addition of a protective layer moves the stability of thermal dye transfer prints much closer to conventional photographic prints.

12.7.4 Future Outlook for Thermal Dye Transfer Printing

The Mavica film camera and Mavigraph color printer were originally introduced as an alternative to conventional photography. Image quality of the early systems, however, with input from still video cameras tied to the resolution of commercial television signals, fell short of photographic prints. Since then, systems have been optimized; still video cameras were replaced by digital cameras; camera and printer prices have come down drastically; and printing speed has increased (Egashira et al. 1992). In the meantime, ink jet desktop printers can now produce photographic quality prints.

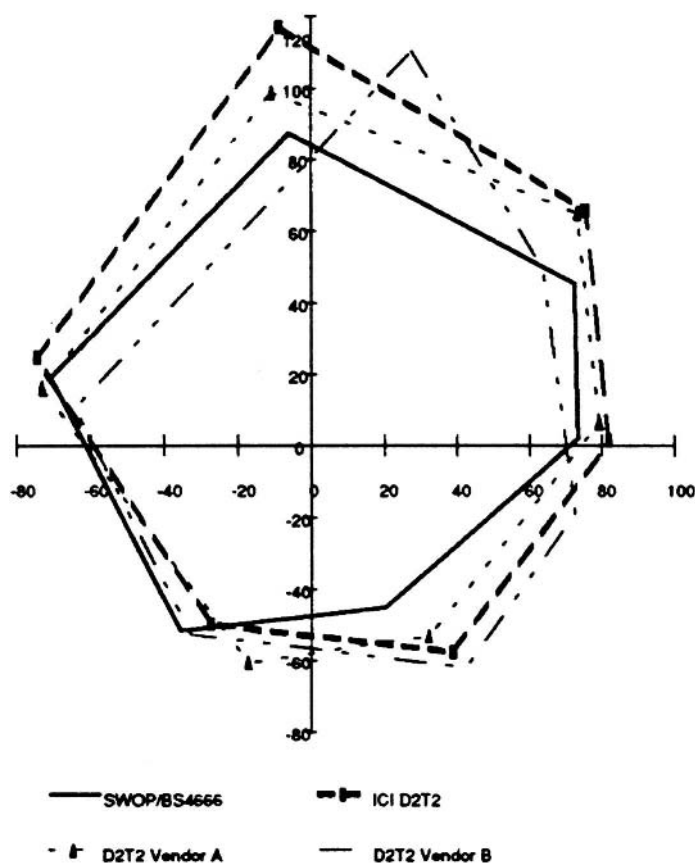


Figure 12.26 a^*b^* plane of maximum chroma at primary and secondary colors for thermal dye transfer proofs and BS4666/SWOP proofs and inks. (From Hann, 1994. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

In the medical market, the introduction of new diagnostic tools and the expanded use of workstations have increased the need for a high quality, color output system. Environmental concerns and the need to simplify and expedite medical examinations have created opportunities for thermal dye transfer printing (Defieuw et al., 1995). Graphic arts are expanding their use of thermal dye transfer printers. The color gamut of thermal dye transfer proofers exceeds the SWOP standard, with only a part of the a^*b^* plane being inaccessible (Fig. 12.26).

Special printers, capable of printing text and images directly onto plastic cards, have established a use in security applications. The undesirable trait of the dye to retransfer is used in the production of novelty items through a second transfer of the printed image to another receptive coating applied to a ceramic tile, mug, or T-shirt.

12.8 LASER THERMAL PRINTING

Laser thermal printing is not new, dating back over three decades. The earliest report of a thermal imaging process is from an RCA worker in 1970. Then, a typewriter ribbon

was used a color donor, with paper as the receiver. Focusing a laser beam through the base of an inked ribbon caused the illuminated ink to transfer (Levene, 1970). The fundamentals of the process have not changed much since. Meyers (1971) reported a laser writing process in which spots of metal one-third to two-thirds smaller than the nominal diameter of the laser beam were visibly altered by coalescence. In 1977 IBM workers reported laser thermal dye transfer images using off-the-shelf dyes such as crystal violet and methyl green coated in a nitrocellulose binder. They showed the future by using a computer to control the position and modulation of the laser beam (Bruce, 1977).

