High-Technology Applications of Organic Colorants

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High-Technology Applications of Organic Colorants

Peter Gregory

Specialties Research Centre
ICI Specialties
Imperial Chemical Industries PLC
Blackley, Manchester, England

For my wife,
Vera,
and my two sons,
Andrew and Michael

Preface

The traditional use of organic colorants is to impart color to a substrate such as textiles, paper, plastics, and leather. However, in the last five years or so organic colorants have become increasingly important in the high-technology (hi-tech) industries of electronics and particularly reprographics.

In some of these reprographics applications the organic colorant is used in its traditional role of imparting color to a substrate, typically paper or plastic. Examples are dyes for ink-jet printing, thermally transferable dyes for thermal transfer printing, and dyes and pigments for colored toners in photocopiers and laser printers. In other applications it is a special effect of an organic colorant that is utilized, not its color. Examples are electrical effects, such as photoconduction and the electrostatic charging of toners, both of which are essential features for the operation of photocopiers and laser printers, and the selective absorption of infrared radiation, which is utilized in optical data storage.

In electronic applications the organic colorant is often employed in a device. Typical examples include liquid crystal dyes, laser dyes, electro-chromic dyes, dyes for solar cells, dyes for micro color filters, and dyes for nonlinear optical applications.

These hi-tech applications present many challenges to the dyestuff chemist to devise dyes to meet the often demanding criteria required. This book describes how those challenges are being met in the important electronics and reprographics technologies. It also illustrates the vital role that organic colorants play in these applications. Indeed, it gives a chemist's view rather than a physicist's or engineer's view of the electronics and reprographics technologies.

The traditional uses of colorants are well documented in books such as those by Gordon and Gregory,[1] Allen,[2] and Zollinger,[3] and especially in the comprehensive volumes of Venkataraman;[4] they are not discussed further here. Neither are some of the less traditional, more diverse uses of colorants,

such as their applications in medicine, security, toiletries, fuel and metal coloration, thermochromic systems, photochromic systems, and many other areas. Modern biological uses of dyes, such as affinity chromatography to obtain highly pure enzymes from gross mixtures, also are not discussed, since these are treated adequately elsewhere.[5]

Acknowledgment

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Contents

I

Historical Perspectives

Can you imagine a world without color? A world of black, white, and shades of gray. A world devoid of the immense variety and brilliance of both man-made and natural color. A dull world indeed! However, color is so common that we tend to take it for granted. Indeed, although everyone is not only aware of but surrounded by color, very few people understand the origins of color and fewer still have any idea of the substances responsible for producing color, namely dyes and pigments.

Mankind has been fascinated by color for several thousands of years. In ancient times man used color to decorate both himself and his surroundings. Even today, thousands of years later, man still uses color for these purposes. However, unlike the ancient Britons and native Americans who daubed the colors directly on to their skin, people nowadays usually confine the color they wear to their garments.

Until the middle of the nineteenth century man obtained his colorants from natural sources.[1] These were of both animal and vegetable origin. For example, the dye prized so highly in ancient Rome, namely Tyrian Purple (**I-1**), was obtained from the mollusc *Dicaithus orbita*.[2] In contrast, the red dye Madder or Alizarin (**I-2**) was obtained from the root of the plant, *Rubia tinctorum*.[3]
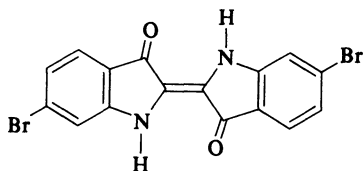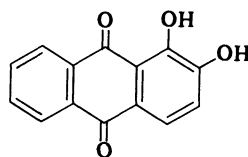
I-1   I-2

Obtaining dyes from natural sources was a slow, inefficient, and very wasteful process. For instance, many thousands of molluscs were required

to produce just one gram of Tyrian Purple. Consequently, a better route for obtaining dyes was obviously needed.

This better route was provided by Perkin. In 1856 Perkin, while attempting to prepare the antimalarial drug quinine, obtained instead the mauve dye Mauveine (**I-3**).[4] This somewhat fortuitous discovery of the first synthetic dye not only heralded the beginning of a major new industry, the dyestuffs industry, but also initiated the pioneering work upon which our present knowledge of organic chemistry rests.[5]

I-3
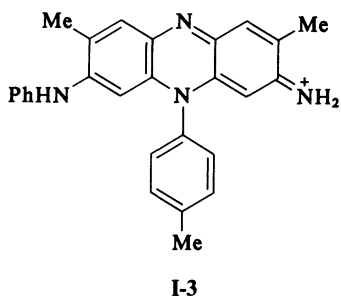
In addition to being strongly colored, dyes and pigments have other unique properties that are readily being applied in some of the high-
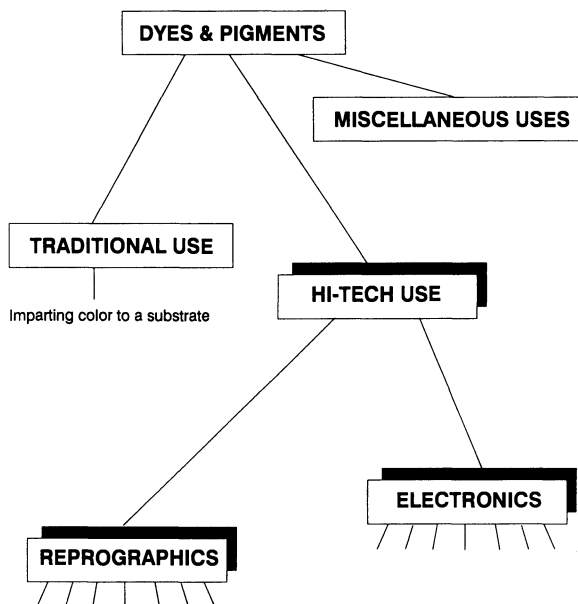
Figure I.1. Uses of dyes and pigments.

technology (hi-tech) industries. In most cases, however, novel dyes and pigments are required for these new outlets.

The two most important hi-tech areas as far as colorants are concerned are the electronics industry and the reprographics industry (Fig. I.1), and each of these may be subdivided further. In the subsequent discussion particular emphasis will be given to the reprographics technologies, which are probably less familiar and have been discussed less than the technology applications in the electronics area.

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II

Colorants for Electronics

The age in which we live may well be referred to by future historians as the electronic age. Silicon chip technology pervades many aspects of our lives and, as far as one can ascertain, will continue to do so at an ever-increasing rate. We have already witnessed several examples where electronics technology has replaced traditional technology. For instance, the switch from
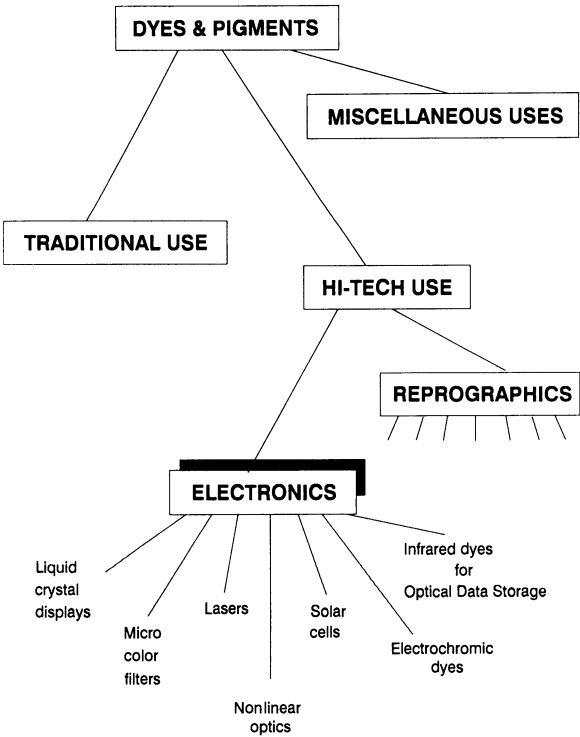
Figure II.1. Uses of colorants in the electronics industry.

conventional watches to digital (electronic) watches and the growth in electronic toys, including microcomputers, at the expense of conventional toys. There are many other familiar examples of electronics technology. For example, electronic calculators, solar cells (used increasingly to power the calculators), video recorders, laser and light emitting diode (LED) readers at supermarket checkouts and, more recently, electronic photography. A number of these new electronics technologies require colorants with special properties. Occasionally, existing dyes and pigments, specially purified, will suffice. Usually, however, completely new molecules are required to meet the challenges presented for colorants in the electronics industry.

The major areas where colorants are required in the electronics industry are shown in the Fig. II.1. Some of the "older" areas, such as liquid crystal dyes, laser dyes, and solar cells have been discussed elsewhere[1] and are therefore treated only briefly here. However, some of the "newer" areas, such as nonlinear optics, micro color filters, and electrochromic dyes, are treated more fully. The use of infrared dyes in optical data storage is discussed in Chapter 11.

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1

Liquid Crystal Dyes

1.1. INTRODUCTION

In recent years liquid crystals have made a significant impact commercially as a result of their application in electro-optical devices such as digital watches (and clocks), calculators, and instrument display panels, for example, in cars and airplanes. The main reasons for the success of these liquid crystal displays are their visual appeal and, more importantly, their extremely low power consumption, which results in a longer battery life for portable units. Only the recent advances of incorporating dyes into liquid crystals are considered in this chapter; for a review of the theory of liquid crystal displays, references should be consulted.[1,2,3,4]

Liquid crystal displays devoid of dyes are defective in several respects. For instance, the color contrast is an unsatisfactory gray on dark gray; the angle of vision is limited, i.e. the display is only visible when the face of the display is viewed obliquely; and finally, troublesome polarizers are required.

Incorporating suitable dyes into a liquid crystal overcomes the above disadvantages. Thus, a whole range of highly desirable color contrasts are possible, including high-contrast black on white, from just three dyes, viz. a yellow, a red, and a blue; also, the need for polarizers is eliminated and the angle of vision is widened. Unfortunately, because of the exacting criteria that must be met, only a few of the enormous number of commercially available dyes are useful in liquid crystal displays. Dyes for liquid crystal displays must be (1) non-ionic, (2) soluble in (compatible with) liquid crystals, (3) highly pure (this is not a regular feature of most commercial dyes), (4) have a high order parameter,[1] and (5) produce the correct viscosity for a rapid response rate.

The first three properties are self-explanatory; however, the fourth requires some explanation. The order parameter of a dye is a measure of how perfectly a dye molecule aligns itself with the liquid crystal molecules.

This parameter is measured on a scale of 0 to 1, where 0 indicates no alignment and 1 signifies perfect alignment. Ideally, a dye should have an order parameter of 1, since this gives the best contrast between the "on–off" states of the liquid crystal device. The on–off states of a liquid crystal are induced by the presence/absence of an electric field which can be applied to selected elements of the liquid crystal cell, thus allowing areas of switched molecules to coexist with areas of unswitched molecules. This, of course, permits the desired information to be displayed. In one state the rod-like liquid crystal molecules are aligned parallel to the electrode surfaces of the liquid crystal device, whereas in the other state they are aligned orthogonally to the electrode surfaces. (The type of liquid crystals and the nature of the electrode surfaces determine whether the on state corresponds to a parallel or orthogonal alignment of molecules; Fig. 1.1). This means that the molecules undergo a 90° rotation from the x to y axis (or vice versa). Therefore, if a dye molecule is perfectly aligned, it too will undergo a corresponding change in direction. Since the dyes used in liquid crystals have their transition dipoles oriented in just one direction, the light is only absorbed in one of the states, on or off, i.e., when the transition dipole of the dye lies perpendicular to the
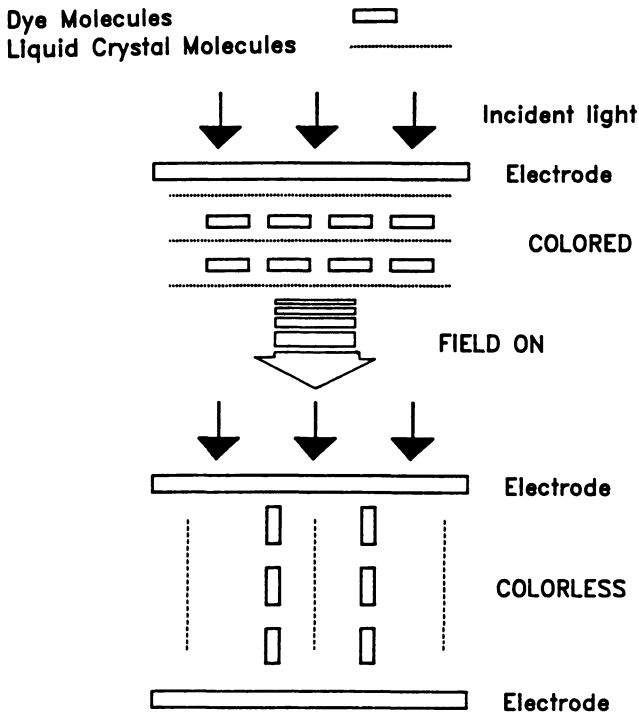
Figure 1.1. Orientation of dyes in on-off states of a liquid crystal.
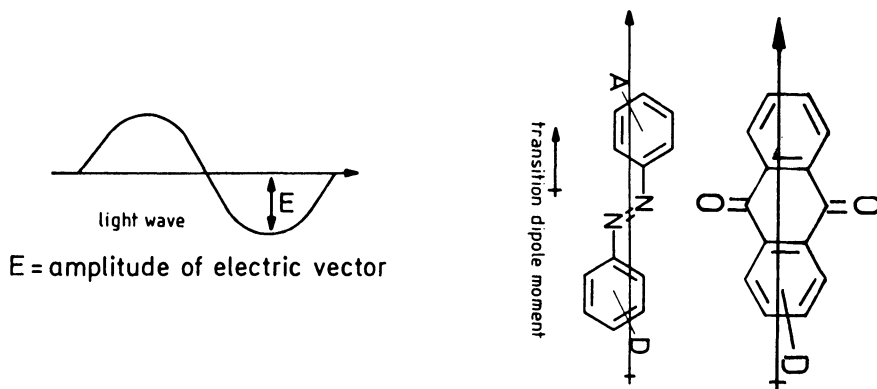
Figure 1.2. Orientation of azo and anthraquinone dyes for maximum absorption of radiation.

direction of propagation of the light source (Fig. 1.2). Thus, a change is observed from colorless to the color of the dye in the portion of the liquid crystal device that is switched (Fig. 1.1).

1.2. DYE TYPES

Disperse azo dyes fit these five requirements quite well and it is not surprising that these dyes have been examined extensively in liquid crystals.[5,6] It has become apparent that long, "thin" polyazo dyes, such as the yellow dye (**1-1**), the orange dye (**1-2**), and the magenta dye (**1-3**) have

1-1

1-2

1-3
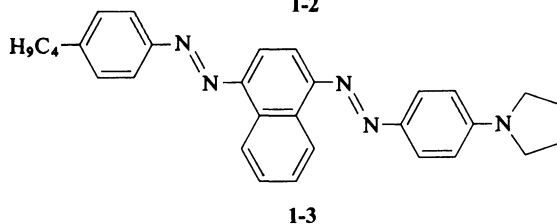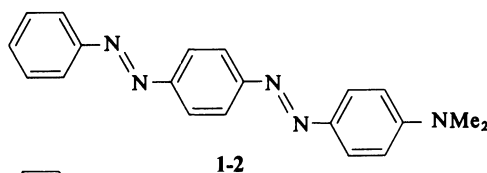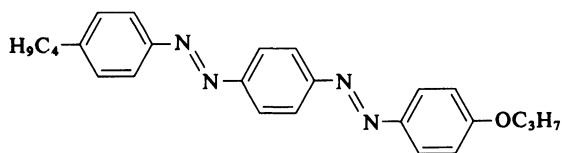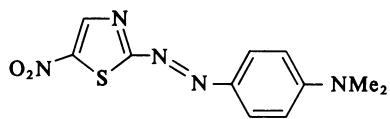
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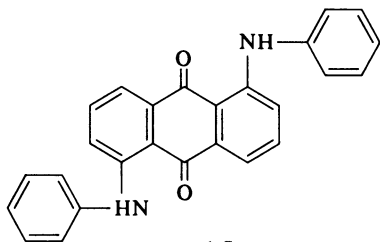
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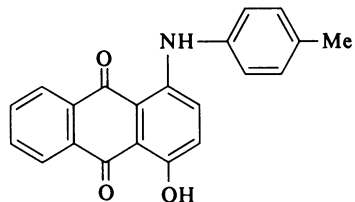
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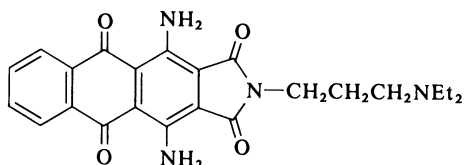
1-7

Table 1.1. Typical Anthraquinone Liquid Crystal Dyes

Dye	Color	Order parameter (E43)
	Yellow	0.80
	Red	0.80
	Blue	0.73

desirable properties. However, a serious defect of azo dyes, particularly blues such as (1-4), is their poor photostability: the ideal liquid crystal dyes should have high photostability, otherwise they will fade too quickly. Consequently, attention has been switched from azo dyes to anthraquinone dyes, which are renowned for their high photostability.[7] Research has rapidly established that anthraquinone dyes such as the bluish-red (1-5), the blue (1-6), and the cyan (1-7) fulfill the criteria for liquid crystal dyes, including that of high photostability. Further research has produced improved dyes with typical structures such as those shown in Table 1.1.[8–10]

1.3. FUTURE TRENDS

Fluorescent liquid crystal dyes are also being evaluated to improve the clarity of the display even further. These dyes must not only fulfill the same requirements as conventional liquid crystal dyes but also exhibit a high fluorescence efficiency. Perylene diesters such as (1-8) are showing promise as fluorescent liquid crystal dyes. These dyes have greater stability to ultraviolet radiation than other perylenedicarboxylic diesters while possessing good fluorescent properties and satisfactory order parameters.[11] The dyes themselves absorb radiation in the 450–500 nm region and are therefore orange in color. The fluorescence arises from energy transfer between the host liquid crystal cyanobiphenyl molecules (1-9) and the dye. The stimulated host molecule transfers its energy to the dye molecule which emits it in the 500–550 nm range (green/yellow) (Fig. 1.3).
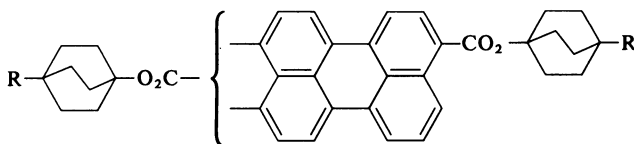
1-8

(Mixture of 5/8 isomers)
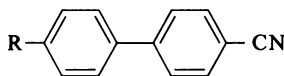
1-9

Chemical modification of the cyan anthraquinone dyes such as (1-7) has produced near infrared dyes for liquid crystals. Typical dyes are **1-10**, **1-11**, and **1-12**.[12]

More novel uses of dyes in liquid crystals which have not yet been realized commercially include flat screen televisions (see *Chapter 2, Section 2*)
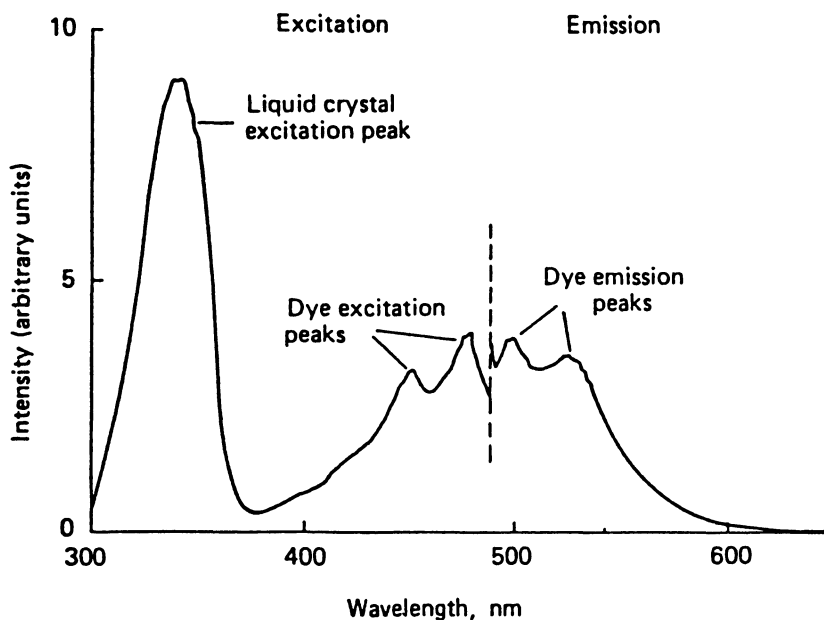
Figure 1.3. Excitation and emission spectra of fluorescent liquid crystal dyes.

1-10 λ_{max} 705 nm

1-11 λ_{max}^{Xylene} 750 nm

1-12 λ_{max} 810 nm
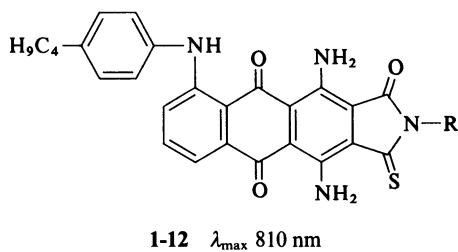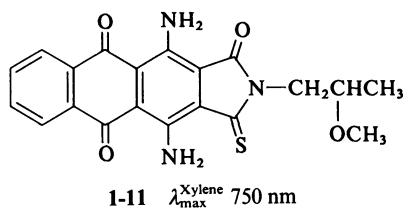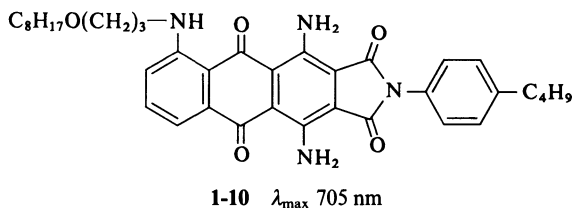
and polymeric liquid crystals.[13] The latter could be used for very large displays in environments such as airports, railway stations, and shops, since the power consumption would be exceptionally low. Liquid crystals are also being evaluated for write–erase optical data storage (see *Chapter 11*).

1.4. SUMMARY

Liquid crystal displays are being used more and more in the electronic age in which we live because of their visual appeal and their extremely low power consumption. Dyes offer many advantages in liquid crystal displays and consequently most displays now incorporate dyes. These dyes must satisfy a number of demanding criteria and it has been found that the anthraquinone class provide the best liquid crystal dyes.

Although the market for liquid crystal dyes will grow, it will never be large in tonnage terms. However, the specialized and ultrapure (anthraquinonoid) dyes are likely to command a very high price, so the sales value could be quite considerable.

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2

Micro Color Filters

2.1. INTRODUCTION

The field of micro color filters[1-3] is another expanding area in which dyes and pigments are being used. A rather unusual aspect of this application is that the three primary *additive* colors of red, green, and blue are required. Normally, it is the three *subtractive* primary colors of yellow, magenta, and cyan that are required for most electronics (and reprographics) applications.
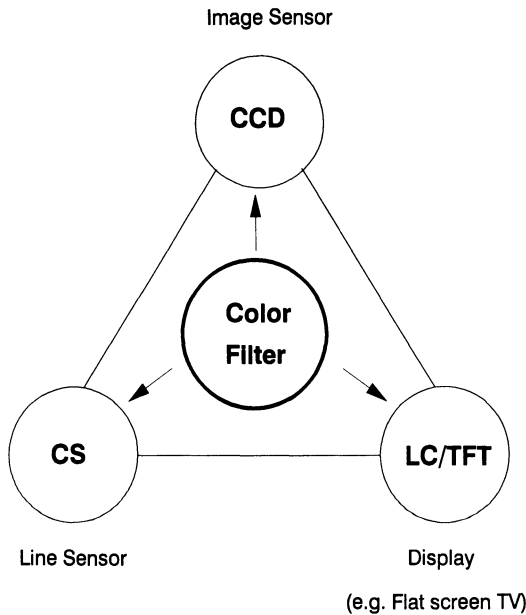
Figure 2.1. Applications for micro color filters. CS, Crystal shutter; LC/TFT, liquid crystal/thin film transistor; CCD, Charge Coupled Device.

The three main applications for micro color filters are shown in Fig. 2.1. Two of these are as sensors in scanning devices to convert colored graphics or text into digitized information: this enables nonimpact printers such as ink jet and thermal to produce a full-color hard copy print. They are therefore essential in devices such as electronic cameras (see *Chapter 8, Section 6.1*) and color copiers (see *Chapter 7, Section 2.3*). The third application, namely displays, is perhaps the most glamorous one. Here, color filters are used in conjunction with liquid crystals, usually twisted nematics, and thin film transistors (e.g., amorphous silicon) to produce full-color flat screen displays, such as flat screen televisions.