The first commercial product using a laser thermal process was the Crosfield Laser Mask, described at an SPIE meeting in 1980 (Gibbs, 1980; DeBoer, 1998). The product consisted of a polymer film base coated with finely dispersed graphite particles in an oxidizing binder such as nitrocellulose. It was exposed through the base with a YAG laser system that ablates the carbon layer transferring it imagewise to a paper receiver in contact. The result was a negative film and a positive proof on the paper. The negative could then be used to burn a lithographic printing plate. In the same year a UK patent application was filed by 3M (Baldock, 1980), describing a method of making direct laser printed images on a rotating drum with a YAG laser.

When high-powered diode lasers became available in the late 1980s, interest in this field was renewed. With these new lasers installed, maintenance-free laser thermal writing systems became a reality.

The field of photothermal and photoacoustic phenomena is an active one. The Gordon Research Conference is devoted to this topic. The field is mostly centered on relatively high-powered effects, where the physics of the material is nearly that of plasma. The regime occupied by graphic arts materials and processes is of considerably lower power, near the borderline between sublimation and ablation.

Compared to printing with a thermal head, the laser thermal process is a powerful approach to imaging. Both sublimation and ablation can be present in any given event. In some discussions it is useful to distinguish between the two processes, but for most events involving the transfer or movements of materials, DeBoer (1998) suggests that it is simpler to lump them together and call it “laser thermal ablation.” This seems reasonable in light of the confusion that arose between sublimation and diffusion in the case of thermal dye transfer printing. As the actual physical and chemical mechanisms are better understood, processes can be more precisely defined (Kinoshita et al., 1998, 2000, 2000a; Koulikov et al., 2000, 2000a; Timpe, 1999). For our purpose, the general term laser thermal printing will be used.

Laser thermal systems are intrinsically capable of higher resolution than resistance head systems. Since the laser can be focused to form a very fine, diffraction-limited spot, this process can produce high quality images. Images with 8 bits of information at 1800 to 4000 dpi have been routinely generated (Patton, 1995) and higher resolutions have been demonstrated (Odai et al., 1996). In the early 1990s two laser thermal printing systems were introduced: Kodak's Approval™ Digital Color Proofing System and Polaroid's Helios Laser System. The printing mechanism of both systems are described in detail.

12.8.1 Laser Thermal Dye Transfer Printing

Kodak's Approval™ Digital Color Proofer is an example of laser thermal dye transfer printing. A schematic of the process is depicted in Fig. 12.27. The beam of a diode laser is focused onto a dye donor sheet, containing a color dye and an infrared dye in a binder of cellulose acetate, coated on a polyester support. The donor is overcoated with a layer

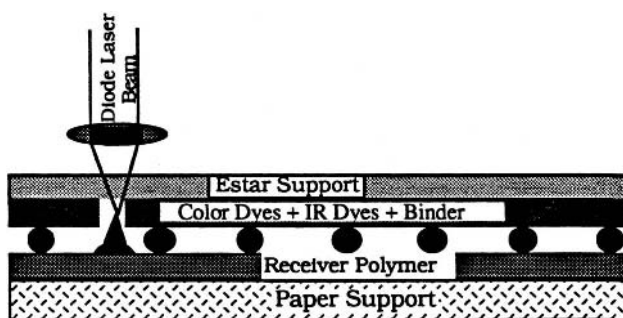


Figure 12.27 Laser transfer printing, dye donor/receiver schematic. (From Sarraf et al., 1993. Reprinted with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners.)

of polystyrene beads, a few microns in diameter, which are held in place by a small amount of binder (PVA emulsion). Both the size and the amount of the beads are important for optimum print sharpness and to prevent the donor from sticking to the receiver. The receiver is coated with a polymer that is a solvent for the dye, e.g., polycarbonate.

The transfer of the dye is a combination of ablation and sublimation mechanisms. Transfer efficiency was found to be a function of air pressure in the printing gap between donor and receiver. Lower than ambient pressure favors higher transfer efficiency, but below a certain level the gap collapses and loss of efficiency occurs.

Unlike thermal dye transfer printing, which is a continuous tone process, laser thermal dye transfer printing is capable of making continuous tone, halftone, and binary images. Images can be produced with a variety of equipment configurations. For high throughput of large format images, use of high-power lasers in a drum type system is favored. The Kodak Approval™ is based on this configuration. Throughput is met by using multiple lasers coupled to optical fibers. Fiber output is managed to provide up to 70 dot/mm (1800 dpi) halftone resolution using a high-power laser in each channel. The system is highly flexible. Screen rulings and screen angles can be specified, five different dot shapes chosen, and dot gain adjusted. The image is built up pixel by pixel through the successive transfer of the three primary subtractive colors and black to a receiver. The Approval™ system employs an intermediate receiver from which the four-color image is transferred to the actual printing stock (Pearce, 1994).