2.2. FLAT SCREEN TELEVISIONS

A flat screen television has several potential advantages over conventional cathode ray tube televisions. These include low power consumption; clear pictures, even in daylight; and the simplicity of the principle upon
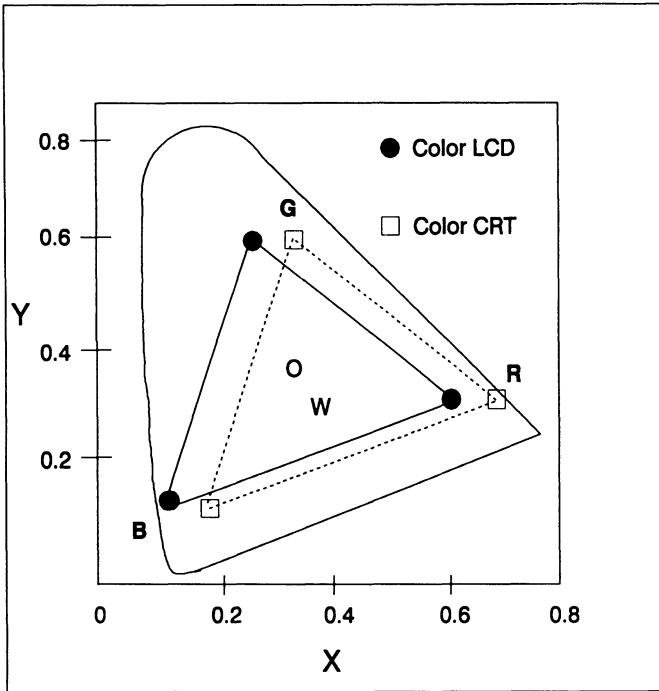
Figure 2.2. Color coordinates for a liquid crystal display TV and a color cathode ray TV, in Commission Internationale de l'Eclairage (CIE) color space. R, red; G, green; B, blue; W, white.

which it is based. However, all these advantages have not yet been realized. The screen is relatively dark because approximately only 30% of the incident light is seen for each primary color of red, green, and blue. To overcome this problem a fluorescent backlight with strong red, green, and blue emission is used, but this adds significantly to the power consumption of the device and therefore offsets one of its main attractions, namely low power consumption.[3] Also, it is proving difficult to produce screens larger than $5 \, cm^2$. As seen from Fig. 2.2 the color space trichromat of a color liquid crystal display flat screen television is comparable to that of a typical cathode ray tube television. This means that it can produce the same gamut of colors. (For details of the construction and operation of flat screen televisions, see refs. 1 and 2).

2.3. COLOR FILTER PREPARATION

There are two major ways of making color filters: by a dyeing method or by a pigment vacuum deposition method. Both use the primary colors for additive color mixing, namely red, green, and blue, as for conventional cathode ray tube televisions. This enables flat screen televisions based upon these color filters to use the same incoming signals as a conventional television.

2.3.1. Dyeing Method

This is a wet process and uses water-soluble dyes. It is an approach being pursued by several companies including Toshiba and Sharp. The simplified process is shown in Fig. 2.3. In the first step, photomicrolithography is used to produce the required matrix for the first color, for example, red. The substance used is normally gelatine or fish glue: this is then dyed with a water-soluble red dye. The process is repeated twice more to produce the green and blue color filters, thereby giving the complete matrix of red, green, and blue (Fig. 2.3a; Fig. 2.3b shows a plan view of the complete matrix).

The red, green, and blue dyes used must be water-soluble, have the correct spectral characteristics, and be capable of dyeing the substrate. They should also have good fastness properties, especially to light. Acid, reactive, or direct dyes are normally used. Typical dyes are CI Reactive Red 120 (**2-1**), CI Acid Blue 83 (**2-2**), CI Acid Yellow 42 (**2-3**), and CI Direct Blue 86 (**2-4**). The yellow (**2-3**) and the blue (**2-4**) are used to produce the green dye, owing to the scarcity of suitable homogeneous green dyes.
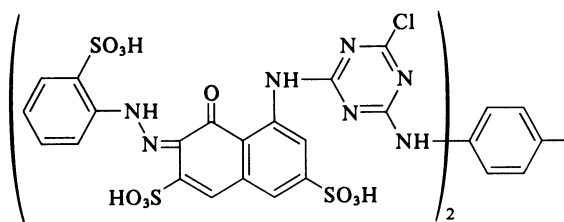
2-1 Red
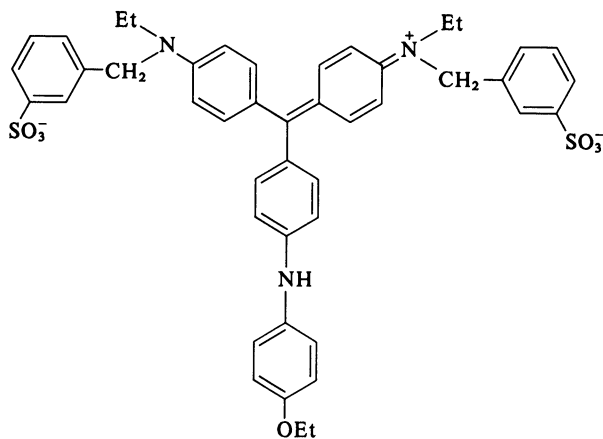
2-2 Blue
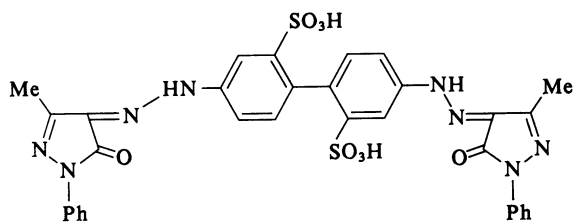
2-3 Yellow

Green
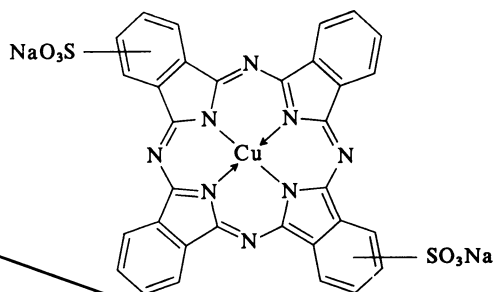
2-4 Blue
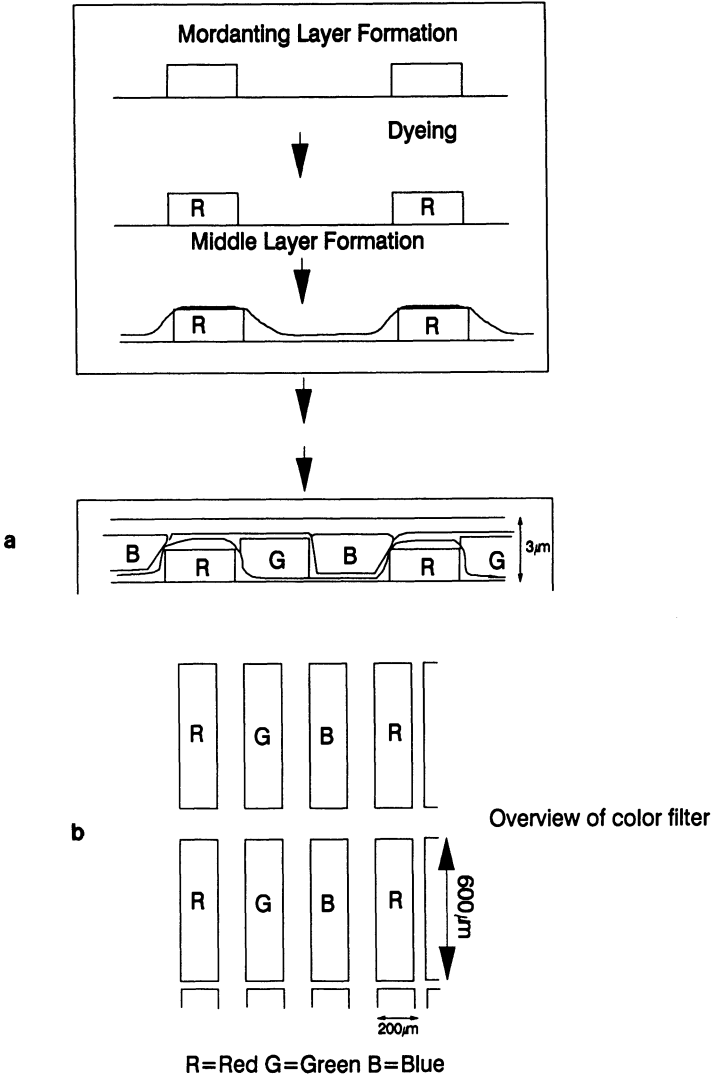
Figure 2.3. Dyeing method: Color filter formation process. R, red; G, green; B, blue. (a) Cross-section and (b) overview of color filter.

2.3.2. Pigment Method

This is a dry method and uses pigments that can be deposited by sublimation *in vacuo*.[2] Again, photomicrolithography is used to produce the matrix. In the first step, the photoresist is deposited on the substrate in those areas in which pigment is not to be deposited permanently. The pigment is
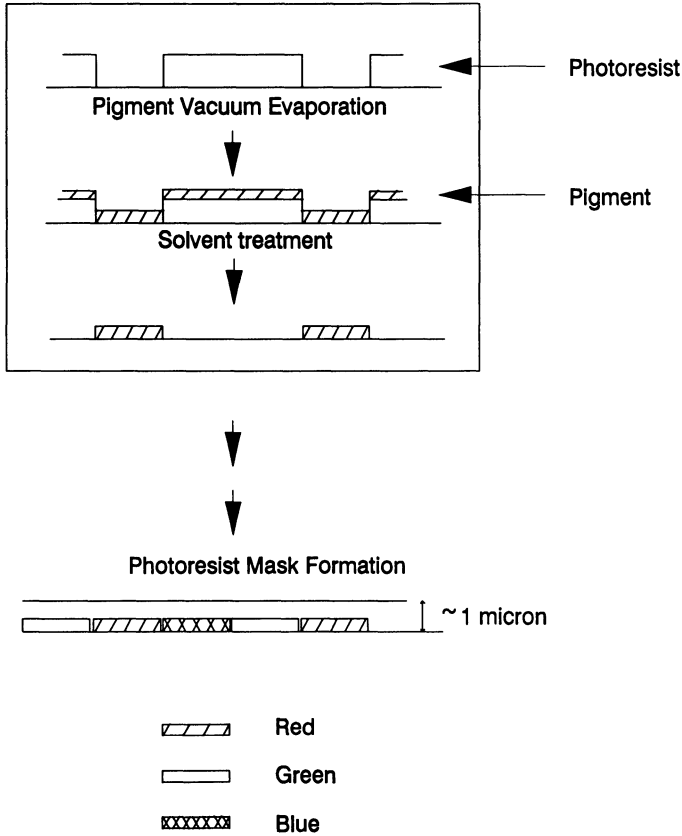
Figure 2.4. Pigment vacuum evaporation method.

then deposited by vacuum evaporation. Treatment with a solvent such as MIBK/isopropanol then removes the photoresist (plus the pigment deposited on it) to give the desired matrix of the pigment. The process is repeated twice more to give the final matrix of red, green, and blue pigments (Fig. 2.4).

The advantages of the pigment process lie in its simplicity, the production of a thinner color layer (typically 0.5μ vs. 3μ for a dye layer) and especially the higher durability of pigments relative to dyes to agents such as light. Canon, among others, seems to be pursuing the pigment approach to color filters.

Typical pigments are the perylene (2-5) for the red, and copper phthalocyanine (2-6) for the blue. These red and blue pigments are generally satisfactory but until recently the green pigment posed a problem. Lead
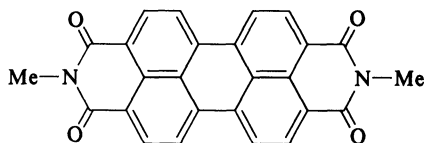
2-5
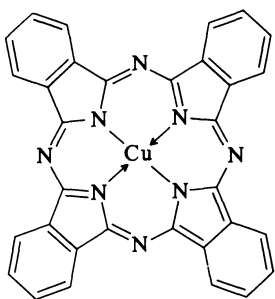
2-6
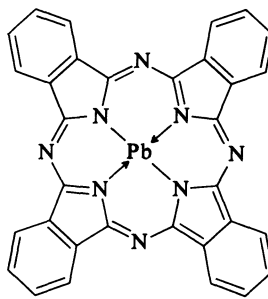
2-7
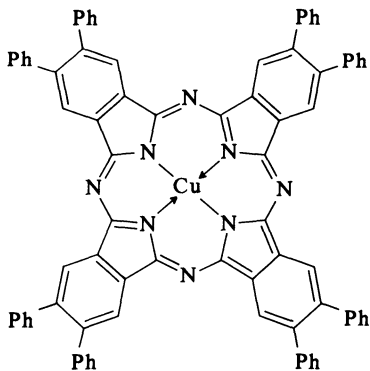
2-8

phthalocyanine (**2-7**) has been used but it is unsatisfactory in several respects. Both ICI[4] and Canon[5] have patented octaphenyl copper phthalocyanine (**2-8**) as a green pigment for color filters. It is claimed to have good properties.
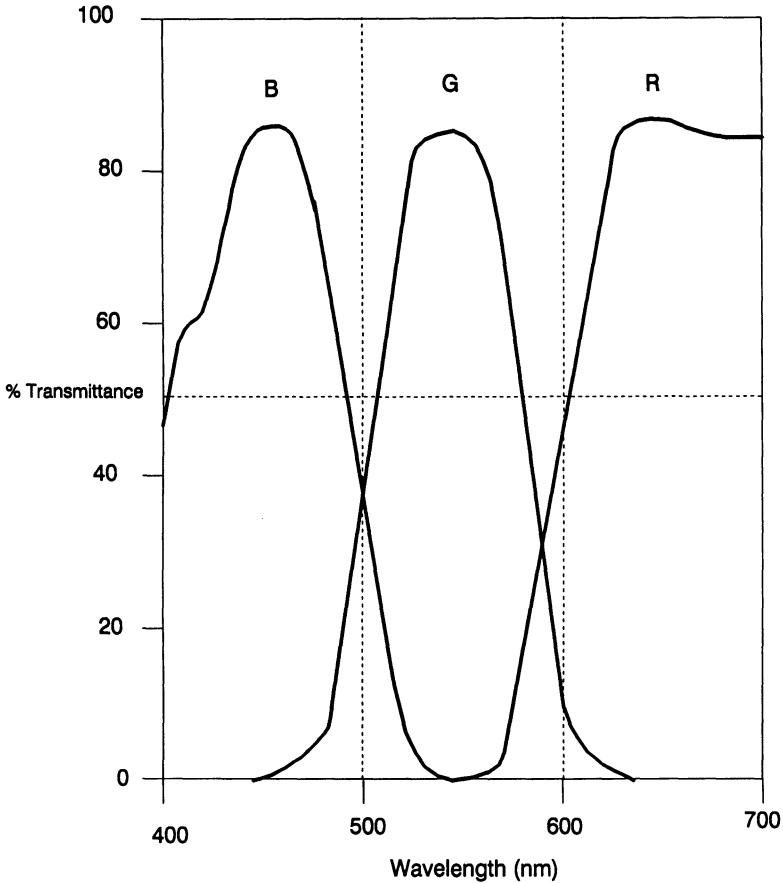
Figure 2.5. Desired transmittance spectra.

2.4. SPECTRAL CHARACTERISTICS

The ideal spectral characteristics of colorants for color filters are shown by Fig. 2.5. As seen from Figs. 2.6–2.8, the spectral curves of the red (**2-5**), green (**2-7**), and blue (**2-6**) pigments are not ideal. However, they are typical of what is currently available. The green is still the least satisfactory—it is too blue. This can be corrected to some extend by adding a small amount of a yellow pigment. Isoindolines such as (**2-9**) have been used.

2-9   R =
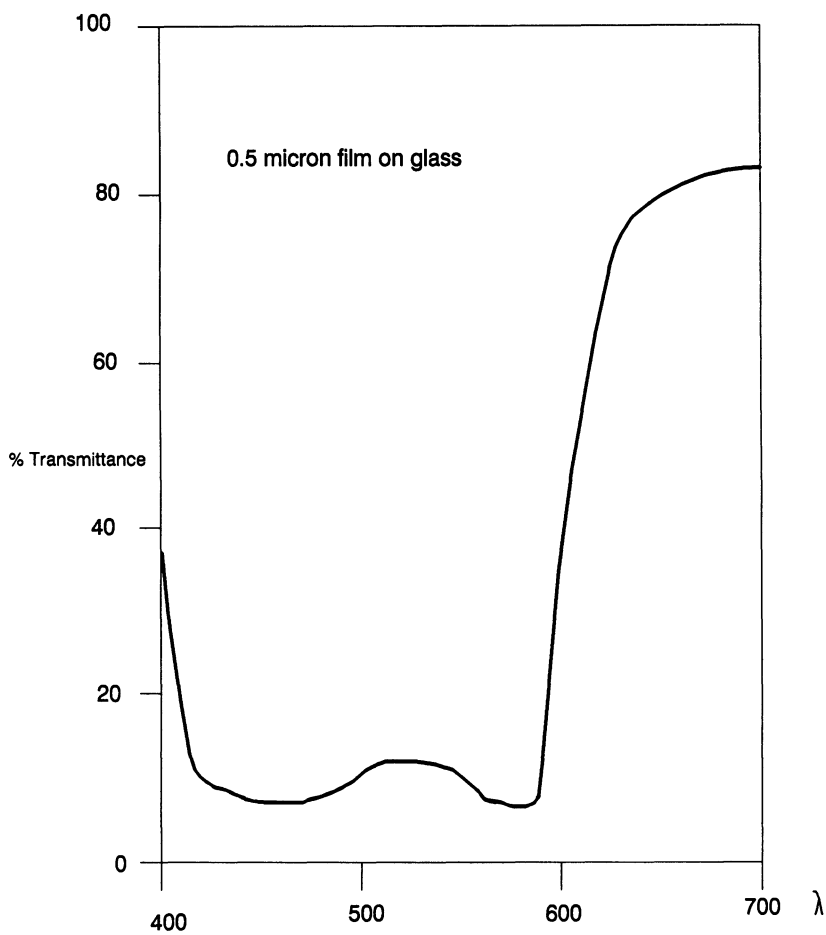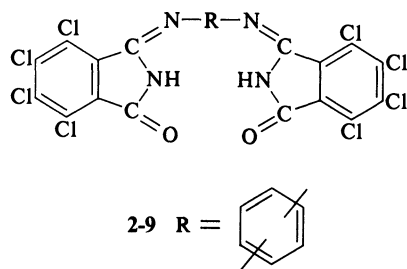
Figure 2.6. Transmittance spectrum of *N,N*-dimethyl perylenetetracarboxydiimide on glass.
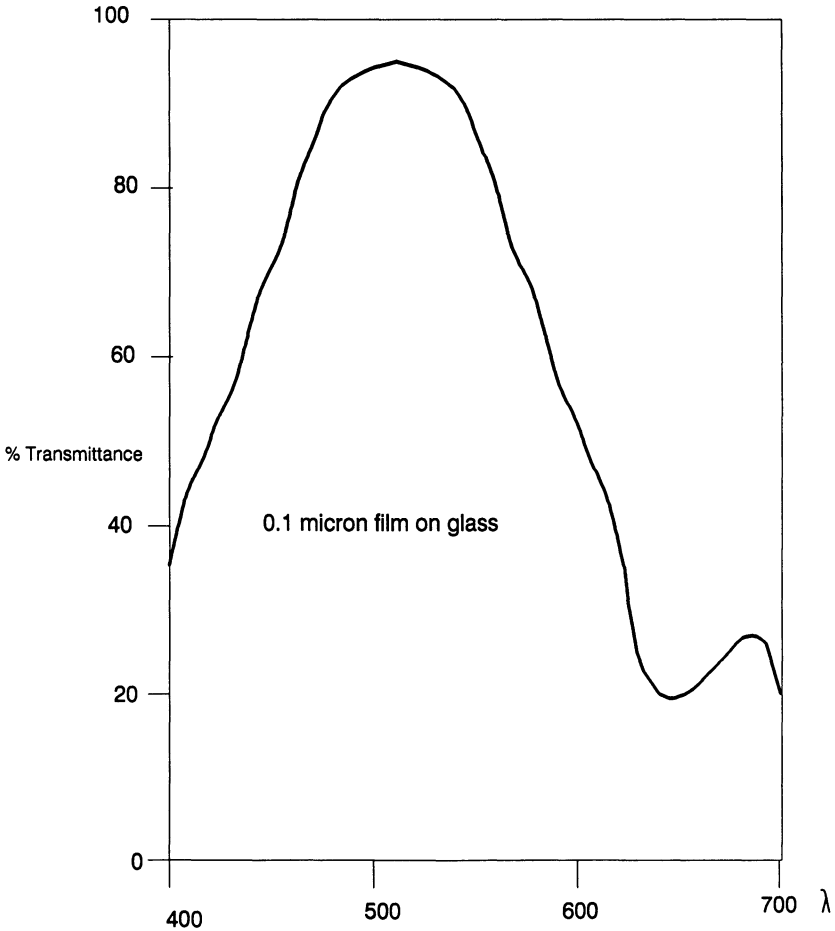
Figure 2.7. Transmittance spectrum of octa-4,5-phenyl copper phthalocyanine on glass.

2.5. SUMMARY

Micro color filters are finding increased use in both scanning devices such as charge coupled devices and in displays such as flat screen televisions. In contrast to the majority of colorants used in hi-tech applications, color filters require the three primary *additive* colors red, green, and blue, not the three primary *subtractive* colors yellow, magenta, and cyan.

Two general methods are employed for the preparation of micro color filters: the dyeing method and the pigment method. The dyeing method is a wet process using water-soluble dyes whereas the pigment method is a dry
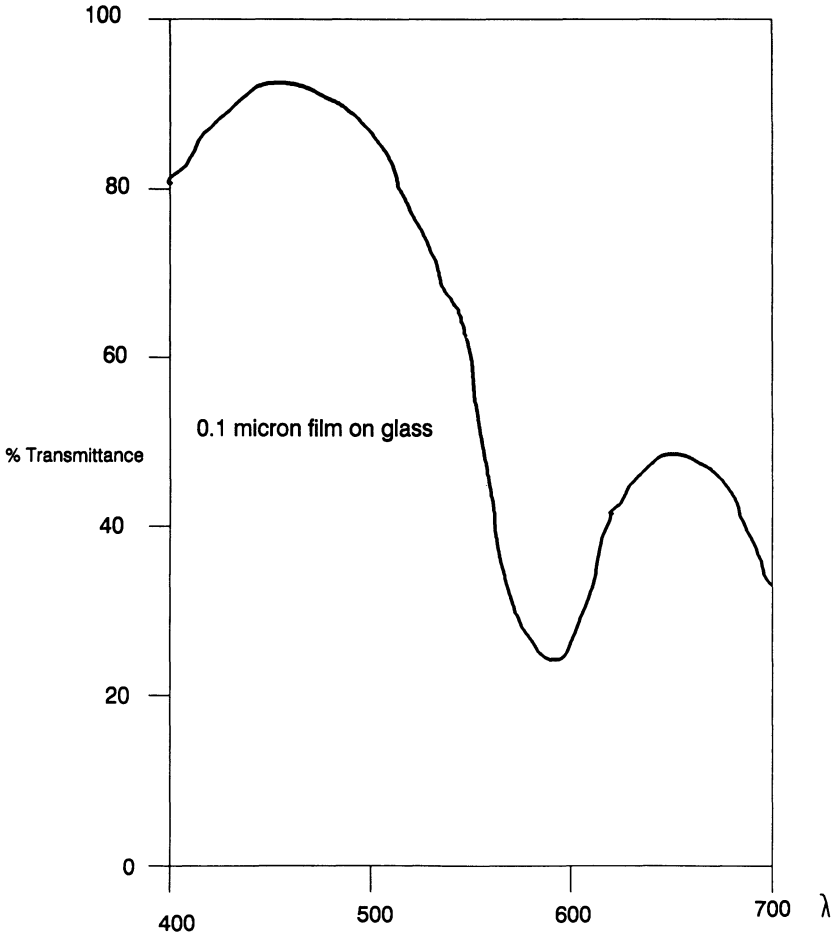
Figure 2.8. Transmittance spectrum of copper phthalocyanine on glass.

process using a vacuum deposition technique. The higher durability of pigments relative to dyes, especially to light, and the advantages of a dry process seem to favor the pigment method.

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3

Laser Dyes

3.1. INTRODUCTION

Laser technology is another area in which organic dyes are beginning to find application. The first continuous laser was demonstrated in 1961 and operated in the near infrared spectrum.[1] Since then, several inorganic lasers have been developed which emit from the ultraviolet through the visible into the near and far infrared regions of the electromagnetic spectrum (Fig. 3.1.). However, the fact that these inorganic lasers emit only at very few specific wavelengths is an obvious drawback. In contrast, dye lasers cover the entire visible and near infrared spectrum from <400 nm to 1000 nm and have a
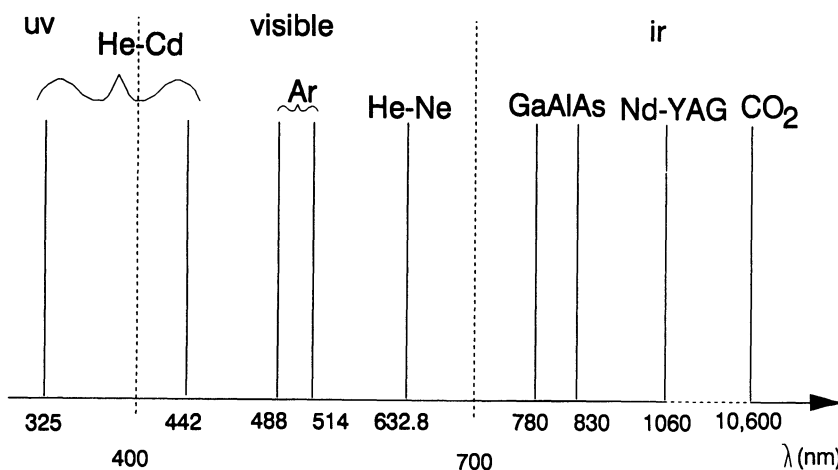
Figure 3.1. Inorganic laser emissions. He-Cd, helium-cadmium; Ar, argon ion; He-Ne, helium-neon; GaAlAs, gallium-aluminum-arsenide; Nd-YAG, neodymium yttrium-aluminum-garnet; CO$_2$, carbon dioxide.

far greater tunability than the inorganic lasers. In contrast to inorganic lasers, which emit very narrow bands (Fig. 3.1), dye lasers emit a broad band of radiation. This means that any lasing wavelength, whether narrow or broad, can be obtained from dye lasers by using appropriate filters (wavelength selectors). Consequently, dye lasers have become increasingly popular, especially in the field of Raman spectroscopy.[2,3]

3.2. BASIC THEORY

Before describing the dyes used it is worth outlining some basic principles of the operation of laser dyes and their properties.[4,5] The word laser is the acronym for light amplification by stimulated emission of radiation. For an atom or molecule to exhibit stimulated emission, it must be capable of excitation to one of its excited levels and must have a vacant energy level of lower energy. Lasing occurs when incident radiation interacts with a molecule that exists in an excited state, thereby causing (or stimulating) the molecule to decay by emission of radiation to a lower energy level. The frequency of the radiation emitted corresponds to the difference in energy between the two energy levels and is found to be in phase with and to travel in the same direction as the incident stimulating radiation. The incident radiation must possess a frequency close to but not necessarily the same as the emitted radiation to stimulate such an emission.

The problem is, of course, that atoms and molecules prefer to exist in their ground state (lowest energy level) and so a means has to be found for promoting a high proportion of them into an appropriate excited state in preparation for stimulated emission to occur. The situation in which the molecules exist predominantly in an excited state rather than the ground state is known as population inversion and is brought about by "pumping" the system with a source of energy. In the case of a dye laser the pump source is usually another laser.

Unfortunately, a good population inversion is not the only criterion for a successful laser dye, since once the inversion has been attained, an efficient decay from the excited state back to the ground state must occur upon stimulation by the incident light. This means that the dye must be an efficient fluorescer and must not lose a significant amount of energy by alternative processes such as nonradiative decay and intersystem crossing.

At this point it might seem that laser dyes offer few benefits: they usually require a second laser to pump them, and their output is lower than that of the pump laser, since the overall process is never 100% efficient and losses are inevitable in practical systems. However, as previously mentioned, the advantage of laser dyes is their tunability. In practice they are used to convert the essentially monochromatic output of conventional lasers into a wider
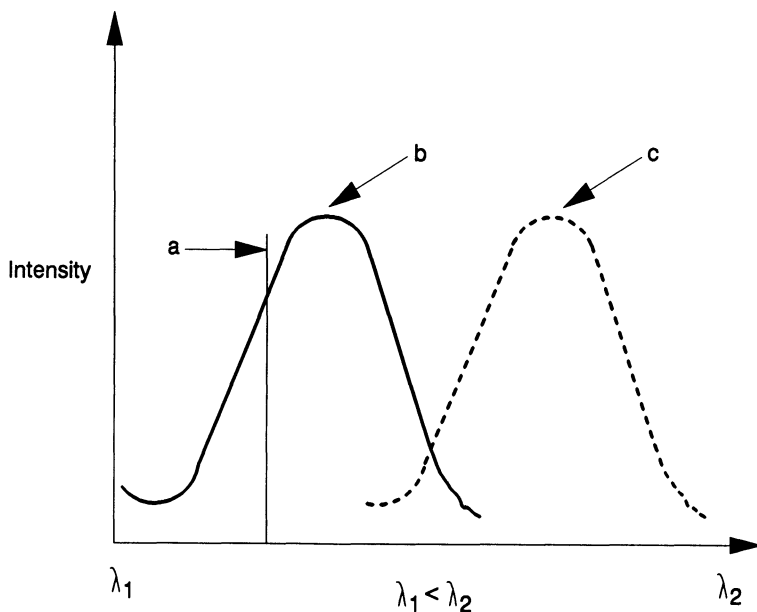
Figure 3.2. Relationship between pump laser wavelength and dye laser wavelength. (a) Pump laser wavelength; (b) laser dye absorption curve; (c) laser dye emission curve.

band of laser wavelengths (Fig. 3.2). The pump laser emits a wavelength (a) coinciding with a point on the absorption curve of the dye (b). This causes a population inversion, and lasing then occurs from the dye (curve c) corresponding to the fluorescence spectrum of the dye.

Because the laser emission is essentially fluorescence of the dye, the wavelength of the dye laser is always longer than that of the pump laser. Wavelength selectors are frequently used to isolate just a portion of the dye laser output, effectively converting the pump laser output into several bands of usable (though less intense) wavelengths of laser light. This means that a rather expensive pump laser can be used to generate a much wider output of laser light using comparatively inexpensive dyes.

3.3. DYE TYPES

As with textile dyes, where many dyes are required to provide a full gamut of shades, several laser dyes are needed to cover the whole region of the electromagnetic spectrum from the ultraviolet to the infrared. Each laser dye is effective only within a 50–100 nm range. Table 3.1 shows how the spectrum from 400 to 1000 nm can be covered using typical laser dyes. In

Table 3.1. Laser Dyes
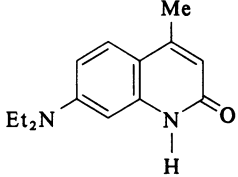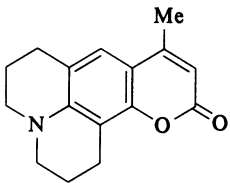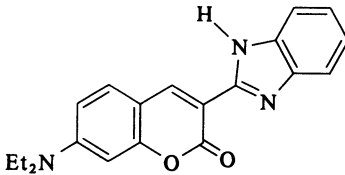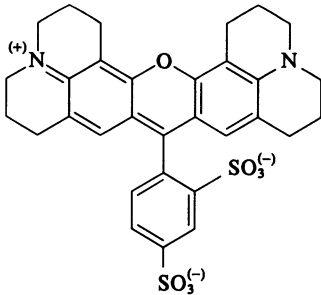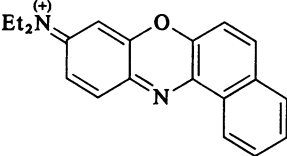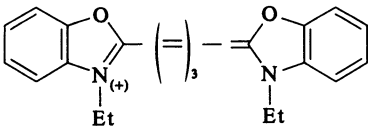
Structure	Absorption max (nm)	Lasing max (nm)	Name
	360	425	Carbostyril 165
	389	480	Coumarin 102
	436	573	Coumarin 7
	576	648	Rhodamine 101
	628	690	Nile Blue
	687	780	DEOTC

Table 3.1. (Continued)

Structure	Absorption max (nm)	Lasing max (nm)	Name
	823	950	Cyanine IR 140

the region from 400 to 500 nm, the carbostyril and fluorescein classes provide effective laser dyes whereas in the region from 500 to 800 nm, xanthenes and the structurally related oxazines dominate. Paradoxically, these classes of dye are among the oldest synthetic dyes and were discovered during the last century. Cyanine dyes are dominant in the infrared region.

Laser dyes have to be very pure since impurities frequently quench the laser output.[6] The dyes are usually dissolved in a very pure solvent such as water, ethanol, or dimethylformamide, and the choice of solvent can affect the strength and position of the laser output. The solvent therefore gives a further parameter for control. Weak dye solutions are generally used (e.g., 10^{-3}–10^{-4} molar), and the dye solution is circulated through a cell upon which a pump laser is focused. The dyes are circulated to prevent rapid overheating, which occurs under the intense irradiation, and a method of cooling is usually incorporated into the circulation system as an extra precaution.

Improvements that could be made to laser dyes include extending their range of output and improving their stability. For instance, lifetimes of laser dyes vary from days to months depending on use. This lack of stability is hardly surprising since fluorescent dyes have notoriously poor light fastness.

The discovery of fluorescence from a new type of excited state, a twisted intramolecular change transfer (TICT) state, provides the possibility of superior laser dyes.[7] Compounds which form TICT states are different from conventional laser dyes and have the advantages over existing laser dyes of (a) increased stability and (b) increased tunability of lasing wavelengths.

3.4. SUMMARY

Laser dyes appear to have established themselves fairly quickly. However, some improvements could be made, such as extending the range of

output of the dyes and increasing their stability. The lifetimes of laser dyes vary between days and months depending on use. This lack of stability is perhaps not surprising in view of the fact that the fluorescent dyes used as laser dyes have notoriously poor light fastness on textiles and thus have little or no importance as textile dyes.

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4

Colorants for Nonlinear Optics

4.1. INTRODUCTION

As the name implies, nonlinear optics[1-3] is concerned with the interaction of electromagnetic radiation with various media to produce new radiation which is altered in phase, frequency, amplitude, etc., from the incident radiation. The rapid growth of laser technology (nonlinear optic effects are only observed with laser light) coupled with the telecommunications industry's need for sophisticated optical switching devices required for data transmission in this computer age has prompted an enormous interest in nonlinear optical materials.

4.2. NONLINEAR OPTICAL EFFECTS AND APPLICATIONS

Equation (4.1) is the basic equation governing optical effects in *molecular* systems:

$$P = \alpha E + \beta E^2 + \gamma E^3 + \cdots \tag{4.1}$$

where P is the polarization induced in a molecule by a local electric field E.

In *macroscopic* systems Eq. (4.2) applies. It is the same as Eq. (4.1) except the coefficients are different.

$$P = \chi^{(1)} E + \chi^{(2)} E + \chi^{(3)} E + \cdots \tag{4.2}$$

The first term represents the *linear* effects and is associated with the refractive index. It is the second and higher terms which represent the *nonlinear* effects. Of these, the most important for practical applications is the second-order

33

Table 4.1. Electric Susceptibility Functions $\chi^{(2)}$, Terminology Used for the Effect, and Known Applications

Susceptibility	Effect	Application
$\chi^{(2)}(0; \omega, -\omega)$	Optical rectification	Hybrid bistable device
$\chi^{(2)}(-\omega; \omega, 0)$	Electro-optic (Pockels) effect	Modulators
		Variable phase retarders
$\chi^{(2)}(-2\omega; \omega, \omega)$	Frequency doubling	Harmonic generation
$\chi^{(2)}(-\omega_0; \omega_a, \omega_b)$	Frequency mixing	Parametric amplifiers
		I.R. up convertors

term, βE^2. There are several nonlinear optical effects (Table 4.1) but the phenomenon known as *frequency doubling* is potentially the most important.

The frequency doubling effect whereby the incident radiation is converted to radiation of double the frequency is especially useful in both telecommunications and optical data storage. For example, in telecommunications the most efficient way to transmit data is by using infrared laser radiation, for example, 1200 nm, produced by an indium-phosphorus laser diode, along optical fibers.[4] However, detection of this long wavelength radiation is inefficient. In contrast, visible radiation is much easier to detect but is an inefficient transmitter of data. Consequently, an important use of nonlinear optical materials would be to convert the infrared radiation to visible radiation by frequency doubling, thus enabling easier detection of the signals (Fig. 4.1).
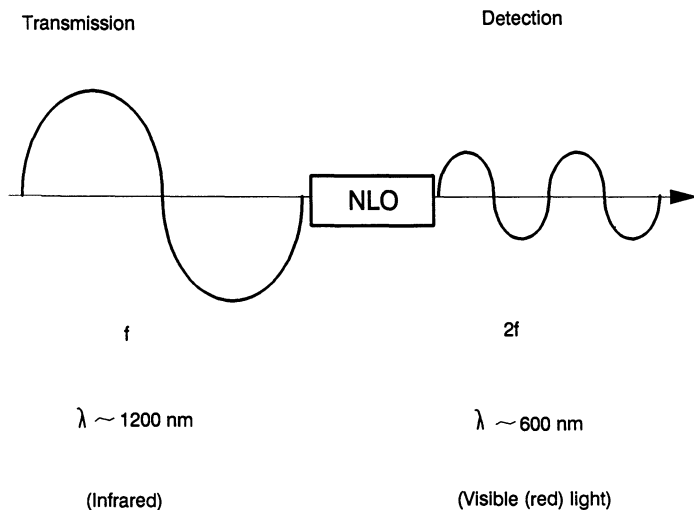
Figure 4.1. Frequency doubling effect for optical communications.
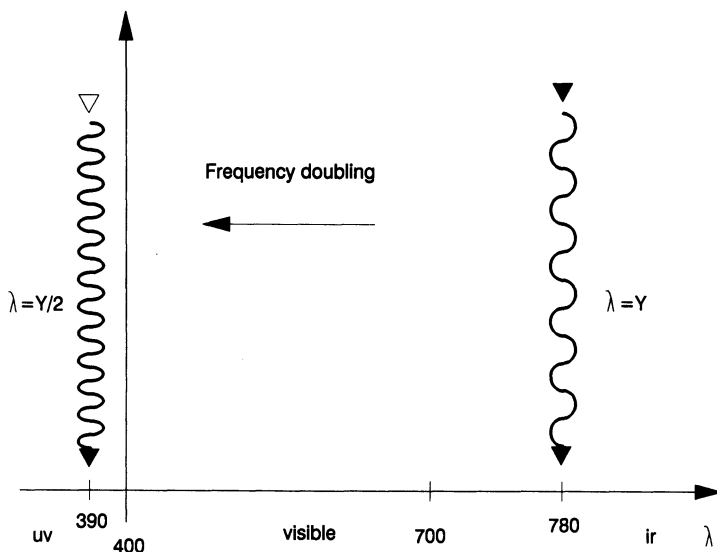
Figure 4.2. Frequency doubling effect for optical data storage.

The second important area for frequency doubling is optical data storage. Currently, semiconductor lasers which emit in the near infrared at 780 nm are used to write and then read the information (see *Chapter 11, Section 4.3.2*). Doubling the frequency of this infrared radiation would produce near ultraviolet radiation at 390 nm (Fig. 4.2). Since the wavelength is inversely proportional to the energy of the radiation (Eq. 4.3), the laser radiation at 390 nm has a wavelength four times less than that at 780 nm, thus enabling four times more information to be recorded on a given area of optical disc.

$$E = \frac{hc}{\lambda} \tag{4.3}$$

where E = Energy, h = Planck's constant, c = Velocity of light, λ = Wavelength.

4.3. MOLECULAR POLARIZABILITY

Molecules capable of high polarizability (hyperpolarizability) give the best nonlinear optical effects. Organic molecules such as **4-1**, which have delocalized pi-electrons and which contain both donor (D) and acceptor (A) groups, have the largest β values. The relationship between hyperpolarizability and some nonlinear optical effects is shown in Fig. 4.3.
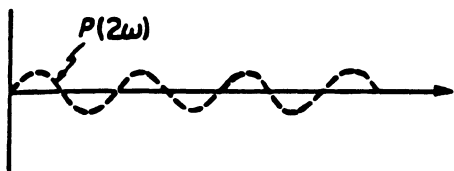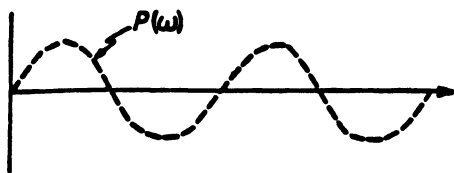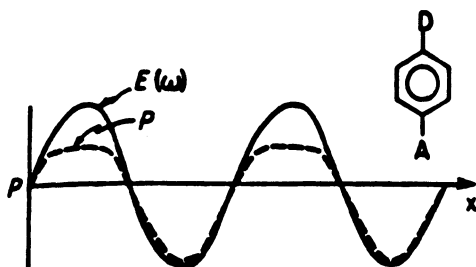
Figure 4.3. Top: Plot of the polarization response P to an incident electromagnetic wave of field strength $E(\omega)$ at frequency ω in a noncentrosymmetric medium. Bottom: Fourier components of P at frequencies $\omega, 2\omega$.
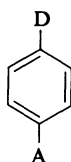
4-1

Molecules with extremely high hyperpolarizabilities (high β values) are known. However, these do not necessarily produce large nonlinear optical effects. To produce large nonlinear optical effects, the molecules need to be aligned correctly: in other words, they must align themselves in the macroscopic world in such a way that the individual effects of the molecules do not cancel each other out (Fig. 4.4). For example, the molecules must crystallize in a noncentrosymmetric fashion if the crystal is to show significant nonlinear optical effects.

4.4. NONLINEAR OPTICAL MOLECULES

Thus far we have seen that certain molecules can interact with electromagnetic radiation to produce nonlinear optical effects and that molecules
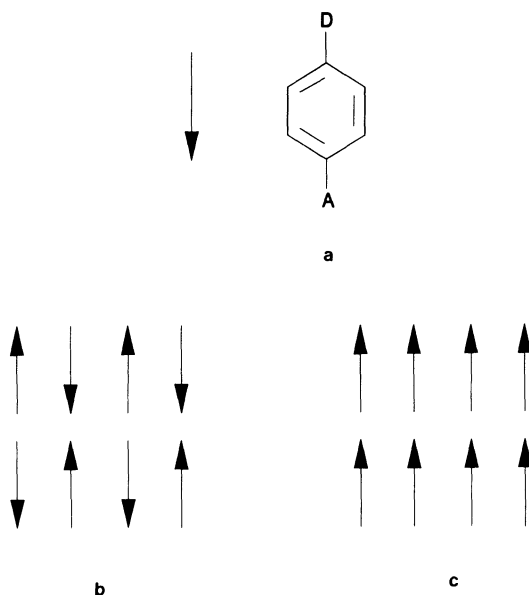
Figure 4.4. Importance of molecular alignment on nonlinear optical (NLO) effects. (a) Individual molecule—high polarizability; (b) centrosymmetric—no NLO effect; (c) noncentrosymmetric—high NLO effect.

with high hyperpolarizabilities are best for this purpose. In order for the effect to be realized practically, the molecules must align themselves correctly in the macroscopic state, i.e. in a noncentrosymmetric arrangement. We will now consider the kind of molecules which give the best nonlinear optical effects and the reasons for this.

Both organic and inorganic molecules can display nonlinear optical properties (Fig. 4.5). Theoretically, organic molecules are capable of producing the largest effects. Molecules containing a delocalized pi-electron system with asymmetrical charge distribution exhibit very large β values. The largest β values are obtained for molecules containing substituents that lead to low-lying charge transfer resonance states: for example, molecules containing a powerful electron-withdrawing group such as nitro conjugated to a powerful electron-donating group such as amino. The length of the conjugated path is also important. Thus, a *para* substituted isomer is the most effective non-linear optical material followed by the *ortho* isomer. The *meta* isomer, for which corresponding charge transfer states are not possible, is the least effective nonlinear material (Fig. 4.6 and Table 4.2).

It is possible to use molecular orbital techniques to calculate the β values of molecules and hence their hyperpolarizabilities. Such calculations indicate that extending the conjugation between donor and acceptor groups should

$\chi^{(2)}$ [esu]

-10^{-5}

InSb

-10^{-6}

$LiNbO_3$ (E.O.)

GaAs

-10^{-7}

$LiNbO_3$

-10^{-8}

KDP

-10^{-9}
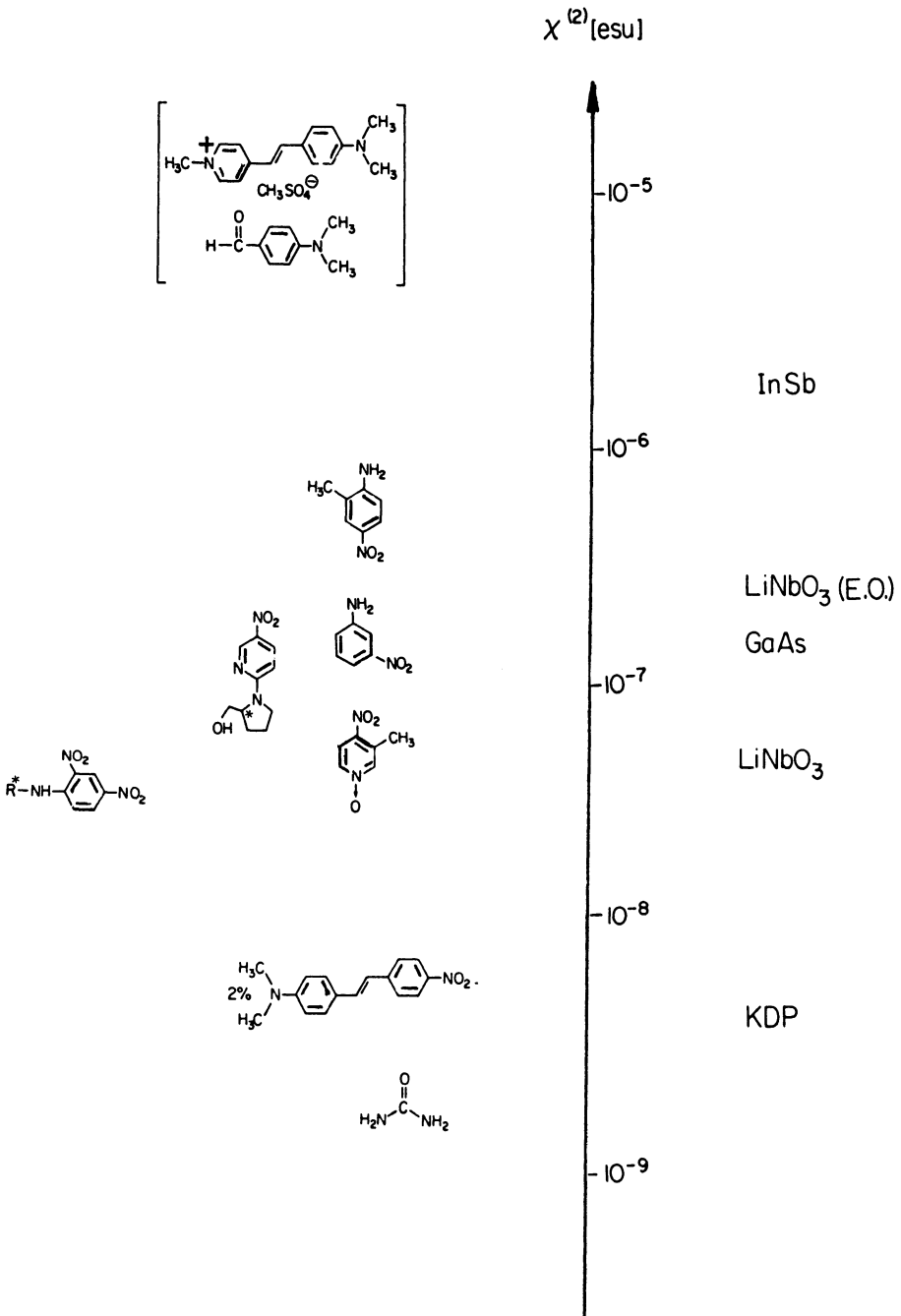
Figure 4.5. $\chi^{(2)}$ scale for various inorganic crystals (**right**) and organic crystals and films (**left**). R*, methoxycarbonylethyl.
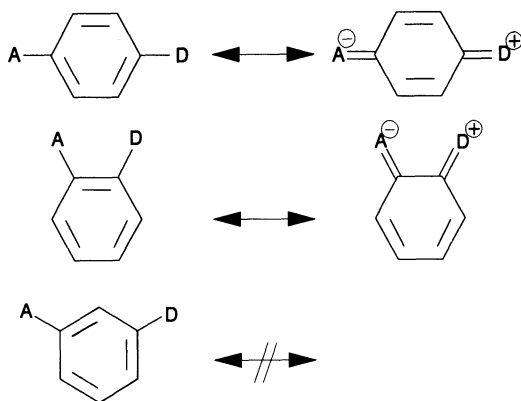
Figure 4.6. Ground-state and lowest energy polar resonance forms for *p*- and *o*-substitution. Resonance is forbidden in the case of *m*-substitution.

produce molecules with large β values. This is the case experimentally (Table 4.3).