Comparing the energy efficiency of the laser dye transfer process with resistive head and resistive ribbon printing, one would expect the most efficient system to be the one where the heat is most localized in the imaging layer, i.e., the laser transfer system. This was confirmed by DeBoer (1991), who found that it takes about 300 mJ/cm² to print a density of 1.0 with laser dye transfer, which agrees well with earlier measurements by IBM workers. In comparison, energies necessary to print a 1.0 density with a 6 micron thick donor film were reported to be 4 J/cm², and for resistive ribbon printing 2 J/cm² were required.

12.8.2 Laser Phase Transition Printing

The image forming mechanism of the Polaroid Helios Laser System film is based on phase transition in a polymer matrix. The imaging layers, consisting of a laser sensitive layer adjoined by an imaging layer, are sandwiched between two transparent polyester substrates

(Chang, 1992). The imaging layer consists of carbon particles in a polymer matrix. The particles have a narrow size distribution that runs between 50 and 100 Å.

In the nonimaged state the sandwich can be separated between the laser sensitive and imaging layer. Imaging occurs when laser energy, produced by high-power gallium arsenide laser diodes, is focused onto the film. Absorbed energy causes a phase transition between the imaging layer and the laser sensitive layer, leading to a strong adhesion between the two layers, only at the site where the laser beam is absorbed. After the spots are formed, the film is “developed” by mechanically separating the sandwich, leaving the written image on one substrate and the negative on the other (Cargill et al., 1992; Habbal et al., 1994).

The Helios Laser System is a high-resolution imaging platform that lends itself to a number of applications (Miller et al., 1994). The film has a single threshold activation energy and writes spots or pixel elements with extremely high definition, as small as a few square microns. The system has been targeted at medical diagnostic applications. The full dynamic range of densities available are between a fixed maximum of 3.5 and a minimum optical density of 0.05. Since the number of available grey levels is over 12 bits, tone scales can be optimized to render the image content of any diagnostic modality.

12.8.3 Future Outlook for Laser Thermal Printing

The future of laser thermal printing seems assured. New fiber lasers offer promise of very high power at reasonable cost. The inherent advantages could make it the printing technology of choice for a variety of applications (Sarraf et al., 1993; Landsman, 1999). Future media for the graphic arts industry will likely be two areas: direct digital color proofing and computer-to-plate (CTP). Direct color proofing will be important for pre-press operations because CTP eliminates the film image, without which conventional proofs cannot be made.

Several direct digital color proofing methods have been demonstrated. One is Polaroid's SUNSPOT, a single-sheet process designed to produce a full-color, high-resolution, transparent image using a set of three diode lasers, each emitting at a different wavelength between 750 and 950 nm (Marshall, 1998). Polaroid has demonstrated a laser ablation color proofing system that can also be used to prepare printing plates from uncoated, grained, anodized aluminum. Konica has described both a laser thermal proofing system and a graphic arts film (DeBoer, 1997).

The Kodak DIRECT IMAGE recording film is a graphic arts film that can be handled under room light and does not require post-image processing (Neumann, 1997). Direct recording films occupy a place with the other direct imaging technologies such as direct digital color proofing, computer-to-plate, computer-to-press, and computer-to-print.

Accelerating patent activities have recently involved laser thermal imaging of lithographic printing plates. Huang et al. (1998) summarized these developments in a paper at IS&T's NIP 14. Kodak introduced the Professional Direct Image Thermal Printing Plate. In this product, the laser thermal heat generates an acid that changes the solubility of the ink receptive polymer layer in an alkaline developer. Recent advances in computer-to-plate technologies have triggered a series of research and development activities in the computer-to-waterless-plate area (CTWP) (Huang, 1999). Presstek is marketing a direct write laser thermal printing plate for the driographic press that uses no fountain solution. Many of the mechanistic details have been described by Hare et al. (1997, 1997a). With the current momentum of research, it is likely that laser thermal printing will become the

primary technology for making direct lithographic plates and will give rise to other direct digital imaging systems.

ACKNOWLEDGMENT

I would like to thank Frederick A. Poole of Felix Schoeller Technical Papers Inc. for preparing the microscopic cross sections.