Molecular orbital calculations indicate that merocyanine dyes such as **4-2** should have large β values. Indeed, a noncentrosymmetric crystal containing the related dye (**4-3**) has one of the largest known $\chi^{(2)}$ values.

Table 4.2. Experimental Values of β for Various Nitroanilines as well as Nitrobenzene and Aniline

Compound	$\beta_{exp} \times 10^{30}$ [esu]	β_{add}	β_{CT}
H₂N——NO₂	34.5	3.4	19.6
H₂N NO₂ (ortho)	10.2	1.7	10.9
H₂N——(NO₂ meta)	6	3.3	4
O₂N——	2.2	—	—
——NH₂	1.1	—	—

^{a} Also listed are the additive contribution β_{add} determined from summing the values for aniline and nitrobenzene and the charge-transfer contribution β_{CT} determined by the two-level model.

$$H_3C-\overset{+}{N}=\!\!=\!\!=CH-CH=\!\!=\!\!=O^- \longleftrightarrow H_3C-N=\!\!=\!\!=CH-CH=\!\!=\!\!=O$$

4-2

$$H_3C-\overset{+}{N}=\!\!=\!\!=CH-CH=\!\!=\!\!=N\overset{CH_3}{\underset{CH_3}{\big\langle}}$$

$$X^-$$
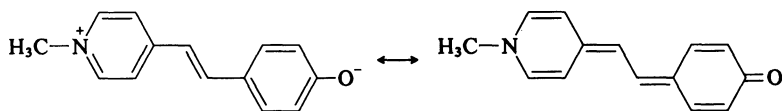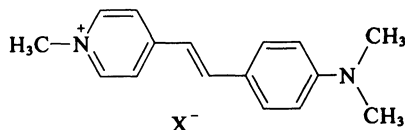
4-3
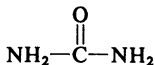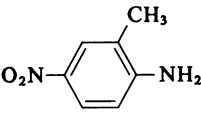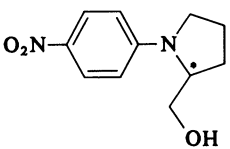
Table 4.3. Theoretical and Experimental β Values for a Series of Benzene and Stilbene Derivatives

Compound	$\beta_{CT} \times 10^{30}$ [esu]	$\beta_{exp} \times 10^{30}$ [esu]
$O_2N-\!\!\langle\ \rangle\!\!-NH_2$	19	34.5
$O_2N-\!\!\langle\ \rangle\!\!-CH=CH-\!\!\langle\ \rangle\!\!-NH_2$	227	260
$O_2N-\!\!\langle\ \rangle\!\!-CH=CH-\!\!\langle\ \rangle\!\!-N\overset{CH_3}{\underset{CH_3}{\big\langle}}$	383	450

4.5. MOLECULAR ALIGNMENT

Although the organic dyes referred to above have extremely high β values this potential is not realized practically because the molecules do not align themselves correctly in the macroscopic state. Hence, many of the β values cancel each other out (Fig. 4.4b). One of the major challenges therefore is to obtain media (crystals, liquids, or polymers) in which the molecules are correctly aligned to express their high β values to the fullest extent (Fig. 4.4c). Unlike the β values, which can be calculated theoretically, it is not possible to either predict or calculate whether molecules will form noncentrosymmetrical crystals. Experimentation is currently the only reliable method available.

Table 4.4. Relative Harmonic Intensity (a Measure of
the β-Value)

Crystalline powder	Rel. harmonic intensity
$NH_2-\overset{\overset{\textstyle O}{\|\|}}{C}-NH_2$	1.0 (0.13)
(MNA structure) 4-4	22.0 (3.0)
(pyrrolidine structure) 4-5	160.0 (21.8)

* Chiral center.

Several approaches are being tried to achieve the desired molecular alignment:

Incorporation of bulky substituents: for example, a methyl group in *para*-nitroaniline to give 2-methyl-4-nitroaniline (MNA) (**4-4**) (Table 4.4).
    Use of bulky counter ions in charged molecules: for example, methosulfate in the dye **4-3** (Table 4.5).
    Introduction of chiral centers: for example, the molecule **4-5** (Table 4.4).

Table 4.5. Harmonic Intensity (Relative to *m*-Nitroaniline)

Crystalline powder	Relative harmonic intensity
4-4	
m-Nitroaniline	1
MNA	3
4-3	
$^{\oplus}I^{\ominus}$	0
$^{\oplus}IO_3^{\ominus}$	0.01
$^{\oplus}NO_3^{\ominus}$	0.5
$^{\oplus}C_6H_5CH=CHCO_2^{\ominus}$	1.5
$^{\oplus}ClO_4^{\ominus}$	5
$^{\oplus}BF_4^{\ominus}$	10
$^{\oplus}ReO_4^{\ominus}$	18
$^{\oplus}CH_3OSO_3^{\ominus}$	30
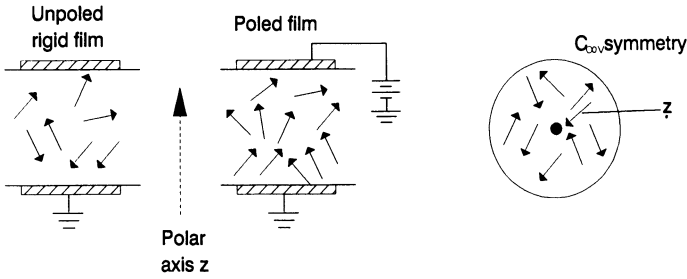
Figure 4.7. Schematic of imparting $C_{\infty v}$ symmetry (polar axis, isotropic perpendicular to the polar axis) to an isotropic medium containing permanent dipoles with an external electrical field E.

Molecularly aligned polymers: for example, heating a polymer to just above its glass-transition temperature, T_g, and then cooling in the presence of an external field (Fig. 4.7).

Molecularly aligned polymers: for example, doping a polymeric liquid crystal with a nonlinear optical material and then applying an electric field (Fig. 4.8).

2% DANS

m=0.5
n=0.5
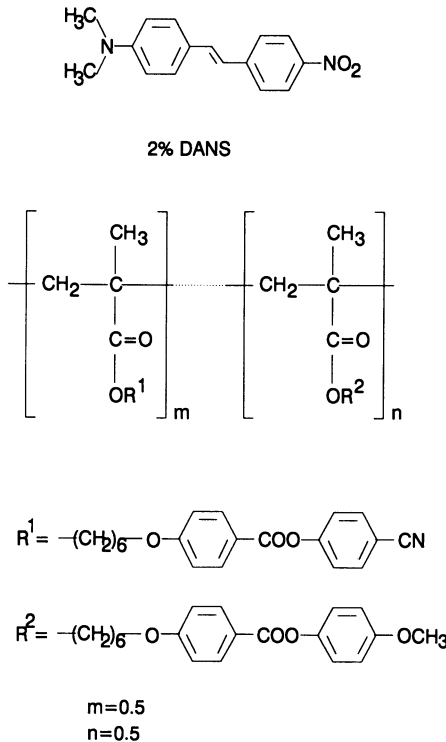
Figure 4.8. Components of a molecularly doped liquid-crystalline polymer film oriented by an external field and which exhibited large second harmonic generation (SHG). m=0.5, n=0.5.

Field-induced alignment of quasicrystalline dye aggregates: for example, photolysis of the colorless spiran dye (**4-6**) in solution to form the cationic dye (**4-7**) and application of an electric field.

4-6   **4-7**
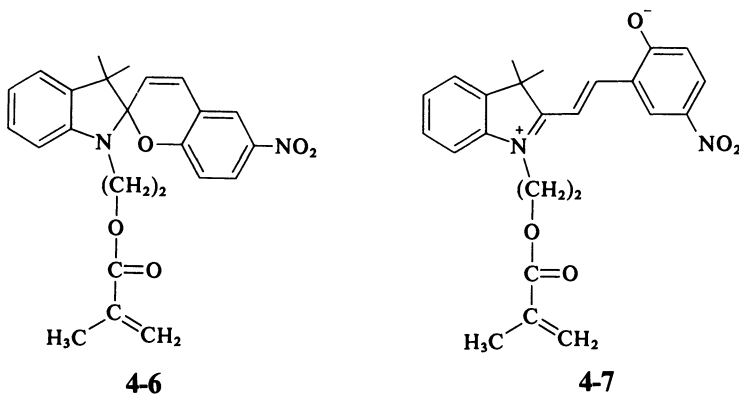
Langmuir-Blodgett techniques: for example, deposition of controlled molecular monolayers.

Of all these techniques, the most promising are the molecularly doped polymers with electric field alignment and Langmuir-Blodgett techniques.

4.6. SUMMARY

Nonlinear optical effects offer important advances in several areas, especially telecommunications and optical data storage. Inorganic and particularly organic materials having high polarizability (hyperpolarizability) are capable of exhibiting exceptionally high nonlinear optical effects on a molecular level; the problem lies in reproducing these effects on a macroscopic level. Several techniques are being evaluated to align the individual molecules to reinforce rather than cancel the individual nonlinear optical effects. The most promising are molecularly doped polymers and Langmuir-Blodgett techniques.

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5

Solar Cells

5.1. INTRODUCTION

The energy output from the sun is enormous; it has been estimated at 3.8×10^{26} W.[1] The amount of energy that falls on the earth's surface in clear weather, with the sun at its zenith, is approximately 1 kWm^{-2}. Nature has been harnessing this energy for millions of years using photosynthesis to convert the radiant energy into chemical energy. With the recent energy crises and the controversies over nuclear power, it is hardly surprising that serious efforts are now being made to convert solar energy into electrical energy.

5.2. PHOTOSYNTHESIS MIMICS

One obvious approach to the conversion of solar energy is to mimic nature's photosynthetic process. In photosynthesis it is the green pigment chlorophyll (5-1) which utilizes solar energy to synthesize carbohydrates

R = Me (chlorophyll a)
R = CHO (chlorophyll b)

5-1

5-2
R^1 – R^4 = alkyl, aryl

45
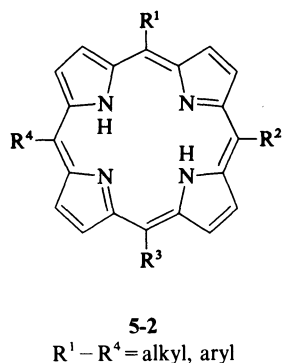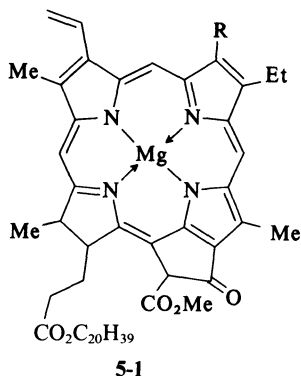
Al | Porphyrin | Au

Figure 5.1. A typical solar cell based upon a porphyrin.

from water and carbon dioxide. Chlorophyll is a porphyrin, and considerable work is being done in synthesizing porphyrins (5-2) as chemicals for converting solar energy into electrical energy.[2,3] For example, Kampas and co-workers[4] have produced cells based on porphyrins with efficiencies up to 1% (Fig. 5.1).

Another group of workers[5,6] has been investigating solar cells based upon merocyanine dyes, such as 5-3, and phthalocyanine pigments, such as 5-4; the latter are close synthetic analogues of porphyrins. A typical cell

5-3   5-4
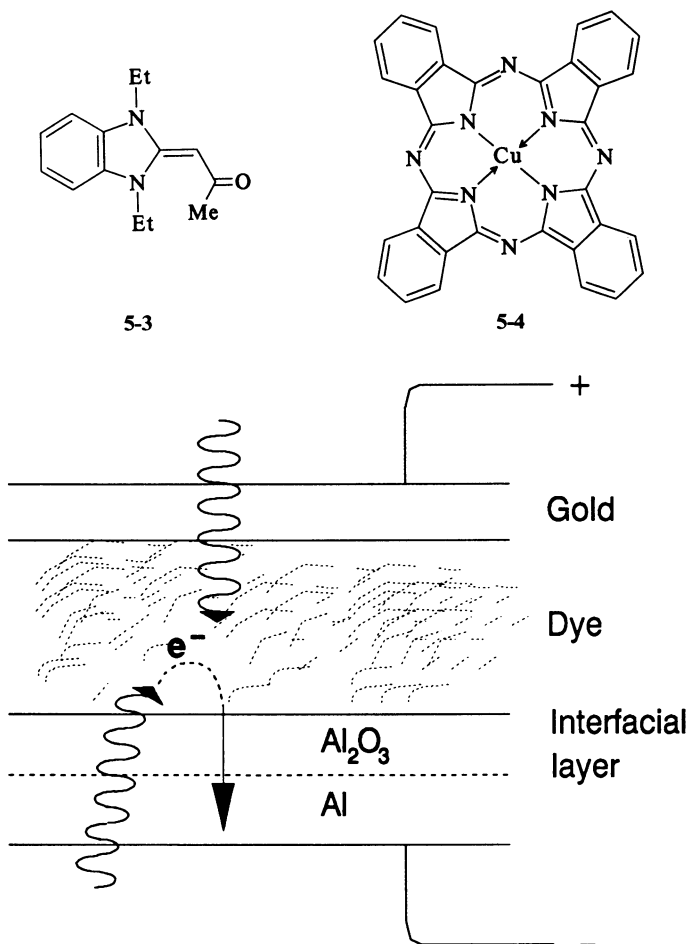
Figure 5.2. A photocell based upon an organic dye.

consists of a dye sandwiched between very thin layers of aluminum/aluminum oxide and gold. Although the mechanism is not fully understood, it is known that light shining through the transparent layers of aluminum oxide is absorbed by the dye which becomes excited and emits electrons. These migrate to vacant sites in the aluminum surface by way of a complex transfer process which is assisted by electronegative dopants such as iodine. The process creates a voltage across the middle layer (Fig. 5.2). Again, the efficiency of the photocell is low (0.31%).

5.3. MISCELLANEOUS COLORANTS

Several major dyestuff companies are also showing an interest in using colorants in solar cells. These include BASF[7] (mainly perylenetetracarboxydiimides) (5-5) and Bayer[8,9] [coumarins (5-6) and 4-aminoanthrimides (5-7)]. Shell, and in particular, the Agency of Industrial Science and Technology (Japan), has several patents on merocyanine dyes[10]; Teijin[11] has a patent on polymeric fluorescent dyes; and Fraunhofer[12] has one on the perylene pigments disclosed by BASF. BASF[13] also has patents on metal complex phenalenes (5-8).

R—N structure 5-5 and R structure 5-6

5-5   5-6

(a) X = N—SO₂—phenyl ; R = H
        |
        R²

(b) X = NR₂³, OR; R = CN

structure 5-7

5-7   5-8
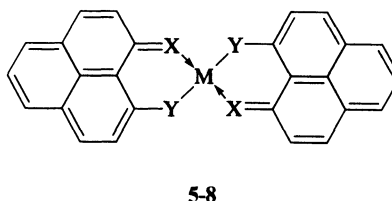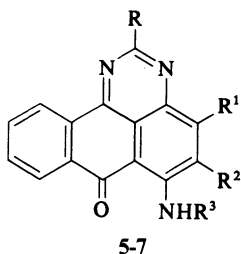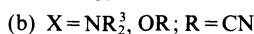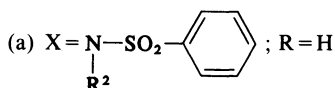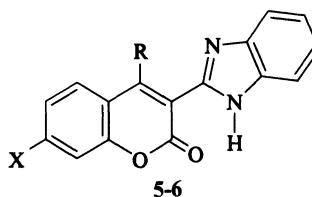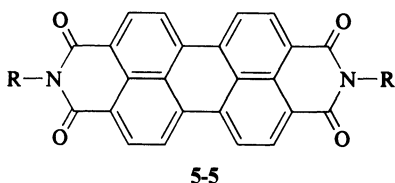
5.4. LUMINESCENT SOLAR CELLS

Dyes are also being used to improve the efficiency of conventional silicon cells. Silicon cells are of low efficiency (15%–20%) because they utilize

Power of photons/
×10³Wm⁻²per nm

Percentage relative response
of Si photovoltaic cell
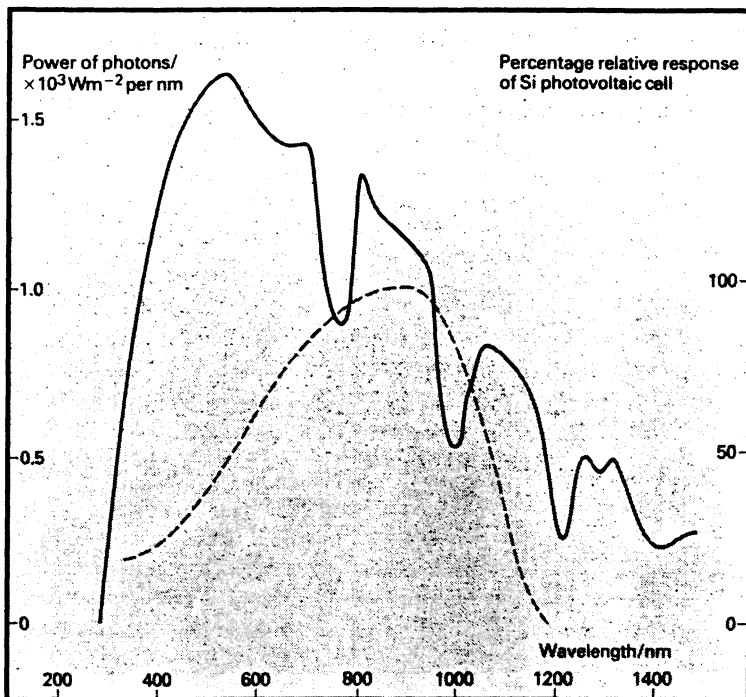
Figure 5.3. *Solid line*: the AM1 solar spectrum as a function of wavelength; AM1 = one standard air-mass screening of the solar radiation; *Broken line*: the spectral response for a silicon solar cell.

only a part of the solar radiation—unfortunately the low energy (near ir) radiation (Fig. 5.3). The cell is not sensitive to the higher energy near ultra-violet and blue radiation which is therefore wasted. If this high energy radiation could be collected and converted efficiently into the longer wavelength (low energy) radiation to which a silicon cell is most sensitive, then the efficiency of the cell should be enhanced greatly. In theory this is possible by using dyes that absorb the ultraviolet and blue radiation and re-emit it at longer wavelengths, viz. fluorescent dyes. In practice the dye would be present in a thin sheet of glass or plastic whose faces and edges are all mirrored to channel the emitted radiation to the edge of the sheet containing the silicon cells. A practical arrangement of the so-called luminescent solar cell[14] is shown in Fig. 5.4.

    Existing dyes do not satisfy the exacting criteria required. The highly fluorescent dyes available, such as fluorescein (**5-9**) and Rhodamine 6GP (**5-10**), have poor photostability and only a small Stokes shift, i.e., the difference between the absorbed and emitted radiation is too small (Fig. 5.5a). Although several dyes could be used in series (Fig. 5.6), this creates additional problems.
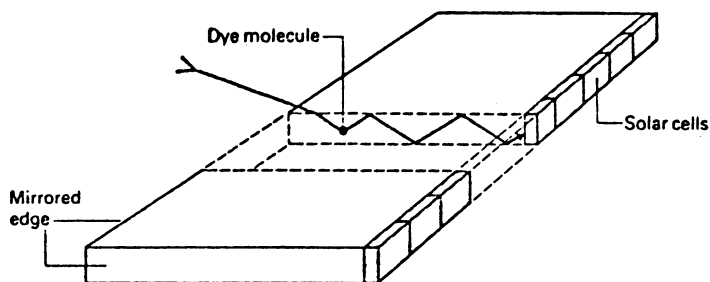
Figure 5.4. Design for a luminescent solar collector.
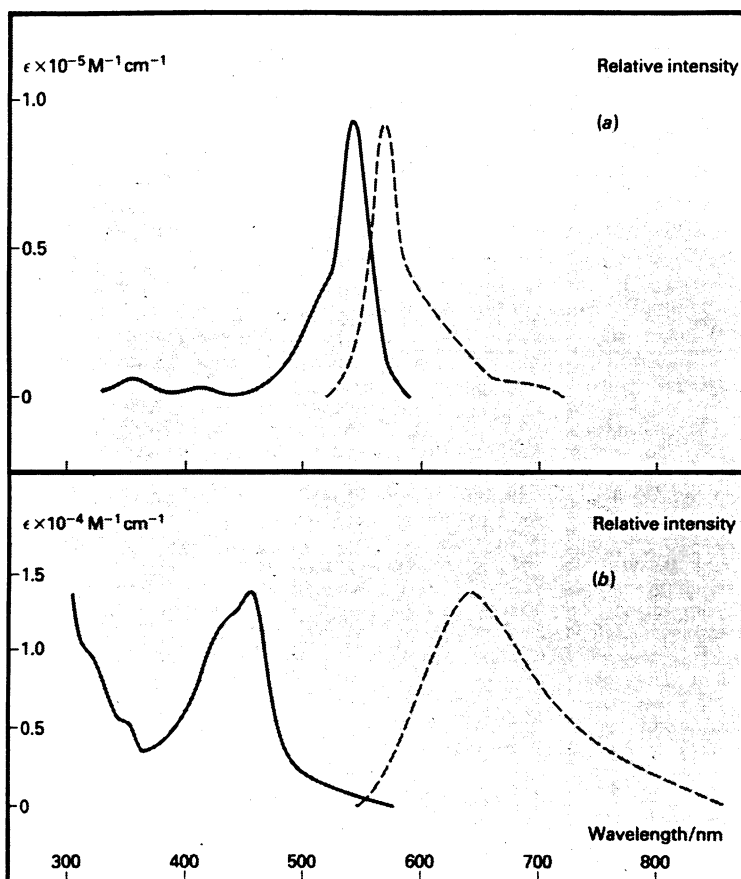
Figure 5.5. The absorption (*solid line*) and emission (*broken line*) spectra for (a) Rhodamine B, (b) the tris complex of 2,2'-bipyridyl with Ru (II).

Na$^+$O$^-$ ... O ... O

5-9

EtHN ... O ... $\overset{+}{\text{NHEt}}$

Me ... Me

CO$_2$Et
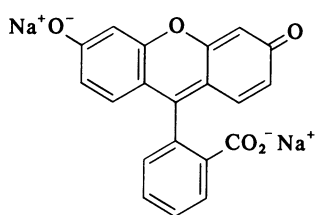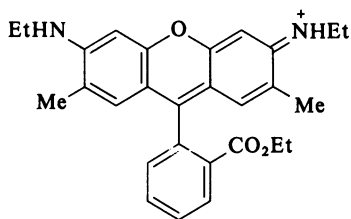
5-10

A different approach to increase the energy separation between the absorbed and emitted radiation is to utilize phosphorescence rather than fluorescence.[14] Phosphorescence is the emission of light from the lower energy excited triplet state, T_1, rather than from the excited singlet state, S_1, as is the case for fluorescence. Phosphorescence is therefore of much longer wavelength than the absorption band (Fig. 5.7). However, it is a spin-forbidden process and occurs either rarely or not at all in dyes. Heavy metals promote phosphorescence by increasing spin-orbit coupling and, indeed, in ruthenium(II) complexes of 2,2'-bipyridyl, for example, **5-11**, the Stokes shift is much larger than for the fluorescent dyes (Fig. 5.5b). However, the compounds have lower extinction coefficients than the dyes (15,000 vs. 100,000) and lower quantum efficiencies (0.3–0.5 vs. 0.6–1.0). Therefore, although these complexes represent a major step forward, the problem is by no means solved.
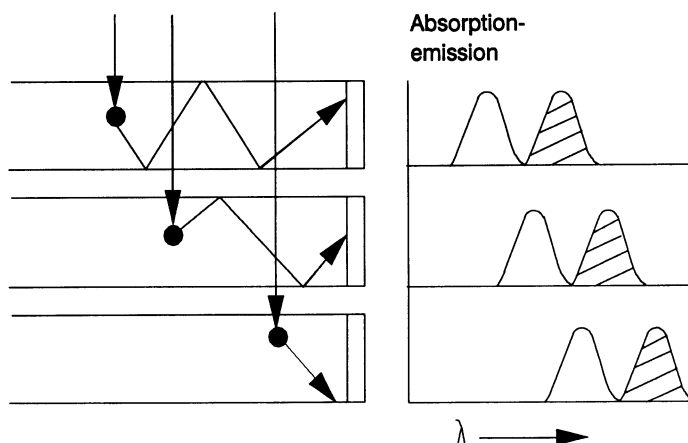
Figure 5.6. A multistack system. The dye in each layer absorbs a particular range of wavelengths (*unshaded curves*). The solar cells at the edge of each plate can be matched to the emitted light (*shaded curves*).
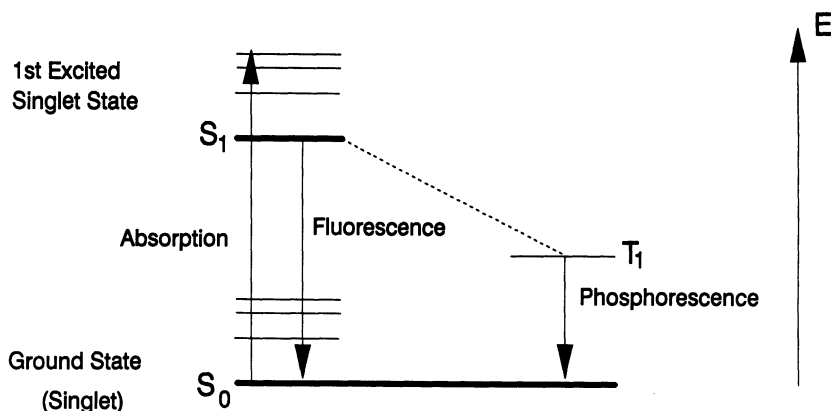
Figure 5.7. Relationship between absorption, fluorescence, and phosphorescence.
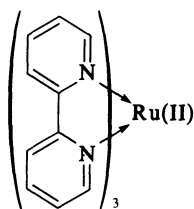
5-11

5.5. APPLICATIONS

Typical uses of solar cells are for powering low energy devices such as liquid crystal displays and traffic lights. Future uses could include the large scale generation of electricity using ground-based solar cells.

5.6. SUMMARY

The recent energy crises coupled with the unpopularity of nuclear power has stimulated the quest for alternative, clean, safe energy supplies. Solar cells offer such an opportunity. The energy output from the sun is enormous and nature already harnesses this energy via photosynthesis. Attempts to mimic photosynthesis by using chemicals closely related to chlorophyll such as phthalocyanines constitutes one approach. However, the efficiency of most solar cells, including those based on silicon, is very low and needs to be improved for them to make a real impact. Luminescent solar cells, although at an embryonic stage, look attractive because they harness more of the electromagnetic spectrum than conventional solar cells.

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6

Electrochromic Dyes

6.1. INTRODUCTION

Electrochromic dyes are those that undergo a color change with electrical energy. Electricity may cause the color change directly, as in dyes for electrochromic displays, or indirectly, as for dyes for electrochromic printing.

6.2. ELECTROCHROMIC DISPLAYS

The principle here is that colorless bis-cationic molecules such as paraquat derivatives are reduced electrochemically to the colored radical cation. For electrochromic displays, the colored radical cation is deposited at an electrode. The basic process is depicted by Eq. (6.1).

$$R-N^{+} \overset{+e}{\underset{-e}{\rightleftarrows}} R-N^{+\bullet} \qquad (6.1)$$

Colorless   Colored (purple)

Paraquat is where R = Me
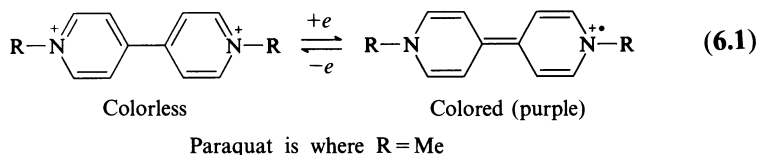
The problem has been to overcome aging. Aging is the phenomenon whereby repeated switching of the display, which is absolutely necessary for practical display devices, causes the deposited molecules to eventually crystallize and thereby inhibit the reverse (oxidation) process. Thus, diheptylviologen (6-1), the most commonly used viologen in experimental electrochromic display rigs, can stand only 5000–10,000 oxidation–reduction cycles.[1] By introducing steric hindrance and asymmetry into the molecules to inhibit crystallization, Barltrop and Jackson have improved the aging properties of viologens.[2] One of the best compounds is 6-2, which gives at least 20,000 cycles without aging.

$C_7H_{15}^n$—N$^+$=⟨⟩—⟨⟩=N$^+$—$C_7H_{15}^n$

6-1

Me

⟨⟩—CH_2—N$^+$=⟨⟩—⟨⟩=N$^+$—CH_2—⟨⟩

Me
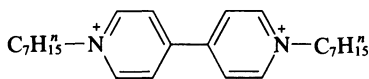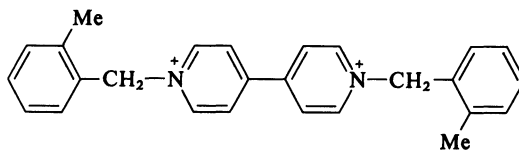
6-2

The work to date has been done primarily by academic researchers although it is obviously being pursued further by IBM.[1] Indeed, IBM has also patented the use of di-phthalocyanines in electrochromic displays.[3] Nippon Chemical Industries also has two patents on dyes for electrochromic displays, although these cover the isomeric 2,2'-bipyridyl system (**6-3**).[4]

=N$^+$ N$^+$=

$(CH_2)_n$
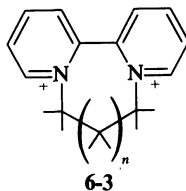
6-3

$n = 0, 1, 2$

It is fascinating that close analogues of powerful weedkillers such as paraquat should be finding use in a totally nonrelated, high-technology application.

6.3. ELECTROCHROMIC PRINTING

These dyes used in electrochromic printing[5] are the same as the colorless leuco dyes used in thermal printing (see *Chapter 8, Section 2*) except that they have been acylated. The dyes are incorporated into a moist paper, together with sodium bromide; electrical oxidation converts the bromide ion to bromine and the latter then oxidizes the leuco dye to the dye proper (Eq. 6.2).

$$\text{Leuco dye} \atop {+ \atop Br^-} \quad \xrightarrow{-e} \quad \left[\begin{matrix} \text{Leuco dye} & & \text{Dye} \\ + & \longrightarrow & + \\ Br_2 & & Br^- \end{matrix} \right] \tag{6.2}$$
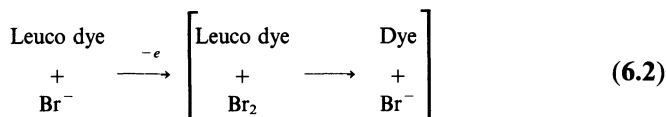
Dyes are available which cover the complete gamut of shades from yellow (**6-4**) to red (**6-5**) to blue (**6-6**).
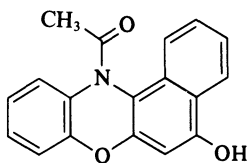
6-4
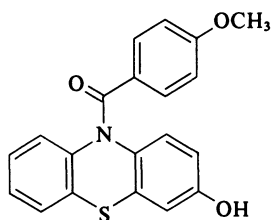
6-5
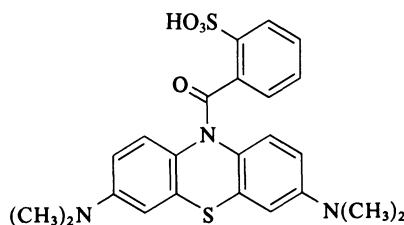
6-6

The leuco dyes are converted into basic dyes such as Methylene Blue (6-7; Eq. 6.3). Consequently, they will have poor light fastness on paper. Therefore, electrochromic printing will have to compete at the cheap end of the market, i.e., that dominated by thermal and pressure-sensitive printing.

6-6   6-7

$$(6.3)$$
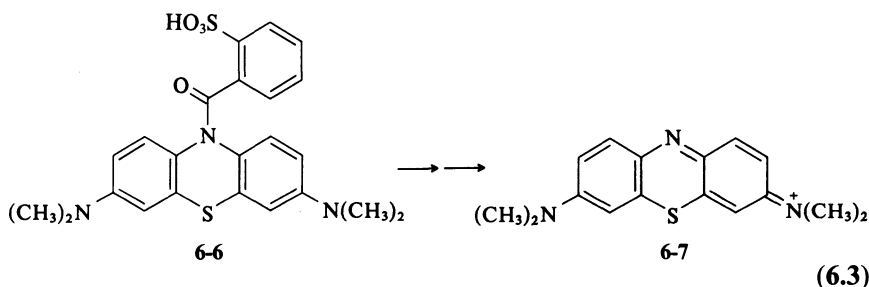
IBM is the most active company in electrochromic printing, having published several recent patents.[6] Other companies also showing an interest include Matsushita[7] and Nippon Telegraph and Telephone.[8]

It is difficult to see any great merit in electrochromic printing, since the acyl leuco dyes will be more expensive than the conventional leuco dyes used in thermal printing (because of the additional acylation step), a moist paper is required, and the fastness properties will be low.

6.4. SUMMARY

Electrochromic dyes are of two types: those used in electrochromic displays and those used in electrochromic printing. In electrochromic dis-

plays the dyes are the colored radical cations formed by electrical reduction of a noncolored bis-cationic compound. The dyes in electrochromic printing are usually acylated leuco dyes. These are present in a moist paper containing bromide ions. Electricity oxidizes the bromide to bromine which then effects oxidation of the leuco dye to the dye proper.

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III

Colorants for Reprographics

Reprography is defined as that area of imaging science lying between conventional photography and conventional printing. Chemicals for reprography is one of the fastest growing areas (ca. 24% per annum) and represents an extremely large, multimillion dollar market. Electrophotography, perhaps more familiar as photocopying and laser/light emitting diode printing, is by far the most important reprographics technology. Thermography and ink-jet printing are other important areas where colorants are used (Fig. III.1). Some of the newer technologies such as ion deposition and magnetography are still in their infancy. Others, such as photoactive pigment electrophoresis, have been around for some time but have yet to be commercialized. All these technologies are discussed in the following chapters with particular emphasis on the three major technologies of electrophotography, thermography, and ink-jet.
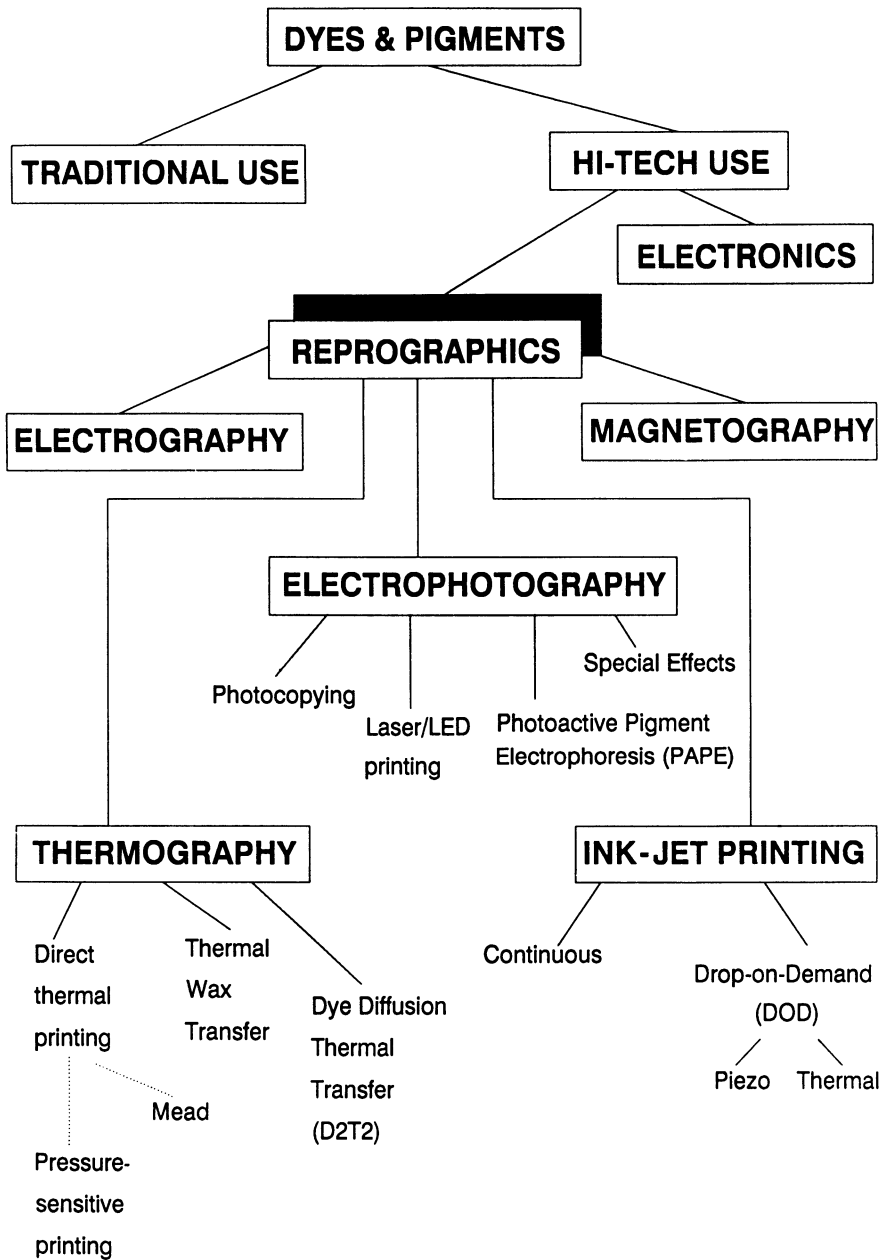
Figure III.1. Major reprographics technologies.

7

Electrophotography

7.1. INTRODUCTION

Most people have probably never heard of electrophotography, yet it is by far the biggest of all the reprographics technologies. These seemingly inconsistent statements make sense only when it is realized that electrophotography comprises the two very familiar and ubiquitous technologies of photocopying and laser/LED (light emitting diode) printing.

Until recently, virtually all photocopiers and laser printers produced only black images. This is beginning to change with the introduction of color copiers and printers by several major companies. A further development is the appearance of "intelligent copiers" which combine the dual functions of photocopying and printing.

Both photocopying and laser printing are well established in the marketplace. A related technology which has yet to establish itself is photoactive pigment electrophoresis (PAPE), also known as photoelectrophoretic (PEP) imaging. This technology combines the principles of electrophotography and electrophoresis. Its attraction is that it can, in theory, produce a full-colored copy by a one-pass process, thus making full-color copying a faster and simpler process.

All these technologies are discussed below, with particular emphasis on the role that organic colorants play in the processes. Some special effects, such as nonphotocopiable documents, photomicrolithography, prepress proofing, and transfer printing toners are also discussed.

We consider first the basic photocopying and laser/LED printing processes.

7.2. PHOTOCOPYING AND LASER/LIGHT EMITTING DIODE PRINTING PROCESSES

Both photocopiers and laser/LED printers use electrophotographic processes to produce an image. Not surprisingly, therefore, there is a great

deal of similarity in the photocopying and laser printing processes. However, there are also some key differences. The major difference as far as the end user is concerned is that photocopiers produce only *copies* of an original document whereas laser/LED printers produce the original document by *printing* text and/or graphics, usually from a computer or word processor. It also follows that laser printers, unlike photocopiers, have to interface with a computer. Differences in the actual processes are explained later.

7.2.1. Photocopying Process

As the name implies, electrophotography involves the interaction of light energy with (static) electricity to produce an image. The basic photo-copying process is best described in six steps[1] (Fig. 7.1):
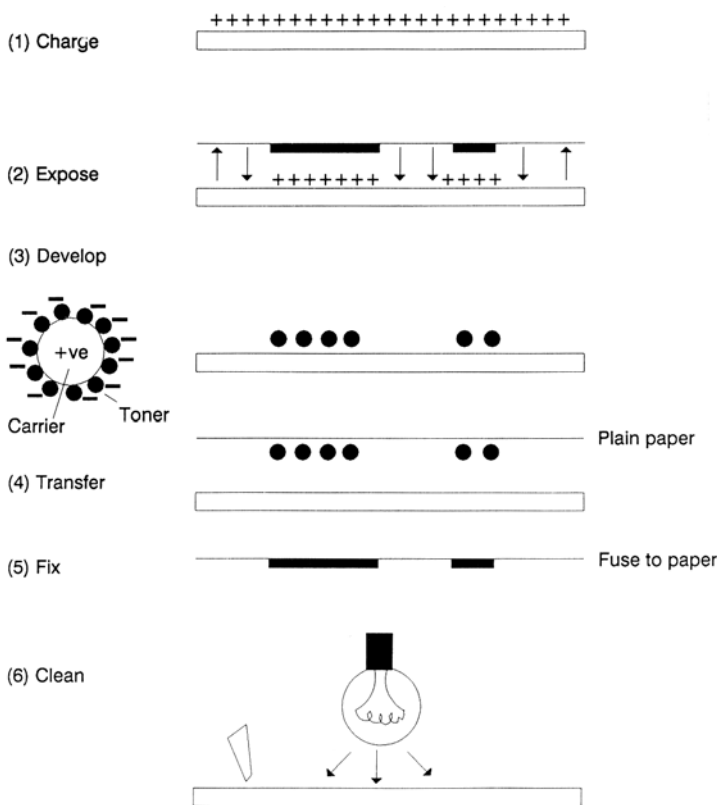
Figure 7.1. The photocopying process using inorganic photoconductors.

1. The photoconductive surface, usually a drum or a belt, is given a uniform electrostatic charge. This is positive for most inorganic photoconductors (the process described) and negative for organic photoconductors (OPCs).
2. The charged drum or belt is exposed to the subject using white light to produce a latent electrostatic image on the photoconductor.
3. The latent electrostatic image is developed by oppositely charged toner particles.
4. The developed image is transferred to a substrate, usually paper.
5. The image is fixed by heat, usually by a hot roller.
6. Finally, the photoconductor undergoes a cleaning step to make it ready for the next copy.

The photoconductor is normally charged to a voltage of 500–1000 V using a corona discharge. Most inorganic photoconductors, such as selenium and its alloys, are charged positive since they function more efficiently with a positive charge. In contrast, OPCs function more efficiently with a negative charge.

As the name suggests, a photoconductor is a *conductor* of electricity in the presence of light: in the dark, it is an *insulator*. In the imaging step, the document to be copied is illuminated with white light: where there is no print, the light is reflected on to the photoconductor and causes the electrostatic charge to be dissipated. In contrast, where there is print (usually black), the light is absorbed and little or no light reaches the photoconductor. Hence, the electrostatic charge remains intact. Thus, after step 2 there is a latent electrostatic image of the document on the photoconductor.

This latent image is rendered visible by development. The most common developer is a dry two-component developer which consists of carrier particles and smaller toner particles. These are agitated in the machine so that they develop triboelectric (static) charges (see *Section 7.5*). For copiers based on inorganic photoconductors such as selenium, the toner particles develop a negative charge and are held to the surface of the carrier, which develops a positive charge, by a weak electrostatic attraction. The developer is then brushed or cascaded over the surface or the photoconductor: in areas where an electrostatic charge remains, the toner particles are plucked from the carrier surface because the attraction between the positively charged photoconductor and the toner particles is greater than the weak attraction between the toner particles and the carrier. At this point, there is a visible toned image of the original document on the photoconductor.

The fourth step simply involves transferring this image from the photoconductor to the substrate, usually plain paper. This is normally done by applying an electrical potential at the back of the paper of opposite charge

to the toner particles. (This potential would be positive in the case of copiers based on inorganic photoconductors.)

The fifth step is that of fixing the image to the paper. This is achieved by a heat treatment which melts the toner resin (see *Section 7.5*) and fuses it to the paper. It is also the reason why copies are warm when they emerge from a photocopier.

The final step involves cleaning the photoconductor to make it ready for the next copying cycle. This is normally done by exposing it to light to remove any residual electrical charge and by removing any excess toner with a doctor blade.

The process for photocopiers based on OPCs comprises the same six steps as discussed above. The only difference is that the OPC has a negative rather than positive charge.[2] Obviously, the toner particles need to be positively charged (Fig. 7.2).
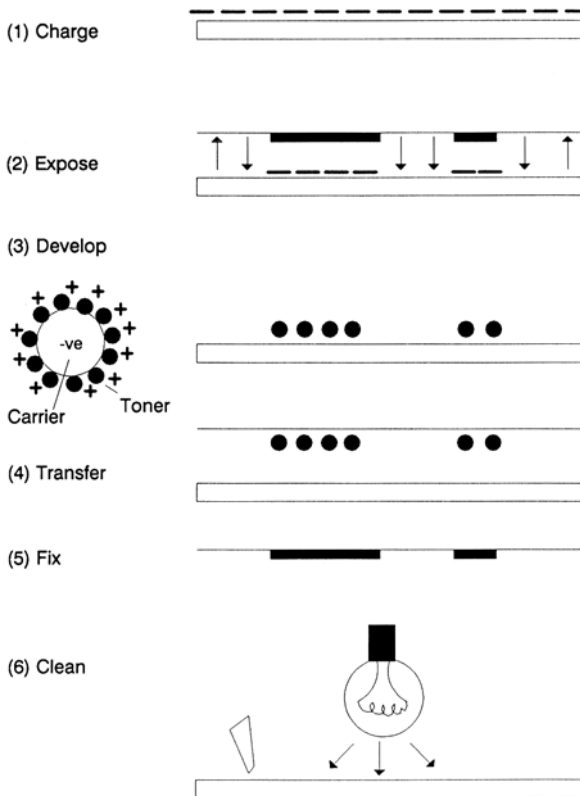
Figure 7.2. The photocopying process using OPCs.

7.2.2. Laser/Light Emitting Diode Printing Process

The laser printing process can also be described in six steps (Fig. 7.3). As in photocopying, the first step involves giving the photoconductor drum or belt a uniform electrostatic charge, shown as negative in Fig. 7.3 (step 1). The second step, the write step, is a complete contrast to the exposure step of photocopying. In the write step, a laser is used to write on the charged photoconductor drum the information stored in the printer's memory. Printers normally store a whole page of information in an all-points address-able manner so that text and/or graphics can be printed. At the points where the laser radiation hits the charged photoconductor, the charge is dissipated. This means that the image to be printed has a *zero* electrostatic charge but the background area remains charged (step 2). This is a complete reversal of the situation in conventional photocopying, in which the image to be
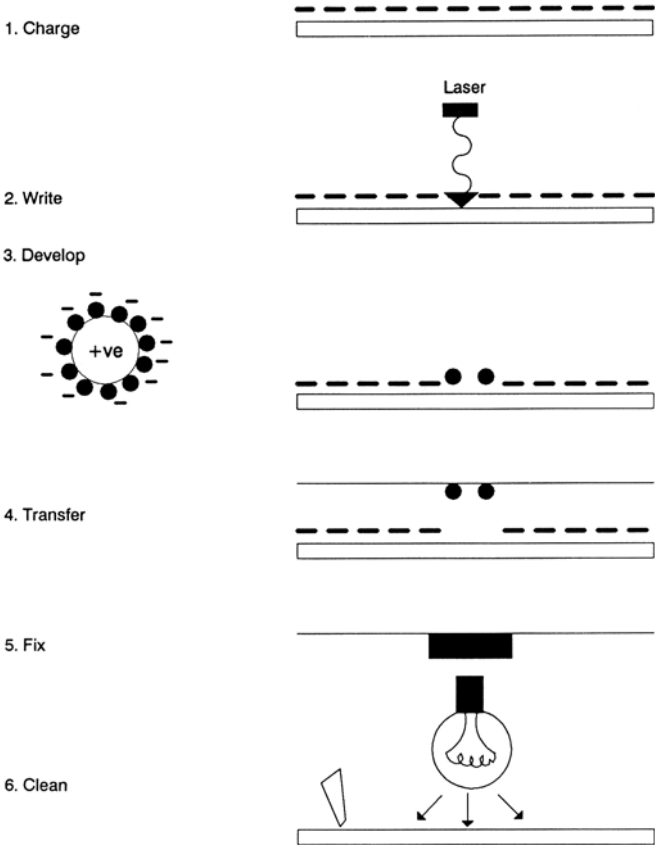
Figure 7.3. The laser/LED printing process (using an OPC).

copied remains charged whereas the background area has zero charge (see *Section 7.2.1*).