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13

Photothermographic and Thermographic Imaging Materials

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13.1 INTRODUCTION

Great strides have been made in the development of the technology of thermally and photothermally generated dry imaging materials (TM and PTM) since the last published reviews. This article is intended to be a review update of the most recent articles (1–9), although it is also intended to be sufficiently complete to provide a basic understanding of the current state of knowledge to give a newcomer to the field a good starting point to begin exploitation of its capabilities.

It is a good time for a technology update, not only from the point of view of the significant advances in the published technology but also because of the substantial increase in industrial and commercial interest. The original promise of high resolution in combination with the demonstrated rapid and convenient format has now been realized in high-quality medical x-ray films, such as DryView™ Medical X-Ray film (Kodak), Dry CR™ DI-AL film (Fuji), DryPro™ (Konica), and Drystar™ (Agfa), and newly emerging products for image-setting films, such as DryView Recording Film™ (Kodak) and DX™ Facsimile Film (Fuji). Furthermore, advances made in the film attributes that previously limited acceptance by a broader market (such as film $D_{\min}$, shelf life, light stability, and slow speed) have been overcome by innovative fixes. Aiding in propelling this technology into the next realm of applications have been the recent advances in (including the availability and manufacturability of) high-power diode lasers and high-resolution thermal heads. Customer appeal of dry film confirms the long-term presence of this technology.

In the most general sense, the basic component lists for thermographic and photothermographic formulations differ only by the presence of a light sensitive source (and sensitizing dyes, depending on the application). Therefore the discussions in the sections

below tend to intermingle the specifics, keeping the great overlap between the two in mind. Thus even though a comment may be made for one, it is assumed to be evident that it often translates to the other. More specifically, the fundamental list comprises four main components: the light sensitive source (with associated sensitizing dyes), a silver ion source to generate the metallic silver particles of the image, a reducing agent for the silver ion source, and a binder to hold everything together on a substrate (opaque or transparent). In addition to this list, the finer properties of the resulting imaging materials for today's demanding applications are achieved by various other components in the formulation, which include "toning agents" (to enhance a black silver image over the natural brown one), stabilizers, antifoggants, supersensitizers, and chemical sensitizers. Finally, material property enhancers are part of the overall construction and include antihalation agents, surface matting agents, and protective topcoats. The advances made in the photographic properties of modern photothermographic imaging constructions by all of these components is summarized below.

The reaction that is fundamental to the image formation in TM, and on which the fundamental basis of all photothermographic imaging constructions are based, is simply the reduction of the silver source to metallic silver:



The difference between the thermographic reaction above and photothermographic imaging is the presence of the latent image on silver halide, which enables the above reaction to proceed at lower temperature.

The fundamental practical difference between the photothermographic and thermographic portions of imaging materials, based on silver halide and an alternate silver source, is the temperature at which development occurs. A D vs. $\log E$ curve illustrating the point is shown for the photocatalytically induced image and the thermally induced image in the same film, in Fig. 13.1.

It can be seen that the thermally induced onset of image formation occurs at a higher temperature than the photocatalytically induced onset. The thermal separation between the curves provides the development latitude of the film. Ideally, the temperature at which

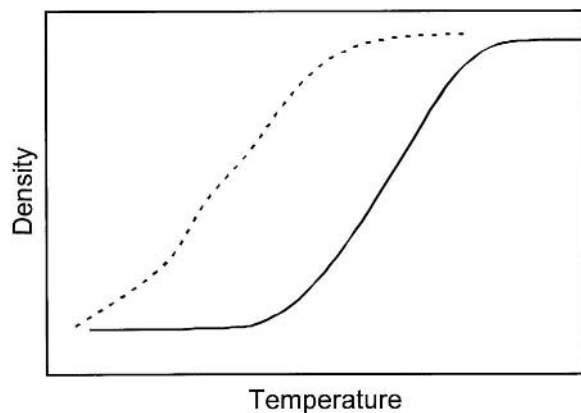


Figure 13.1 Idealized D $\log E$ curve for photothermographic, dashed line, and thermographic, solid line, imaging characteristics.

photocatalytically induced $D_{\max}$ occurs is well below the temperature of the thermally induced optical density. The AgX-free thermographic film clearly has just the one curve, which is typically adjusted to occur at the lowest temperature practically possible without adversely affecting the range of stability properties required.