The third step is the development step. Here, the developer uses a toner which has the *same* electrical charge as the photoconductor, in this case negative, so that it is *repelled* from the negatively charged background into the uncharged image areas (step 3). This technique of development using a toner that has the same electric charge as the photoconductor is termed reverse development. Again, this step is different from the development step in conventional photocopying.

The fourth, fifth, and sixth steps of transferring the developed image from the photoconductor to the final paper substrate, fixing it by heat, and cleaning the photoconductor are the same as in photocopying.

The first commercial laser printer was the Xerox 1200, introduced in the early 1970s.[3] Today, there are many laser printers on the market ranging in price from $2000 to greater than $250,000.[4]

The Xerox 1200 used an array of flashlamps as the light source. Other light sources such as the cathode ray tube have also been used, but, as the name implies, all the current laser printers use lasers as the light source. Until recently the continuous wave gas lasers were used, for example, the helium-neon laser (632.8 nm) used in the IBM 3800 and the helium-cadmium laser (325 and 442 nm). These gas lasers were used because their light output matched the spectral sensitivity of the available photoconductors, i.e. arsenic triselenide and blue OPCs for the helium-neon laser and selenium for the helium-cadmium laser, and because they have a reasonable power output. However, continuous wave gas lasers are relatively large and inefficient and require acousto-optic modulators to digitize the beam.[5]

The solid state semiconductor lasers such as the gallium–aluminum–arsenide laser are used in the new generation of laser printers. They are very small (transistor size), very efficient, and can be current modulated. They emit in the near infrared (780–830 nm) with a lower output power than the gas lasers. Consequently, they require OPCs having a spectral response in the near infrared. Although several of these are now available[5] (see *Section 7.4.3*), there is a need for OPCs with improved sensitivity since this could be a limiting factor in the search for even faster laser printers. For example, in the IBM 3800 the laser energy is 2.5 mW and the dot exposure time is 62.5 nS so that the exposure energy on the photoconductor is only 1.4×10^{-6} J cm^{-2}.

Laser/LED printing has become important because it has combined a well-established technology (electrophotography) with a rapidly emerging technology (semiconductor lasers) to produce printers which are fast (8–250 pages per minute), high quality (up to 600 lines per inch), quiet, and produce both text and graphics. Laser/LED printing is the fastest growing area in reprographics. It has been estimated that the laser printing market will grow

from \$600 million in 1985 to \$8000 million in 1990.[6] Continuing improvements in laser technology and in OPCs will result in even better laser printers which means that laser printers will be a dominant force in page printers for some considerable time.

7.2.3. Color Copying Process

Colored copying[7] can either be monochrome (one color other than black) or full color. With monochrome copying, the process is almost identical to that already described for conventional black copying: the only difference is that the carbon black used as the pigment for a black toner is replaced by a dye or pigment of the appropriate color for a colored toner. These dyes and pigments are discussed in *Section 7.5.3*. The actual copying process for a full-color copy is much more complex than that for a monochrome copy and is described briefly below.

In theory, any color can be obtained by the use of three primary colors. For the subtractive color mixing used in the photocopying process the three primary colors are yellow, magenta, and cyan. Thus, the first requirement for full-color copying is having yellow, magenta, and cyan toners. The next requirement is having photoconductors that are sensitive to red, green, and blue light. This may be achieved by using a single panchromatic photoconductor or three different photoconductors. Here, OPCs are utilized increasingly because of the ability to fine tune their properties, including spectral sensitivity (see *Section 7.4.3*).

As in conventional monochrome copying, the first step is to give the photoconductor a uniform electrostatic charge. The colored document to be copied is then exposed to blue light (by using a blue filter). As seen from Fig. 7.4 blue light is absorbed by the color yellow; therefore, the yellow parts of the document do not reflect any of the blue light on to the photoconductor and so the charge remains intact in the areas of the photoconductor corresponding to the yellow areas of the document. The same is true of the black part of the document, since black absorbs all visible radiation. In contrast, the magenta and cyan areas of the document will reflect the blue
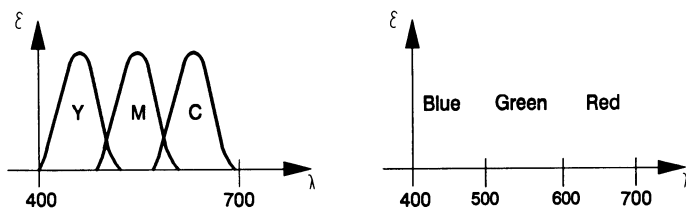
Figure 7.4. Absorption curves of the yellow-magenta-cyan (YMC) trichromat and the complementary spectral colors.

Expose   Develop   Transfer
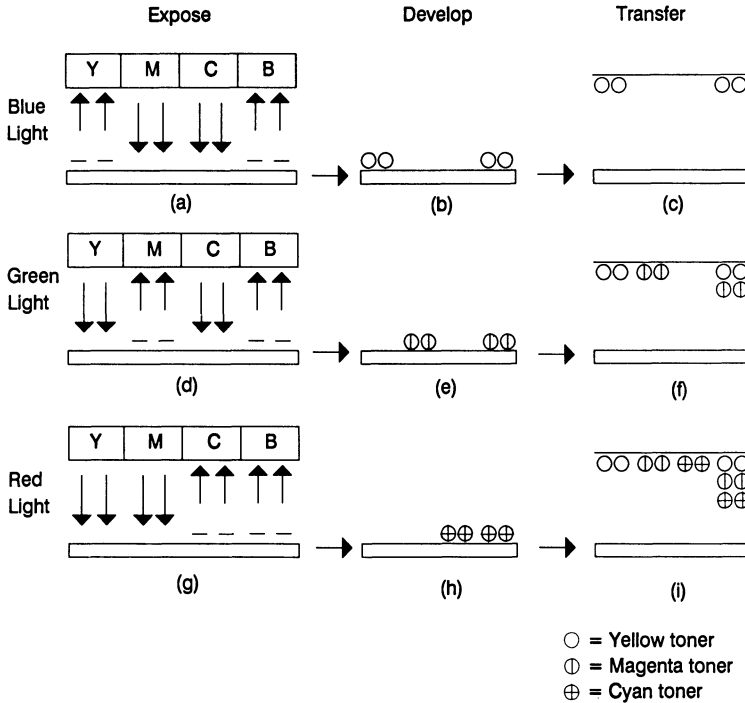
Figure 7.5. Principle of full-color photocopying.

light on to the photoconductor and dissipate the charge (Fig. 7.5a). The latent electrostatic image on the photoconductor is then developed with a yellow toner (yellow being the complementary color to blue) (Fig. 7.5b) and the developed image is transferred to paper (Fig. 7.5c).

The document is then illuminated with green light. In this case, the magenta and black portions of the document absorb the green light and the yellow and cyan portions reflect it (see Fig. 7.4). The resulting latent electrostatic image (Fig. 7.5d) is developed with a magenta toner (magenta being the complementary color to green) (Fig. 7.5e), and the developed image is transferred to paper (Fig. 7.5f).

Finally, the document is exposed to red light. Here, the cyan and black parts of the document absorb the red light; the yellow and magenta areas reflect it on to the photoconductor. The resultant latent electrostatic image (Fig. 7.5g) is developed with a cyan toner (cyan being the complementary color to red) (Fig. 7.5h), and the image transferred to paper (Fig. 7.5i).

The latest generation of color copiers, such as Canon's Color Laser Copier, are based on semiconductor lasers. The process is somewhat different than the conventional color copying process described above. In a color laser copier, light scans the original document and is reflected on to a charge

coupled device (CCD) line sensor. The 5000 CCDs which make up the array are grouped into units of red, green, and blue filters (see *Chapter 2, Section 3*). Each filter screens out two colors, allowing only light of the filter color to reach the sensor. The CCD converts the light into a digital signal which is sent to the copier printing unit. A semiconductor laser then writes the digitized data on the photoconductor. The resulting electrostatic image is then developed with a toner and transferred to paper. The process is carried out four times, one each for the yellow, magenta, cyan, and black toners, to produce the full-color copy. The image is then fused to the paper.[8] Laser copiers still require a four-pass process but the digitized image allows easy electronic manipulation such as image enlargement or reduction. Also, a photoconductor sensitive to the 780 nm radiation emitted by the semiconductor laser is required rather than a panchromatic photoconductor as for conventional color copiers (see *Section 7.4*).

Full-color copying is a complex process that results in a number of associated technical problems. Some of these are machine problems, such as keeping the photoconductor and paper in register during the three passes (expose–develop–transfer); some involve the photoconductor; some involve the charge control agent, (CCA) (see *Section 7.5.2*); and some involve the dyes and pigments used in the colored toners (see *Section 7.5.3*). All are being addressed with some degree of success. For example, a recent innovation by Colorocs[9] is to use an intermediate transfer belt upon which the three color images are superimposed before final transfer to the paper followed by fusion. This is considered to improve the registration of the image.

Color copying is receiving increasing attention from the traditional major players such as Xerox and Canon as well as many others, including Eastman-Kodak (Color Edge), Colorocs, Ricoh, Sharp, and Toshiba.

7.3. KEY CHEMICAL COMPONENTS

As is evident from *Section 7.2* the two key chemical components for both photocopying and laser/LED printing are the photoconductor and the toner. The photoconductor is a chemical or combination of chemicals which makes the whole electrophotographic process work. It can be either an inorganic-based material such as selenium or an OPC. With OPCs, one of the chemicals, the charge generating material, is normally colored. The other chemical, the charge transport material, is normally noncolored.

The toner is the chemical that produces the final visible image on the paper. It is usually black but, as already mentioned, color is also becoming more evident. The toner always contains a colorant. It normally contains a CCA also. This is typically a dye in the case of black toners. The interrelationships described above are illustrated in Fig. 7.6.

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                    ┌─────────────────────┐
                    │    PHOTOCOPYING     │
                    │        and          │
                    │  LASER/LED PRINTING │
                    └─────────────────────┘
                               │
               ┌───────────────┴───────────────┐
        ┌──────────────┐                  ┌─────────┐
        │PHOTOCONDUCTOR│                  │  TONER  │
        └──────────────┘                  └─────────┘
            │                                  │
      ┌─────┴──────┐                    ┌───────┴────────┐
 ┌──────────┐ ┌─────────┐         ┌──────────┐      ┌──────┐
 │INORGANIC │ │ ORGANIC │         │ COLORANT │      │ CCA  │
 └──────────┘ └─────────┘         └──────────┘      └──────┘
                   │                   │                │
             ┌─────┴─────┐       ┌─────┴─────┐    ┌─────┴─────┐
         ┌───────┐ ┌───────┐
         │  CGM  │ │  CTM  │
         └───────┘ └───────┘
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Carbon black (black toners)	YMC dye or pigment (colored toners)	Dye (black toners)	Noncolored (colored toners)

Colored molecule   Noncolored molecule
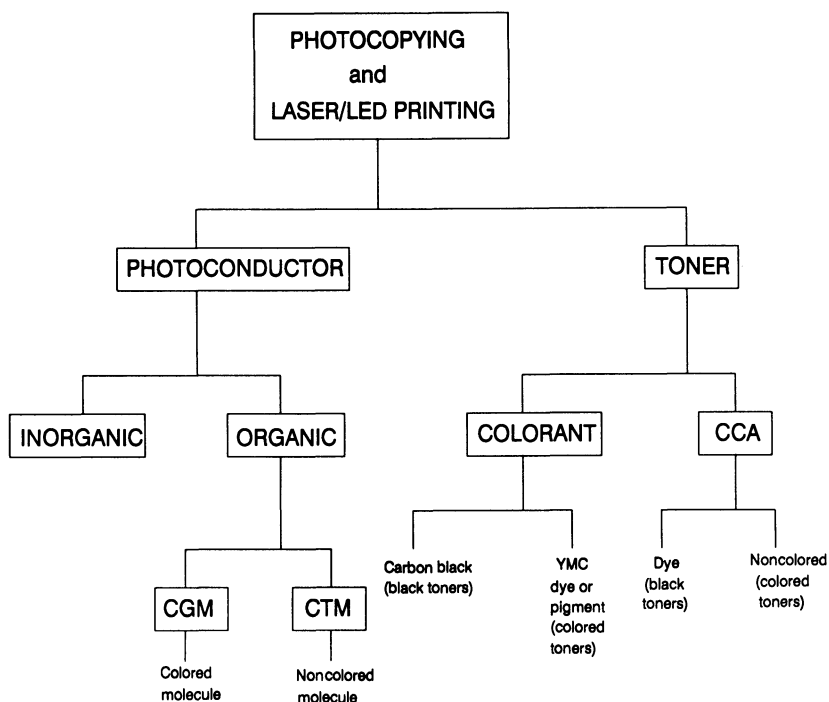
Figure 7.6. Interrelationships between key consumables and chemicals in photocopying and laser/LED printing. CGM, charge generating material; CTM, charge transport material.

The two key chemical components, namely the photoconductors and the toners, used in both photocopiers and laser/LED printers, are discussed in more detail below.

7.4. PHOTOCONDUCTORS

Photoconductors may be divided conveniently into inorganic photoconductors and OPCs. However, certain properties apply to all photoconductors and these are discussed first.

7.4.1. General Features

The spectral response or spectral sensitivity of a photoconductor is a parameter of paramount importance. It determines both the radiation source with which the photoconductor is compatible and, in the case of photocopiers, the color of print which can be copied.

Figure 7.7. Emissions of lasers/LEDs and white light.

Photocopiers use white light as the radiation source. White light comprises the radiation spanning the whole of the visible spectrum, i.e. from 400 to 700 nm (Fig. 7.7). In contrast, laser/LED p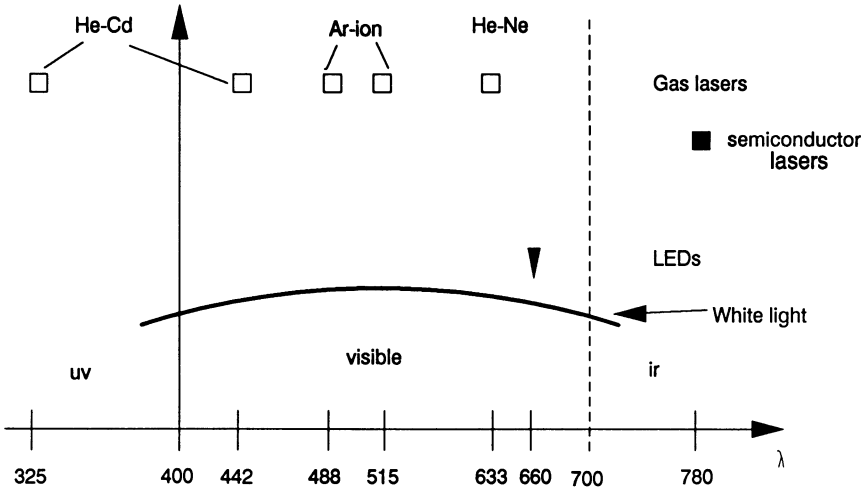rinters use radiation of a wavelength specific to the laser or LED being used. As mentioned earlier the older laser printers used gas lasers such as helium-cadmium, argon ion, and helium-neon, all of which emit in the UV/visible region (Fig. 7.7). However, the new generation of laser printers use the solid state semiconductor lasers such as the gallium-aluminum-arsenide laser which emits in the near infrared at 780 nm. LEDs emit in the red region at 630–660 nm (Fig. 7.7).

The ideal spectral sensitivity of a photoconductor for copiers is 400–700 nm to match the white light source. As seen from Fig. 7.8, which shows the spectral response of inorganic photoconductors, this is not always possible in practice. Selenium has no sensitivity beyond 600 nm. Selenium/tellurium alloys are better, as are cadmium sulphide and especially arsenic triselenide. Indeed arsenic triselenide is the best panchromatic inorganic photoconductor, having good sensitivity across the whole of the visible spectrum.

In copying black print, especially where the colorant is carbon black, photoconductors with limited spectral sensitivity, such as selenium, perform satisfactorily. However, problems occur when colored print has to be copied. Thus, colors that absorb radiation *outside* the sensitivity range of the photoconductor will not be copied. In the case of selenium, this applies to blue and cyan colors since these absorb in the red region of the visible spectrum (Fig. 7.9).
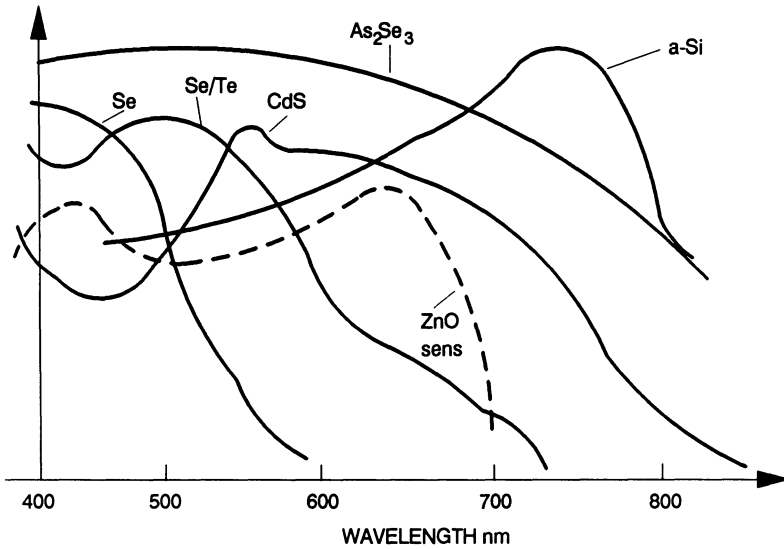
Figure 7.8. Spectral sensitivities of some inorganic photoconductors. Se, selenium; Se/Te, selenium/tellurium; CdS, cadmium sulfide; As_2Se_3, arsenic triselenide; ZnO, zinc oxide (sensitized); a-Si, amorphous silicon.
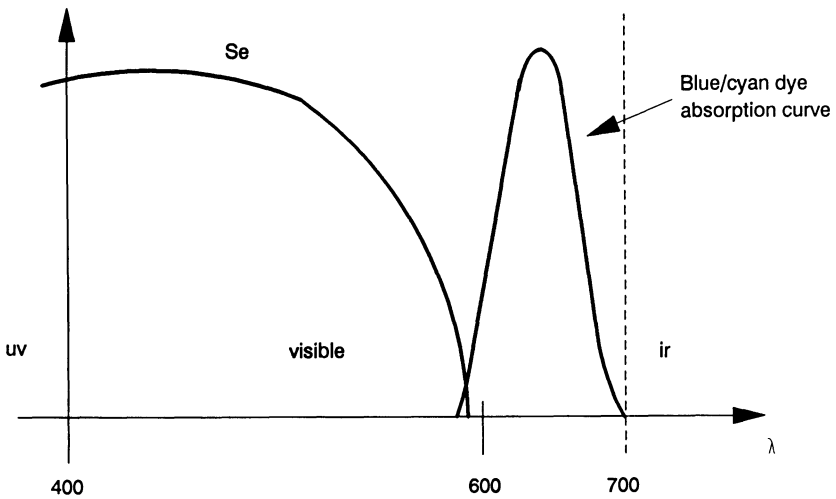

Figure 7.9. Spectral sensitivity of selenium photoconductor and absorption curve of blue/cyan dyes.
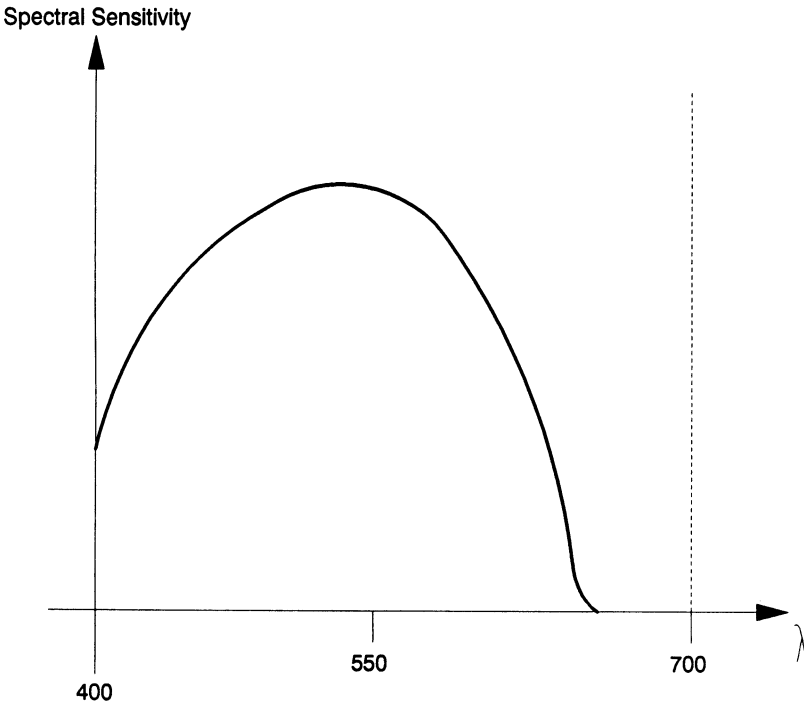
Spectral Sensitivity

Figure 7.10. Spectral sensitivity of a typical red OPC.

One of the major advantages of OPCs is the ability to fine tune their receptiveness to light of almost any wavelength. Red OPCs are commonly employed for white light copiers. Red pigments have maximum absorption at the middle of the visible spectrum (550 nm), so they provide maximum spectral sensitivity across the visible spectrum (Fig. 7.10). (The spectral response of a charge generating material is very similar to its absorption curve.)

For the new generation of laser/LED printers the photoconductors have to match the outputs of these devices. These occur in the near infrared at 780 nm for the lasers and the red at 630–660 nm for the LEDs. OPCs fit these requirements best. Indeed, some OPCs, especially phthalocyanines such as X-form metal-free phthalocyanine*, are ideally suited for both lasers and LEDs, since the spectral response matches the output of both devices (Fig. 7.11). The spectral sensitivity of the photoconductor is also important in designing nonphotocopiable paper (see *Section 7.7.1*).

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* X-Form metal-free phthalocyanine, also known as the tau-form, is one of three metastable polymorphs; the other two are alpha, the least stable polymorph, and gamma. The beta form is the most stable polymorph.
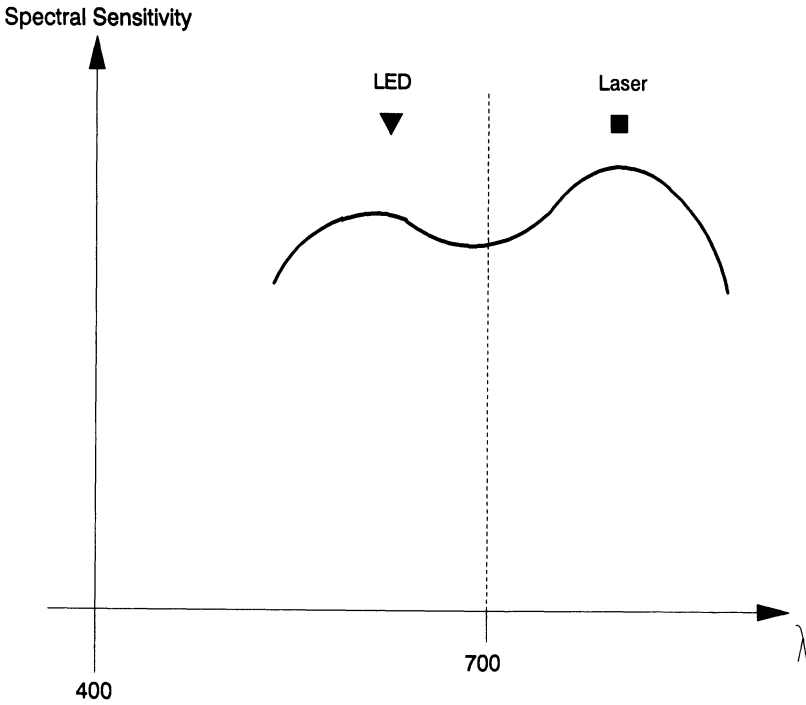
Spectral Sensitivity

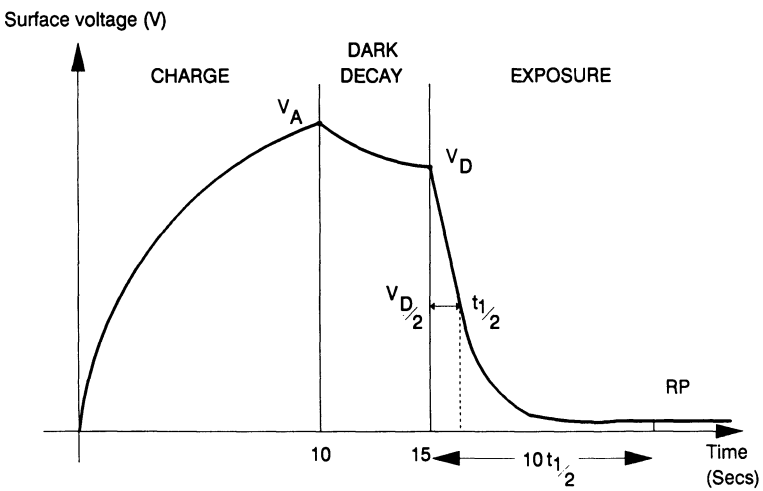**Figure 7.11.** Spectral sensitivity of X-form metal-free phthalocyanine.