A note is necessary regarding the focus on specific primary components in the photothermographic imaging construction discussed in this review. Silver bromide, silver carboxylates, hindered phenols, and polyvinylbutyral are, by far, the most important classes utilized for those individual fundamental properties listed above, respectively. As a result, while various silver halides and their mixtures are used as the light harvesting component (2), other silver sources are disclosed in the patent literature, silver benzotriazole (10) and acetylide being the second most cited sources (11–13). As a result, while other silver sources are disclosed in the patent literature, such as silver benzotriazole (10) and silver acetylide (11–13), far less information on these secondary choices is generally available outside of the references noted. The same can be said for polymers, which exhibit the properties needed as binders in these types of constructions (2,14), as well as for other classes of organic developers (2). Therefore this discussion will naturally gravitate to the most important components noted, although references and comments related to these others will be included whenever appropriate.

Finally, while the discussion below utilizes a compartmentalization approach for each component, it should be emphasized that, for the first time, chemical bonding interactions between certain components have been clearly demonstrated (15,16). These interactions mean that each individual component often cannot be regarded as an independent variable even though it may be discussed as such.

The cross section of a typical photothermographic film construction is shown in Fig. 13.2.

In general, the topcoat provides protection for the softer silver image layer beneath, especially during thermal processing and, depending on the T_g of the underlayers, only needs to be a few microns thick. The silver imaging layer contains all the components necessary for the formation of the silver image on thermal development and must be thick enough to provide sufficient $D_{\max}$. This is the primary functional layer and therefore contains the silver source, a latent image capturing material, and developer. This layer also contains various components to maximize the image quality, including antifoggants, ton-

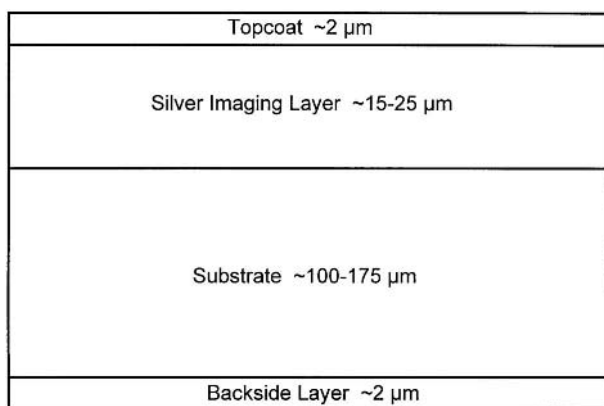


Figure 13.2 Generic cross section of thermally developed imaging materials.

ers, and stabilizers. The substrate layer is typically a clear film base, such as polyethylene terephthalate, whose thickness is dictated by the intended application; but it can be paper as well. The substrate may contain filter or antihalation dyes and may also be coated with a subbing layer to enhance coated layer adhesion. The backcoat is a thin polymer layer that incorporates components needed to improve physical handling such as antistats and matte particles.

A note on what is not covered in this review is also in order. Photothermographic and thermographic process technology are not included. The interested reader may be referred to some of the most significant patent literature on this topic (3,17). In addition, the color-based photothermographic imaging materials reported in the literature have been partially reviewed (5) and will be subjected to a limited update below. Also, thermally developed constructions based on silver halide and color couplers only, without a major portion of the construction providing silver ion from an alternative source, are not included.

With this overview, the following discussion demonstrates the advances made in the state-of-the-art of photothermographic and thermographic imaging materials and illustrates the potential for future applications.

13.2 PROPERTIES OF Ag^+ SOURCES USED IN TM AND PTM APPLICATIONS

Photothermographic and thermographic imaging materials utilize a non-silver halide source of silver ions to form the bulk of the black image (Ag°). Although many classes of silver compounds have been reported in the patent literature (18,19) there are only three classes that have found practical use, silver carboxylates (20), silver benzotriazoles (10), and silver acetylides (11–13). By far, silver carboxylates, nominally abbreviated as $\text{Ag}(\text{O}_2\text{CR})$ but more accurately as $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ (see below), where $x = 12\text{--}22$, have been the source of choice, as can be seen by the number of companies utilizing it (20–25).

Silver carboxylates are often referred to as soaps, because of the long saturated hydrocarbon chain similarity with sodium and potassium soaps, typically $\text{C}_{16}\text{--}\text{C}_{22}$, although, as will be shown below, this is where the similarity ends. It should be further pointed out that the silver carboxylate used in the commercial formulations can be a mixture of primarily stearic ($\text{HO}_2\text{C}_{16}\text{H}_{31}$) and behenic ($\text{HO}_2\text{C}_{22}\text{H}_{43}$) acids with smaller fractions of palmitic ($\text{HO}_2\text{C}_{14}\text{H}_{27}$) and arachidic ($\text{HO}_2\text{C}_{20}\text{H}_{39}$) [for example, (20)] or pure silver behenate (21). In addition, there are always low levels of unsaturated carboxylic acids in the fatty acid source, which may contribute to printout instability in the nonexposed areas (26). Longer chain silver carboxylates prepared from these unsaturated carboxylic acids have been known for some time to exhibit poor stability (27,28). On the other hand, the structurally characterized silver tiglate (2-methyl-2-propenoate) complex has been found to be quite stable (29), as have the short chain di-carboxylates, silver fumarate, and silver maleate (30).

This discussion on the silver sources attempts to bring the physical properties of silver sources in line with their photothermographic properties, as illustrated for silver soaps in Table 13.1.

The fundamental properties of $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ that can be associated with the characteristics of photothermographic imaging chemistry (D_{max} , D_{min} , speed, stability, etc.) are summarized in Table 13.1 and are discussed in more detail under each category.

Table 13.1 Properties of $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ Related to Photothermographic and Thermographic Processes

Properties	Basis of property	Consequence of property
1. $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimer structure	Ag—O covalent bonds	Imaging reactivity characteristics
2. Three-coordinate silver	Two strong Ag—O bonds, one weaker Ag—O bond	Preferred crystal growth in <i>a</i> – <i>b</i> plane forms flat, tabular crystals; poor solubility
3. $2.9 \text{ \AA}$ Ag $\cdots$ Ag separation in $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$: same as in metallic Ag°	Bridging carboxylates create the $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimer structure	Possible effect on growth of Ag° image or latent image
4. Reactivity	Coordinatively unsaturated Ag on crystal edge, or lattice defect sites	Reaction with compounds having an affinity for silver ion
5. Solubility limitations	Strong Ag $\cdots$ O interactions between $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimers	Poor solubility, small ($500 \text{ \AA}$) crystallite size, film stability
6. Nonlinear solubility temperature dependence	Possible micelle properties	Krafft temperature ~ 50 – 60°C
7. Thermal stability	Crystal defects, impurities, chain length	Possible effect on fog center formation, latent image centers
8. Multiple thermal transitions prior to and including the development temperature	Straight chain hydrocarbon and its chain length	Unreported
9. $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ color	$\lambda_{\text{max}} = 250$ – 260 nm	Colorless construction
10. Refractive index	Dominated by Ag and hydrocarbon content	Haze
11. Photostability	$\lambda_{\text{max}} = 250$ – 260 nm	Print stability
12. Conductivity	$\text{Log } \sigma = -16$	Insulator

13.2.1 The $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ Dimer Structure

In discussing silver carboxylates, it should be first emphasized that the “salt” nomenclature utilized in the imaging literature and patents implies an ionic $\text{Ag}^+(\text{O}_2\text{CR})^-$ species and is misleading. The molecular structure of the silver stearate complex, $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$, where $x = 18$, which was previously understood since 1949 only by its unit cell parameters (31), has recently been published (32). The structure consists of three-coordinate silver covalently bound in 8-membered dimer rings of $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ (see Fig. 13.3). The silver is three-coordinate because of two strong Ag—O bonds and a weaker Ag—O bond between dimers. The weaker, interdimer Ag—O bond may be more accurately labeled as a supramolecular synthon, as this interaction plays a major role in determining the properties of the material in the solid state (33,34). The chemical literature clearly shows that, within the range of typical linear carboxylic acids, the same fundamental 8-membered silver carboxylate dimer results in all cases (33 and references therein, 35) where there are no additional ligand groups. As a result, the “salt” nomenclature conflict is more than semantic, as the reaction chemistry related to these silver com-

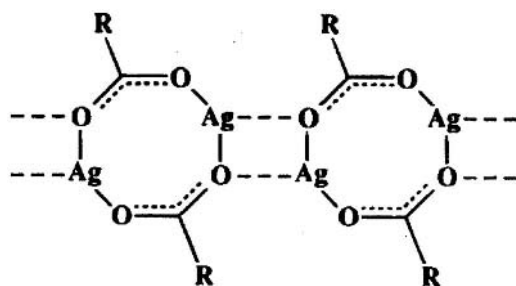


Figure 13.3 Ag—O dimer and neighbor bonding interactions in $[\text{Ag}(\text{O}_2\text{CR})]_2$.

pounds becomes more clear and understandable when viewed as a covalently bonded $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimer, as will be seen in the various individual property sections below.