Figure 7.12. Test cycle for a potential OPC.

In addition to spectral sensitivity, there are four other important parameters for a photoconductor:

1. Charge acceptance (V_A)
2. Dark decay $\left(\dfrac{V_A - V_D}{V_A} \times 100 \right)$
3. Sensitivity (photodischarge) ($t_{1/2} \times I$)
4. Residual potential (RP)

These four basic parameters are measured for any potential photoconductor, usually by using the Kawaguchi Electrostatic Paper Analyser, model SP 428 (see Fig. 7.12).

Charge acceptance (V_A) is the electrical potential in volts of the photoconductor surface after exposure to a corotron (a corona enclosed on three sides with metal plates) for a certain time period (usually 10 sec in a test machine). A high charge acceptance is desirable since this results in a better electrical contrast between the charged and uncharged areas in the latent electrostatic image, and leads to better print quality.

The dark decay measures the insulating properties of the photoconductor in the dark. It is normally expressed as a percentage (Eq. 7.1). Ideally it should be as low as possible.

$$\text{Dark Decay} = \frac{V_A - V_D}{V_A} \times 100 \qquad (7.1)$$

The photodischarge sensitivity measures the amount of radiation that is needed to discharge the photoconductor. The photodischarge sensitivity should be as high as possible. In other words, a minimum amount of energy should be able to discharge the photoconductor. High sensitivity is especially important in high speed copiers and printers. The sensitivity in lux-sec is the light energy (intensity × time) required to reduce the surface voltage to half its value (Eq. 7.2). The sensitivities of commercial photoconductors range from about 0.5 to 10 lux-sec.

$$\text{Sensitivity} = t_{1/2} \times I \qquad (7.2)$$

$$I = \text{light intensity (lux)}$$

$$t_{1/2} = \text{time taken to reduce } V_D \text{ to } V_D/2 \text{ (in seconds)}$$

Figure 7.13 shows the evolution of photoconductor sensitivity.[10] There are several noteworthy features. The first is the enormous overall improvement in sensitivity. As expected, this was particularly marked during the
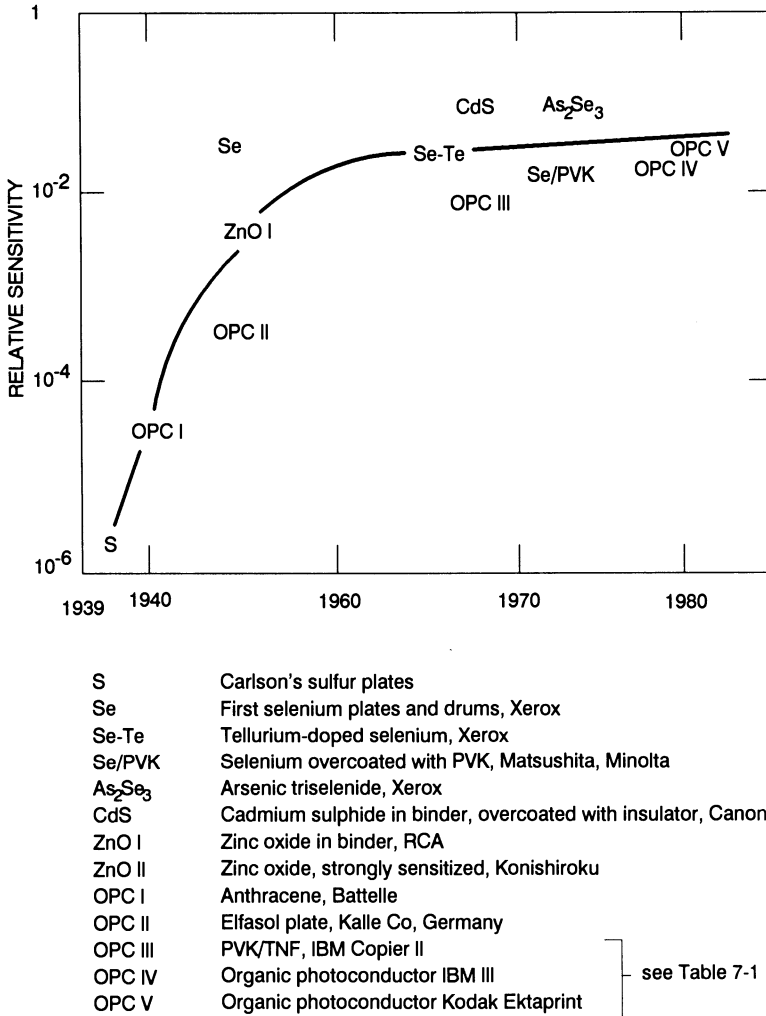
Figure 7.13. Evolution of photosensitivity of photoconductors.

S	Carlson's sulfur plates
Se	First selenium plates and drums, Xerox
Se-Te	Tellurium-doped selenium, Xerox
Se/PVK	Selenium overcoated with PVK, Matsushita, Minolta
As_2Se_3	Arsenic triselenide, Xerox
CdS	Cadmium sulphide in binder, overcoated with insulator, Canon
ZnO I	Zinc oxide in binder, RCA
ZnO II	Zinc oxide, strongly sensitized, Konishiroku
OPC I	Anthracene, Battelle
OPC II	Elfasol plate, Kalle Co, Germany
OPC III	PVK/TNF, IBM Copier II
OPC IV	Organic photoconductor IBM III
OPC V	Organic photoconductor Kodak Ektaprint

OPC III, OPC IV, OPC V — see Table 7-1

early period of development. Thus, from 1939 to 1959 the sensitivity improved by a factor of 10,000! During the next 20 years the sensitivity only improved by a factor of 100. The second feature is the step change that occurred in switching from the early photoconductors, such as Carlson's sulfur plates and anthracene (OPC I), used at the Battelle Institute, to the selenium family of photoconductors. Finally, there is the steadily improving performance of the organic photoconductors which now rival and even surpass the best inorganic photoconductors in terms of sensitivity.

As the name implies, the residual potential (RP) is the electrical potential that remains after exposure of the photoconductor to radiation. Ideally, it should be zero. The measurement is normally taken at $10t_{1/2}$ (Fig. 7.12).

7.4.2. Inorganic Photoconductors

Selenium is the most widely used inorganic photoconductor. It may be used alone; as an alloy with other materials (notably tellurium); or as a chemical compound, as in arsenic triselenide. Other inorganic materials also function as photoconductors. The most important commercial materials are cadmium sulphide and dye-sensitized zinc oxide. More recently, amorphous silicon has also been employed.

Inorganic photoconductors were the first photoconductors to find widespread commercial use. In fact, until the mid-1980s inorganic photoconductors dominated the photocopying market due to a number of attractive properties: they can be fabricated as a single layer on a drum, have a long life (100,000–500,000 copies), have good abrasion resistance (are robust), and have good photoconductive properties. However, they also have a number of important limitations:

1. *Toxicity*: Selenium, arsenic, cadmium, and tellurium are toxic, and special precautions have to be taken in the manufacture, use, and disposal of these types of photoconductors.
2. *Wastage during manufacture*: Selenium photoconductor units are made batchwise, resulting in a 30%–40% scrap rate.
3. *Limited spectral sensitivity*: They are generally unsuitable for infrared laser imaging (Fig. 7.8).
4. *Unsuitability for high speed copiers*: This is due to their lack of flexibility in belt form.

It is for these reasons that the use of selenium-based and indeed other inorganic-based photoconductors is declining.[10,11]

The only other area of inorganic photoconductors in which considerable research is being done is amorphous silicon. However, this is very high technology including plasma deposition and many problems are encountered.[12] Nonetheless, Canon use an amorphous silicon photoconductor in their 7550 machine.[13]

7.4.3. Organic Photoconductors

Because of the deficiencies of inorganic photoconductors, tremendous efforts are being made to design photoconductors that are superior to selenium and the other inorganic-based photoconductors. The bulk of this
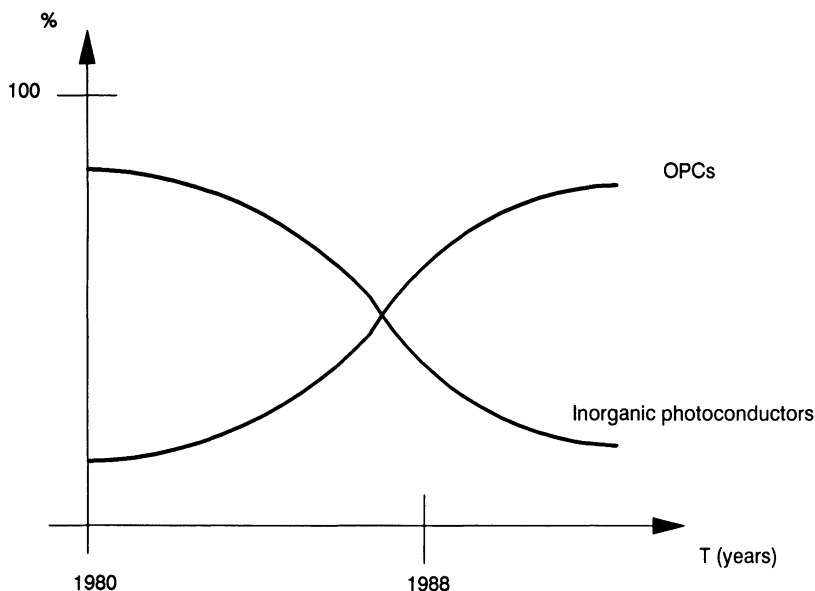
Figure 7.14. Trends in OPCs and inorganic photoconductors.

effort is being directed toward OPCs.[10,11,14,15] Activity is so intense that more than 3000 patents have already been filed on OPCs. Indeed, over 600 relevant patents appeared in one year (1983).[16] Most of the patents are Japanese, with the three leading companies being Canon, Ricoh, and Konishiroku. As seen from Fig. 7.14, this increased activity is reflected in the marketplace where greater than 50% of copiers and printers are now based on OPCs, and this trend is continuing apace.[17]

The lure of OPCs is the virtually unlimited number of structures that can be synthesized and tailored for optimum performance. OPCs can be designed to be nontoxic, although the earlier ones, such as polyvinylcarbazole-trinitrofluorenone (PVK-TNF), were Ames positive because of the trinitroflurenone moiety. In addition, they can be designed to have the correct spectral sensitivity. Furthermore, OPCs are more cost effective and are easier to manufacture than inorganic photoconductors. OPCs also have high flexibility in belt form and are therefore suitable for high speed copiers and printers.

The pioneer of electrophotography, Chester F. Carlson, originally used organic materials such as anthracene as the photoconductor.[18] Anthracene is a planar organic molecule with a system of delocalized pi-electrons. This description also applies to most dyes and pigments and therefore it is not surprising that all the OPCs in use today are based upon dyes or especially pigments.
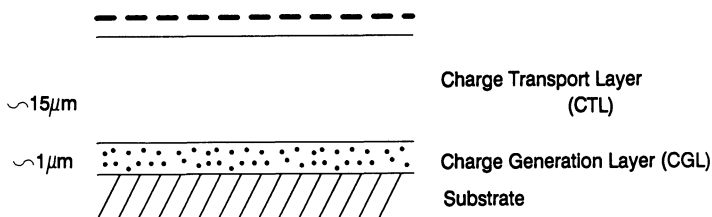
Figure 7.15. Construction of a typical OPC.

OPCs are rarely single compounds and tend to be a composite of what is called a *charge generating layer* and a *charge transport layer*. Indeed, virtually every commercial OPC is of this dual layer type (Fig. 7.15).
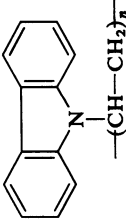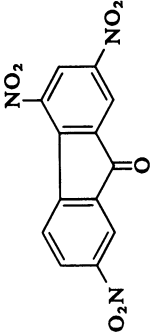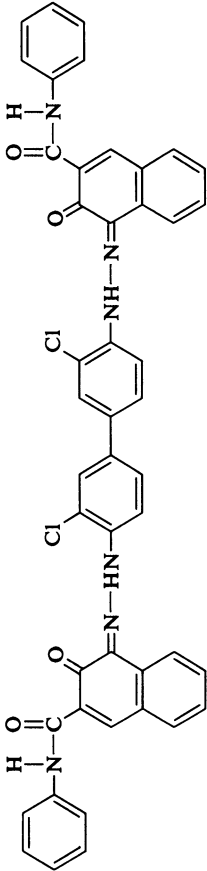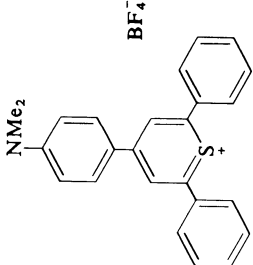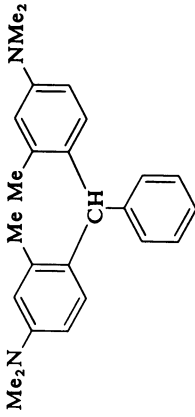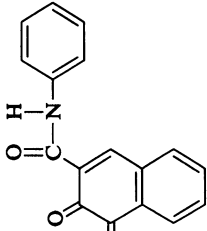
Figure 7.15 shows the most common arrangement of an OPC.[10] The base substrate is electrically conducting and is either an aluminum drum or aluminized polyester film (for belts). Next is a thin charge generation layer, typically 0.1–3.0 μ, comprising the charge generating material dispersed in a polymeric binder, usually a polycarbonate (e.g. LEXAN 141). In some cases a very thin (e.g. 0.1 μ) subbing layer is applied to the aluminum to improve the adhesion of the charge generating layer. The top coat consists of a much thicker charge transport layer, typically between 10 and 30 μ, containing the charge transport material in a binder, usually polycarbonate.
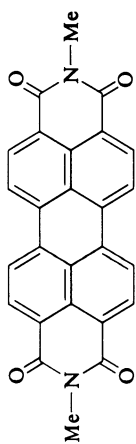
The charge generating materials in the charge generating layer are invariably pigments, and the charge transport materials in the charge transport layer are electron-rich organic compounds which are usually noncolored or only slightly colored (e.g. pale yellow).

A variety of organic pigments have been used for charge generation including polyazos, perylene tetracarboxy diimides, polycyclic quinones, phthalocyanines, squariliums, and thiapyryliums[10] (see Tables 7.1 and 7.2 for structures). The pigments used as photoconductors must be extremely pure and possess the correct morphology, otherwise their performance is impaired. For example, traces of impurities can alter deleteriously the photoconductive characteristics of a compound. In some cases, the pigments are purified by sublimation whereas in others a less expensive crystallization treatment is possible. The crystallinity of a pigment and its particle size are often important parameters in determining OPC performance.
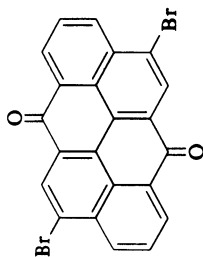
The charge transport materials are *p*-type semiconductors (these transport a positive hole), the main types being aryl hydrazones, pyrazolines, stilbenes, leuco di- and tri-phenylmethanes, aminoaryl heterocycles, and highly conjugated arylamines.[10] Obtaining a good charge transport material necessitates a trade-off between good OPC performance on the one hand and good environmental stability, especially to light and aerial oxidation, on the other hand.

Table 7.1. Typical Combinations of Charge Generating Materials and Charge Transport Materials for Photocopiers

CGM	CTM	Company

PVK [19-24]

IBM II

Azo [25]

TNF [23,24] (Ames + ve)

IBM III

Hydrazone

Kodak
Ektaprint

Leuco-triphenylmethane

Thiapyrylium [26]

Kalle

Oxadiazole

Konica

Diphenylalkylmethane

Canon

Hydrazone

Perylene tetracarboxydiimide[27]

Dibromoanthanthrone[28]

Azo
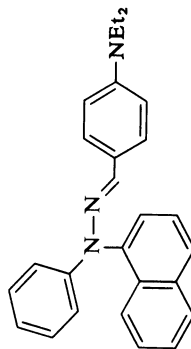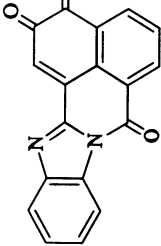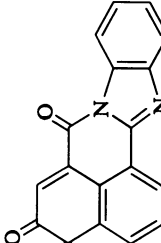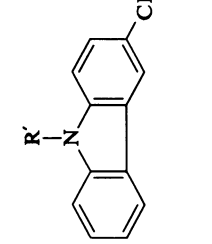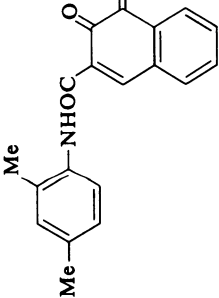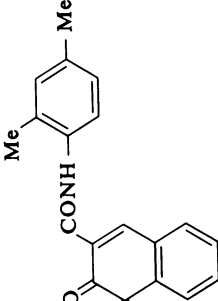
Table 7.1. (Continued)

CGM	CTM	Company

Mitsubishi

Ricoh

Hydrazone

Azo

Azo[29]

Me

Me

CONH

Me

NHOC

Me

CH=N–N–R

R'–N

Ricoh

NEt$_2$

Stilbene

Ricoh

CH=N-N-CH$_3$

N-C$_2$H$_5$

Hydrazone

CONH

Cl

O

H
N-N

O

H
N-N

Cl

O

HNOC
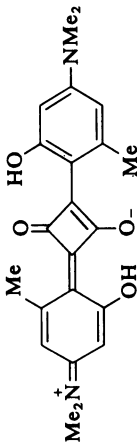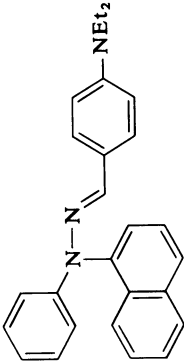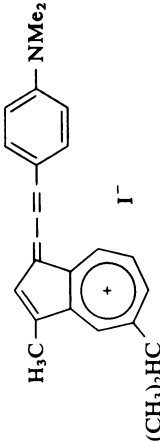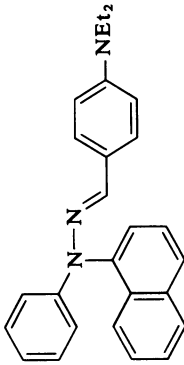
Azo[30]

Table 7.2. Typical CGM/CTM Combinations for Laser/LED Printers

CGM	CTM	Company
Squarilium[31]	Hydrazone	IBM Xerox
Azulenium	Hydrazone	Canon

Ricoh

CH=N—N
Me

Hydrazone

N—Et

Et

CONH

HO

N=N

HN

C₂H₅

HNOC

N
H

HO

Z=Z

N

NH

N=N

OH

HNOC

C₂H₅

Azo
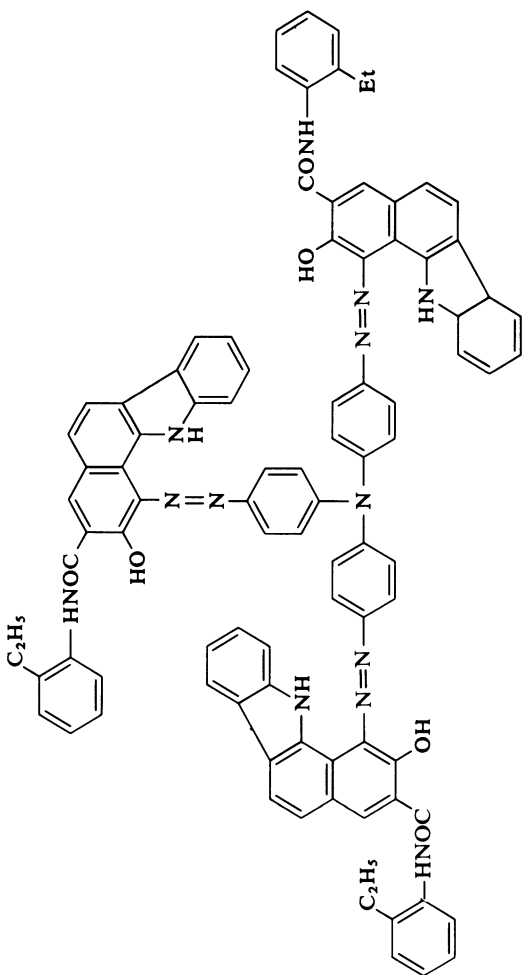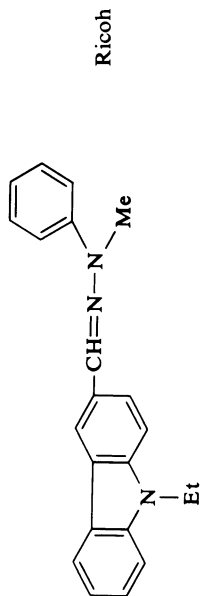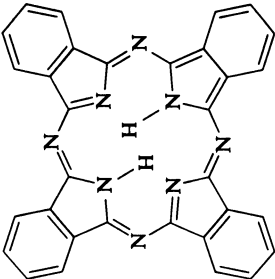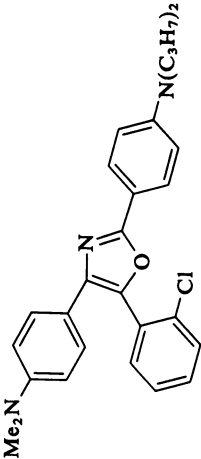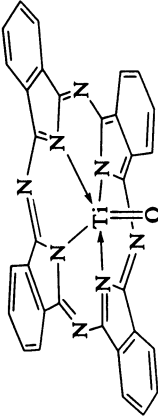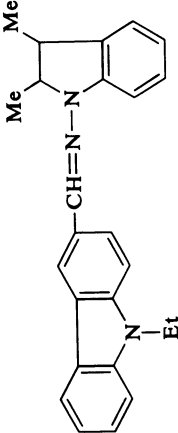
Table 7.2. (Continued)

CGM	CTM	Company
		Hitachi

Me$_2$N — N(C$_3$H$_7$)$_2$ — Cl

Oxazole

Me   Me

CH=N—N

Et

Hydrazone

DIC

Phthalocyanine[32] (x or tau form)

Phthalocyanine (TiOPc)

Arylamine

Xerox

Arylamine

Xerox

Phthalocyanine[33] (VOPc)

Phthalocyanine[34] (ClInPc)

In general, a particular combination of charge generating and charge transport material works best. Some examples of such optimum combinations are shown in Tables 7.1 and 7.2. Table 7.1 shows typical OPCs for white light copiers and Table 7.2 shows typical combinations for laser/LED printers.

7.4.4. Photoconductive Mechanism

How do photoconductors work? In step 2 of both the photocopying process[25,35] (Figs. 7.1 and 7.2) and the laser/LED printing process[25,35] (Fig. 7.3), the electrostatic charge disappears as if by magic when it is struck by radiation. How this occurs in an OPC is shown by Fig. 7.16.

Radiation, which can be either reflected white light in the photocopying process or laser radiation for laser printers, upon hitting the OPC, passes through the transparent charge transport layer (hence the need for a non-colored charge transport material) and hits the opaque (colored) charge generating layer. The charge generating material absorbs the radiation and in doing so ejects an electron to form a transient ion-pair complex. The conductive aluminum substrate is held at a positive potential and attracts the electron to earth. This leaves a positive hole, i.e. a positively charged pigment molecule. This positive hole then migrates to the charge generating/charge transport material interface attracted by the negative potential at the surface of the OPC: any defects in the charge generating material crystallinity
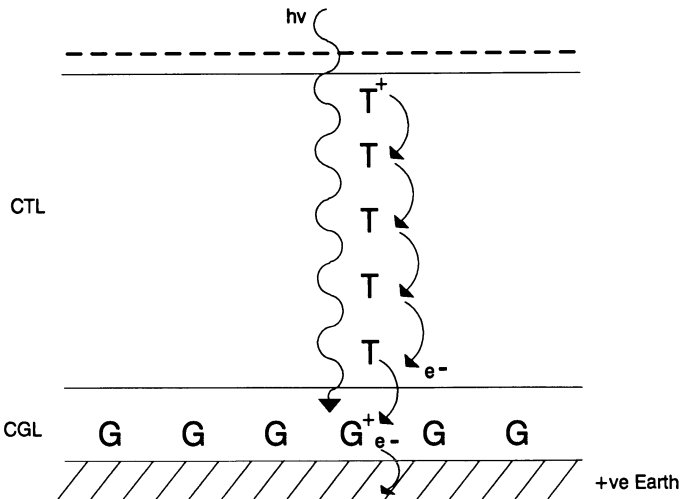
Figure 7.16. The photoconductive mechanism for an OPC. G, charge generating molecule; T, charge transport molecule.

hinders this hole transport by a trapping mechanism. Hence, the need for high purity, high crystallinity pigments as charge generating materials. At the interface, an adjacent charge transport material molecule donates an electron to the positive hole to regenerate the neutral pigment molecule and, at the same time, form a positive hole in the charge transport layer. This explains why charge transport materials need to donate an electron easily. In other words, they must have low ionization potentials and be easily oxidized. The positive hole is then transported to the surface by a hopping mechanism, attracted by the negative charge. Once at the surface, it neutralizes the negative charge.