Formally, there are six available coordination sites around the silver, although silver normally prefers 3–4 coordination sites occupied in molecular structures (35). The silver atoms in the dimer located on the crystal edge, therefore, are coordinatively unsaturated and easily accessible to compounds having the ability to coordinate to silver. From the photothermographic imaging chemistry point of view, components in the imaging formulation having the ability to coordinate to silver may react with the silver carboxylate at this location. The components having silver binding functionality include toners, development accelerators, and stabilizers. Specific examples of silver complexes of components contained within the coated film are discussed in the individual sections below.

By way of comparison, much less has been reported about the molecular structure of either of the other main commercially important silver sources, silver benzotriazoles and silver acetylides. The only silver benzotriazole structure reported in the literature contains the benzotriazole in its neutral, nondeprotonated form, $\{\text{Ag}(\text{benzotriazole})_2(\text{NO}_3)\}$ (36); this clearly has only limited relevance to the silver benzotriazole used in photothermographic imaging materials. The poor solubility of silver benzotriazole, in which it has commonality to silver carboxylates, is considered to be a good indication of a polymeric structure. Auxiliary ligands, such as aromatic nitrogen heterocycles, thioureas, and phosphines, have been claimed as compounds suitable for improving the solubility of silver benzotriazoles in photothermographic imaging constructions (37). The molecularly simpler silver imidazole, which also is poorly soluble and is also used as a silver source (38), has recently had its molecular structure clarified by Rietveld analysis of powder diffraction data (39). In this case, the structure is well resolved and shows that the complex is, in fact, polymeric.

The molecular similarity to benzotriazole may be sufficient to conclude a similar connectivity and explain both solubility and the lack of thermal phase changes within the temperature range of the development processes.

Silver acetylides comprise a class of compounds for which analogs also must be used in order to explain properties relevant to photothermography. These complexes, similar to silver benzotriazoles and carboxylates, typically exhibit poor solubility and are thereby considered polymeric (40) or at least complex oligomers (41). Little more can be said regarding the structures of the silver acetylides such as those used in photothermography. An interesting variation on the silver acetylide theme is the incorporation of carboxylates where, in all probability, the coordination occurs through the carboxylate; but the triple bond may be important (40). Silver acetylides incorporating phosphine derivatives are

more soluble, presumably by replacement of alkyne cross-linking groups with terminal phosphine ligands. From the molecular structures reported in the literature, the polymeric nature inferred for the silver acetylides used in photothermography can be assumed to be likely.

It is concluded that the thermo- and photothermographic consequences of the poor solubility of silver carboxylates may be considered relevant in the discussion of silver benzotriazoles and silver acetylides equally.

13.2.2 Three-Coordinate Silver in $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$

In the solid state, three-coordinate silver is the rule, in which there are two strong Ag—O bonds and one weaker Ag—O bond [2.2 and 2.6 Å, respectively (32)]. The weaker Ag—O bond between $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimers (shown in Fig. 13.3) is common in silver carboxylates and is the source of many silver carboxylate solid state properties.

The silver soap structure can be considered to be a linear coordination polymer because of the extended Ag—O bond between $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ units. The consequence of the extended Ag—O bonding, in combination with the weak hydrocarbon interactions between terminal methyl groups in the structure, is highly preferred crystal growth in the a–b plane of the crystal lattice (that is, the plane resulting in sheets of Ag atoms). As a result, a large volume of hydrocarbon chains encompasses a thin sheet of silver atoms, but the attractive forces between the hydrocarbons is sufficiently weak that only extremely thin crystallites are formed in the preparation of silver carboxylates under aqueous conditions (42–45). The tabular plate structure of the silver carboxylate can be illustrated by recrystallized silver behenate (Fig. 13.4) and is typical, although not exclusive, for all long chain silver carboxylates.

Whereas there are strong interactions between Ag ··· O pairs in the a–b plane and weak interactions between the terminal methyl groups, the process of preparing the $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ soaps (from water at $>60^\circ\text{C}$) leads to rapid precipitation of the insolu-

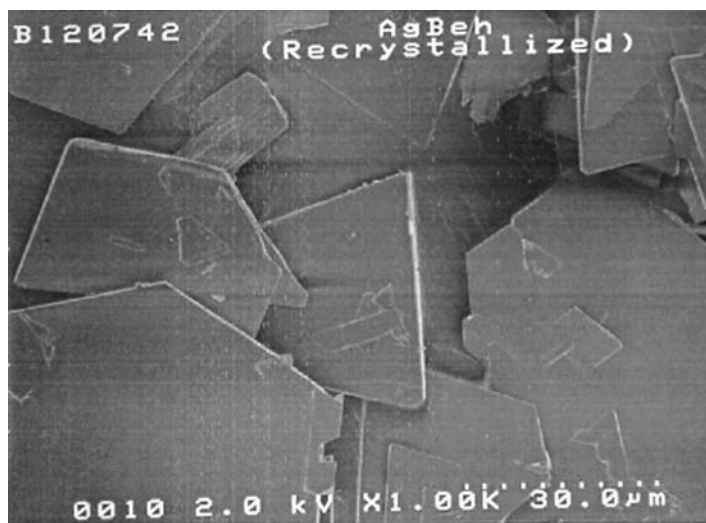


Figure 13.4 Recrystallized $[\text{Ag}(\text{O}_2\text{C}(\text{CH}_2)_{20}\text{CH}_3)]_2$ (99%)

ble solid. The ratio between the hydrocarbon surface, the (001) plane, and exposed silver atom surfaces, the (010) and (100) planes, therefore, becomes quite large, approximately 100:1, as can be quickly ascertained from scanning electron microscopy (SEM), such as in Fig. 13.4. This ratio suggests that reactivity of the silver soap is at least partially controlled by the low level of available silver atoms. Halidization of the silver soap, for example, would be expected to occur primarily on these silver exposed planes, and this is precisely what is seen (44,46).

Recently, imaging films having improved image tone have been claimed by increasing the percentage crystallinity of the silver carboxylate incorporated into the film (42,43). In this case, phosphonium compounds are incorporated into the silver carboxylate preparation procedure, which are claimed to promote the crystallinity of the resulting product. Crystallinity is defined as the ratio of the sum of the silver behenate diffraction lines to the sum of the diffraction lines of an Al_2O_3 reference. Crystallinity greater than 0.85 is preferred.

A slightly different approach to changing the structure of silver carboxylates is to focus on the odd-numbered chain lengths. A material based on a 9:1 mixture, by weight, of $\text{C}_{20}\text{H}_{41}\text{COOAg}$ and $\text{C}_{22}\text{H}_{45}\text{COOAg}$ gave slightly better D_{max} and D_{min} values than one based on silver behenate when fresh and much better values are found after incubation for 2 days (47).

13.2.3 Ag ... Ag Separation in $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$

An interesting consequence of the bridging nature of the carboxylate groups in $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ compounds is the location of the silver atoms at an unexpectedly close proximity to each other, 2.9 Å (34,48–50). While this distance is common for silver carboxylates, it happens to be the same as in metallic silver. The basis of this proximity is the fundamental M-M bridging properties of the carboxylate ligand in the $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimer structure, which is a well-established carboxylate bonding mode (51). However, this short distance and the similarity to the distance in metallic silver suggest possible bonding interactions between these metals in the dimer. The potential for bonding between the Ag^+ atoms is the subject of continuing debate (52–56). The consequence of such close $\text{Ag} \cdots \text{Ag}$ proximity is still uncertain in photothermographic imaging materials, although possible routes to the growth of Ag° have been postulated (1), because addition of one electron to the dimer could produce an incipient Ag_2^+ species, the well-known precursor to the latent image in conventional AgX systems (57).

13.2.4 Reactivity of $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$

The open coordination site on the silver in the $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimer in the edge of the crystal lattice can be expected to be very reactive with compounds having the ability to bond silver. This type of reaction chemistry results in the facile formation of stable complexes, such as the formation of in situ AgX by the reaction of $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ with halides, and toners as described below. Furthermore, this reaction chemistry can also be illustrated by the extreme reactivity of neutral donors having strong affinity for silver, such as phosphine-based (58) and sulfur-based (59) ligands. Triphenylphosphine is a particularly good ligand to convert the insoluble $[\text{Ag}(\text{O}_2\text{C}_x\text{H}_{2x-1})]_2$ dimer to derivatives having differing reactivities and solubilities. Novel silver carboxylate silver sources have been disclosed as a result of the affinity of the silver ion for neutral donor ligands (60,61).