Inorganic photoconductors function in a similar way except in this case it is an electron, not a positive hole, that has to be transported to the surface (to neutralize the positive charge). For single layer photoconductors a single material has to perform the dual functions of charge generation and charge transport. However, some inorganic photoconductors have dual layer structures like the organic photoconductors—one layer for charge generation and one for charge transport.

Although OPCs are becoming increasingly popular and have several advantages over inorganic photoconductors, they do have one defect, namely their shorter lifetime. Typical inorganic photoconductors produce 100,000–500,000 copies. In contrast, the current OPCs only produce 10,000 copies. In practice, this is not a serious drawback. Several manufacturers make disposable cartridges for copiers and printers. These contain sufficient materials to produce 10,000 copies. After that, they are discarded and a new cartridge inserted. An aftermarket has also developed whereby only the OPC drum is discarded, not the entire cartridge. In machines using belts, the belt automatically moves to a new portion after 10,000 copies have been produced, so that 100,000 copies can be made by using a belt of the appropriate length. There is little doubt that the intense research activity on OPCs will continually produce improved products.

7.5. TONERS

The toner is the second key component of electrophotography. As described in *Section 7.2*, toner is the material that produces the final, visible image on the paper. It is the dye or pigment used as the colorant that produces the observed color. However, colorants are also used in toners for producing effects other than color. For example, they may be used as CCAs for controlling the electrostatic charge on toner particles. The main types of toners, their preparation and some basic properties, are described below, followed by a discussion of CCAs. Special effect toners, such as transfer printing toners, are discussed in *Section 7.7.4*.

7.5.1. General Features

Toners may be either dry or liquid. Dry toners may be subdivided further into two-component and monocomponent toners, and the latter may be magnetic or nonmagnetic (Fig. 7.17).

At present, dry toners are by far the most important commercially, especially dry two-component toners. Dry toners have larger particle sizes than liquid toners, typically 10–25 μ compared with less than 1 μ for liquid toners. The quality produced by dry toners is adequate for most applications, including the current full-color copiers, but liquid toners are normally used when very high resolution is required, as in prepress proofing.

The dry two-component toner system is still the most ubiquitous, although dry monocomponent toners are becoming increasingly important. A dry two-component toner system is composed of toner particles and much larger carrier particles. A mixture of the two is known as a developer. This system was used to illustrate both the photocopying and laser/LED printing processes (*Section 7.2*).

In monocomponent magnetic toners the carrier and toner are essentially combined into one particle. Ideally, the core consists of the magnetic carrier material such as iron, steel, or magnetite coated with a matrix containing the resin, colorant, and other additives such as surfactants and CCAs. However, in practice it is more like a "plum pudding" whereby several magnetic particles are dispersed in the resin matrix (Fig. 7.18). A monocomponent nonmagnetic toner is like a magnetic toner but devoid of the magnetic material.

Toner particles are composed mainly of resin: the other three ingredients are the pigment, which is usually carbon black, an antioffset wax, and the CCA (Fig. 7.19). The resins must have low softening points (typically
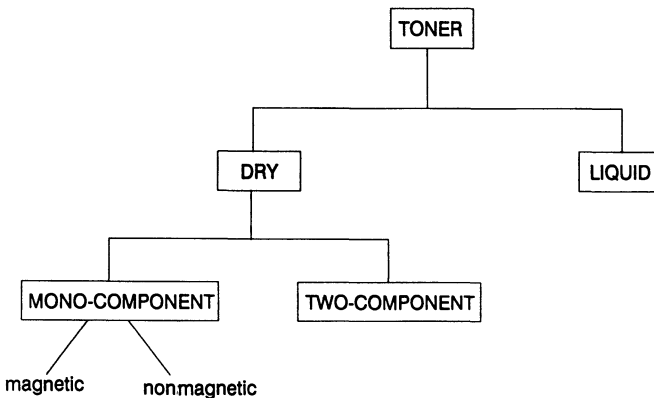
Figure 7.17. Main types of toner.
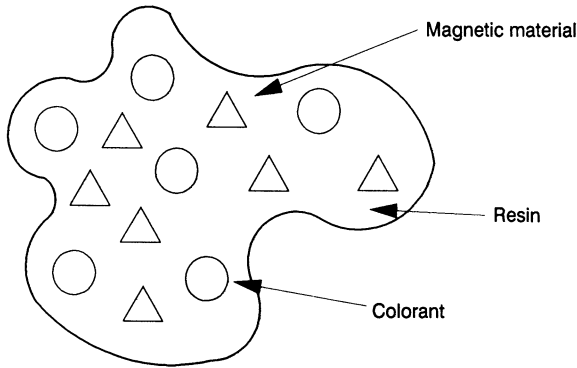
Figure 7.18. Typical monocomponent magnetic toner.
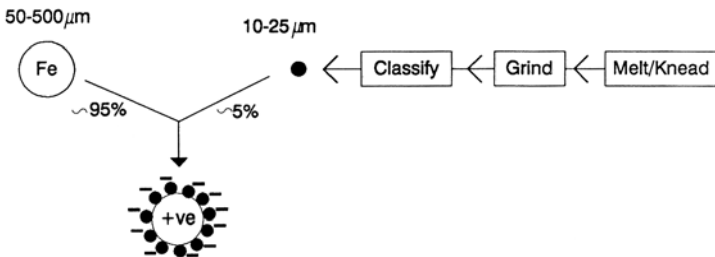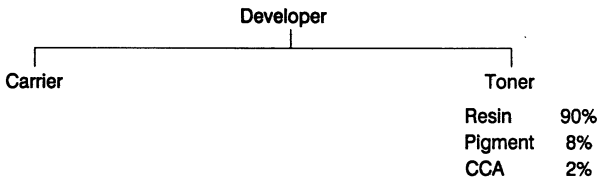
Figure 7.19. Dry two-component developer for use with copiers using inorganic photoconductors.

60–70°C) but high melt viscosities in order to facilitate the final fusion step to the paper, and they must be good insulators in order to accommodate an electrostatic charge. Styrene-acrylic resins, such as styrene-*n*-butyl methacrylate, are by far the most important resins, accounting for about 80% of the toner resins used. Polyester resins are the other important resins.

Dry toners can be prepared by a number of methods including suspension polymerization of a pigmented monomer, but the most widely used method remains hot melt kneading followed by grinding and classification.

In the hot melt kneading process the ingredients are premixed and then hot melt kneaded at 150–200°C. The melt is cooled, crushed, and ground, usually by jet milling, and toner particles of the desired particle size (10–25 μ) are obtained by classifying (Fig. 7.19). The toner is then made into a developer by adding a carrier (usually iron, steel, or ferrite) and the suitability of the toner is assessed by measuring its triboelectric charge using the so-called "Blow-Off" test.[36] The triboelectric charge is expressed as microcoulombs per gram (μCg^{-1}): typical values are 10–40 μCg^{-1}. If the triboelectric charge is satisfactory, then the ultimate test is to use the toner in a machine to produce copies: this can involve running as many as 50,000 copies continuously. In the machine test, properties such as toner usage, solid area density, resolution, and background density (fogging) are assessed.

Basically, liquid toners consist of a dispersion of the toner particles in an insulating liquid. The toner particles may be the colorant itself, the colorant containing a binder such as linseed oil or an alkyd resin, or toner particles similar to the dry toners containing a binder resin and other additives such as charge control agents.[37] The insulating liquid, which must not dissolve the toner particles, is usually a hydrocarbon from petroleum distillates. Isopar G and Isopar H are typical liquids.[37] The electrical charge on toner particles dispersed in a liquid depends upon parameters such as zeta potential rather than triboelectric effects. The emergence of color copiers (*Section 7.2.3*) coupled with the Landa technology[38] (which essentially uses a gel rather than a liquid) is expanding the viability of liquid toners.

7.5.2. Charge Control Agents

A CCA is a chemical that imparts and regulates the electrostatic charge on a toner particle. It ensures that the toner particles acquire the correct level of triboelectric (static) charge, i.e. that the charge is neither too high nor too low, and it keeps the charge constant over long periods of time. This produces high quality copies with very sharp, distinct images (black or colored) on a pure white background. Without a CCA, poor quality copies result, viz. less distinct images on a fogged (gray) background. Most people are probably unfamiliar with CCAs, because they are a relatively new discovery and most of the information on them is contained in the patent literature.

CCAs are used primarily in the most important type of toner, the dry two-component toner, but are also used in monocomponent and liquid toners.[39,40] As noted above, dry two-component toners (developers) consist of carrier particles and much smaller toner particles. The developer is agitated in the photocopier machine, causing both the carrier particles and the toner particles to develop electrostatic charges; this results in the toner

particles forming a monolayer on the carrier surface (Figs. 7.1–7.3). In practice, a nonideal, incomplete surface layer is formed. Whether the toner particles are positively charged and the carrier particles negatively charged or vice versa depends on the materials used for the toner and carrier. Also, whether negatively charged or positively charged toners are required depends upon both the photoconductor (organic or inorganic) and the process (copying or printing) (*Section 7.2*).

7.5.2.1. Negative Charge Control Agents

The two common groups in organic chemistry that carry an inherent negative charge are the sulfonic acid group and the carboxylic acid group. Therefore, it is hardly surprising that many organic molecules containing either sulfonic acid[41] or carboxylic acid groups,[42] or derivatives of these groups,[43] have been evaluated as negative CCAs. Generally, however, they are unsatisfactory. This is probably because the negative charge is localized on the oxygen atoms, which results in an ionic group in the molecule and hinders dispersibility in the toner resin. In contrast, 2:1 chromium complex azo dyes (**7-1**), devoid of sulfonic acid or carboxylic acid groups, have been found to be excellent negative CCAs.[44] Here, the molecule contains a unit negative charge which is delocalized throughout the pi-electron system of the whole molecule. Such dyes exhibit good compatibility with the toner resin. Apparently, this discovery was made by accident. A black metal complex dye was incorporated into a toner containing carbon black in an attempt to modify the shade. Instead, the quality of the copies produced by that toner were so superior to those to which no dye had been added that it was obvious that some unique effect had been discovered!
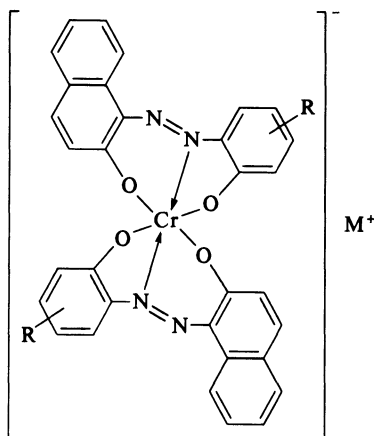
7-1

CI Acid Black 63 (**7-2**), which was marketed by Orient Chemical Industries as BONTRON S31, is typical of the early 2:1 chromium complex azo dyes which function as negative CCAs. However, this compound has two major defects: it is reported to be mutagenic (Ames positive)[45] and has only borderline thermal stability. Therefore, it has been withdrawn from the marketplace.

7-2
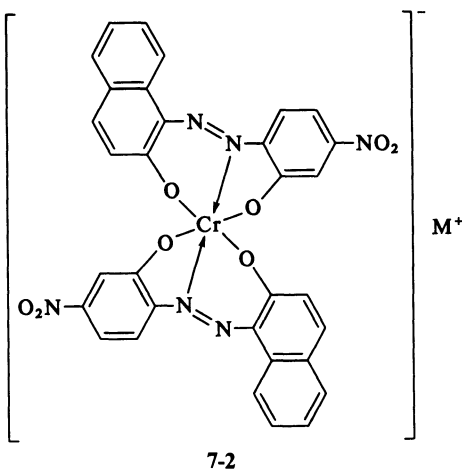
A recent paper[46] implicates the nitro group as the causative agent both for the low thermal stability and the reported mutagenic response. Therefore, it is hardly surprising that subsequent CCAs, which are claimed to be non-mutagenic and have higher thermal stability, are generally devoid of nitro groups. For example, BONTRON S32 (**7-3**) contains a sulfonamido group and BONTRON S34 (**7-4**), which has a chlorine atom and is one of the

7-3   R = SO_2NH_2
7-4   R = Cl

7-5
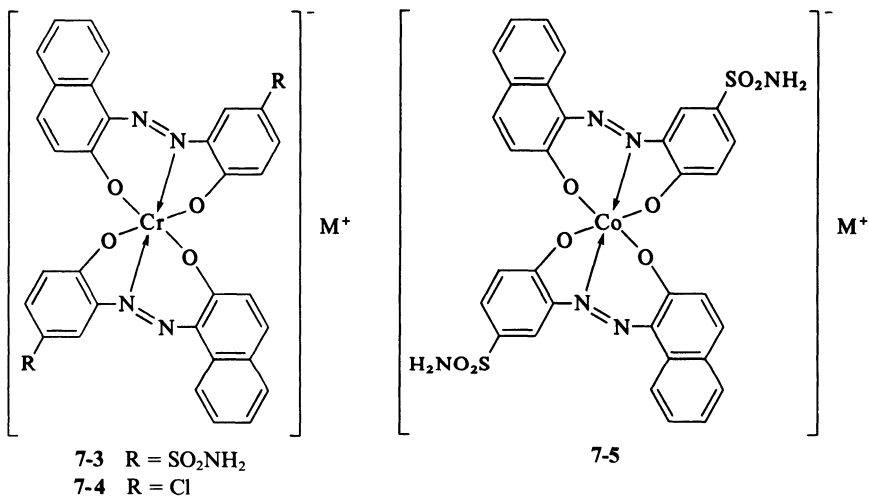
current market leaders. A patent to ICI[47] claims the use of analogous cobalt (III) complexes as negative CCAs. Indeed, CCA 5 (**7-5**) is now on the market.

An alternative approach adopted by Hodogaya is to use more pigmentary type materials as CCAs. True pigments, because of their extreme insolubility, are generally nonmutagenic, even if they contain nitro groups (see *Chapter 12*). Accordingly, Hodogaya's SPILON Black TRH (**7-6**) is a 2:1 chromium complex azo pigment containing several nitro groups based on a BON-acid anilide coupler. It is claimed to be Ames negative.[48]

7-6
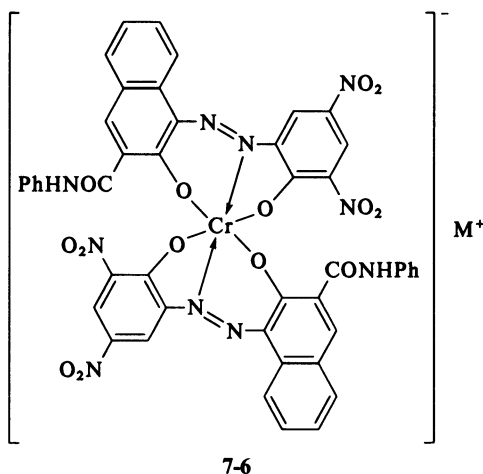
Only a few dyes and pigments are good CCAs. From the many types examined, the best negative CCAs are the 2:1 chromium (III) or cobalt (III) complexes of 1-phenylazo-2-naphthols (**7-7**) devoid of ionizable groups. Even analogous dyes from the isomeric 2-phenylazo-1-naphthol system (**7-8**) perform poorly as CCAs.[46]

Although the structure of the dye is the single most important parameter affecting its performance as a CCA, other parameters are also important (Table 7.3). These include the properties of the counter-ion. In conventional

Table 7.3. Important Parameters Affecting CCA Performance

Parameter	Requirement
Dye structure	$[Dye]^- M^+$
Counter-ion properties	High mobility/compatability enhancement
Thermal stability	High, for processing at 150–200°C
Solubility (in toner resin)	Low
Inorganics (Na^+, Cl^-, . . .)	Low
Water	Low
Particle size	Small
Morphology	Crystalline

1-Phenylazo-2-naphthol
(good)

7-7

2-Phenylazo-1-naphthol
(poor)

7-8
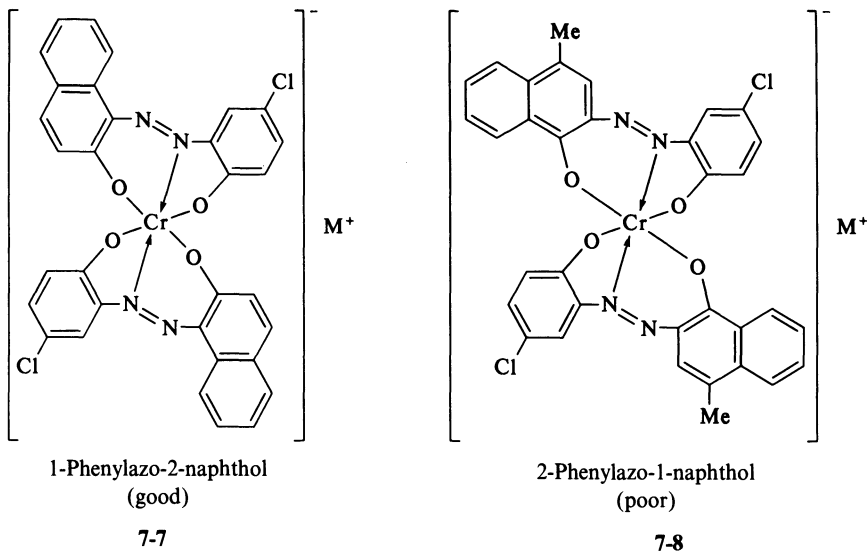
textile dyes, the counter-ion is normally the sodium ion (Na^+) but the best counter-ion for CCA performance has been found to be the hydrogen ion (H^+).[46] This is because it enhances the compatibility of the dye with the resin but primarily because it is small and highly mobile (see *Section 7.5.2.5*).

The thermal stability of the dye must be high and its solubility in the toner resin must be low. These two parameters obviously depend directly upon the dye structure. Further, the dyes must have low levels of inorganic ions, such as sodium and chloride, and water. Particle size and morphology are also important: small crystalline particles are preferable.

7.5.2.2. Positive Charge Control Agents

Positive CCAs are becoming more important as the number of photo-copying machines using OPCs instead of selenium is increasing. Just as negative CCAs are molecules containing an inherent negative charge, positive CCAs are chemicals that generally contain a positive charge.

Nigrosine dyes are the most important type of positive CCA. They are claimed extensively in patents as positive CCAs.[49] Nigrosines are dark blue to black dyes formed by heating nitrobenzene, nitrophenol, or nitrocresol with aniline, aniline hydrochloride, and iron.[50] As such, they are a mixture of various compounds, especially phenazines. The major component is probably of the formula (7-9).[51] Nigrosine oleate is one of the preferred positive CCAs.

Other classes of cationic dyes containing a delocalized positive charge have also been claimed as positive CCAs. The blue triphenylmethane dye (7-10) is typical.[52]

7-9

7-10
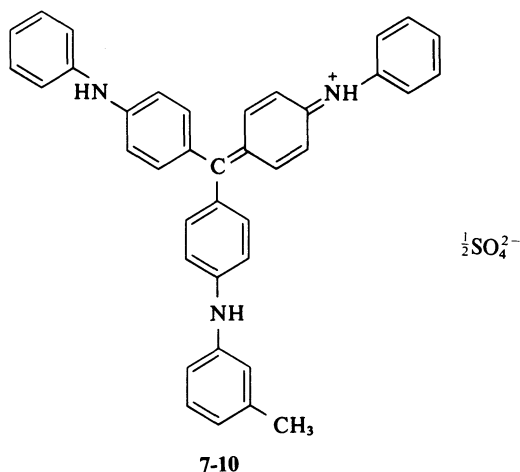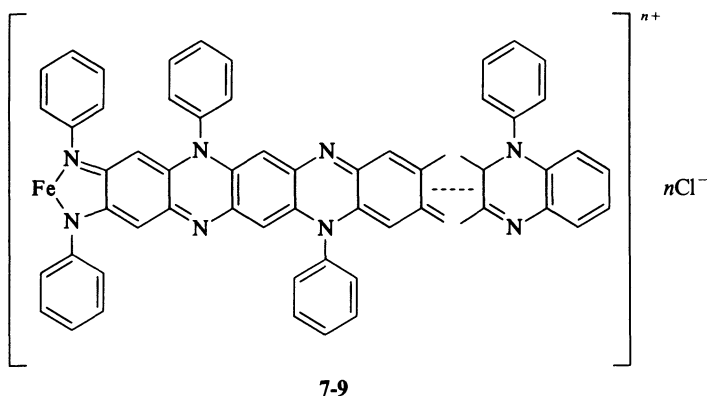
7.5.2.3. Noncolored Charge Control Agents

The 2:1 chromium complex negative CCAs and the nigrosine positive CCAs described above are highly colored compounds. As such, they are useless as CCAs for the colored toners used for color copying, since these use bright yellow, magenta, and cyan pigments and the presence of a dull, intensely colored CCA would obviously destroy the bright colors of the pigments. Instead, noncolored CCAs have to be used. Again, noncolored negative CCAs and noncolored positive CCAs are required.

As mentioned earlier, organic molecules containing sulfonic acid or carboxylic acid groups, such as the surfactant type molecule (**7-11**), are generally poor CCAs. Good noncolored negative CCAs have been obtained by making noncolored analogues of the 2:1 chromium complex azo dyes. This is achieved by making the chromium complex of an aromatic *ortho*-hydroxy carboxylic acid. Typical examples are BONTRON E81[53] (**7-12**) and

BONTRON E82 (**7-13**).[53,54] These complexes are essentially noncolored and are used as CCAs in colored toners.

$$C_{18}H_{37}SO_3^- M^+$$

7-11

7-12

7-13
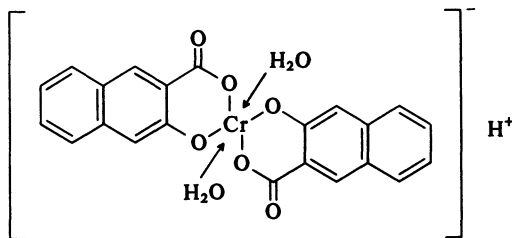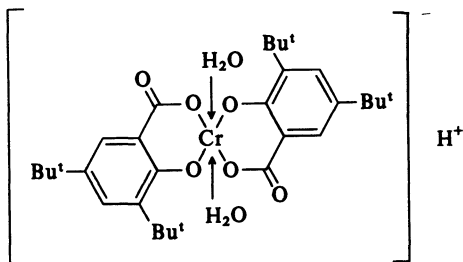
The bulk of the work on noncolored positive CCAs is based on compounds having a quaternary nitrogen atom. The quaternary nitrogen atom may be attached to four hydrocarbon radicals, as in (**7-14**), or may form part of a cyclic structure, as in (**7-15**).

7-14   **7-15**
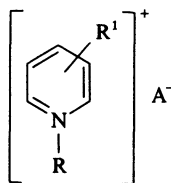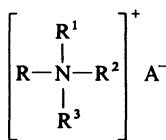
Xerox has been particularly active in this area and has a number of patents on quaternary ammonium compounds of type (**7-14**)[55] and on pyridinium and picolinium compounds of type (**7-15**),[56] such as cetyl pyridinium chloride (**7-16**). Compounds having an aromatic ring, such as (**7-16**), are generally better CCAs.

7-16
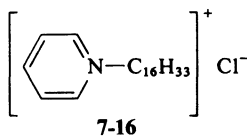
In general, the noncolored CCAs are not as effective as their colored counterparts such as BONTRON S34 and nigrosine.

7.5.2.4. Polymeric Charge Control Agents

Polymeric CCAs are currently being evaluated. The concept here is that a polymeric CCA will be more compatible with the toner resin. There are two basic types: one in which a conventional CCA is attached to a polymer by ionic bonds and one where the polymer itself is the CCA. A typical example of the former type is given by (7-17). Here, a 2:1 chromium complex azo CCA, having a proton as the counter-ion, is mixed with an amino containing polymer such as dimethylaminoethylmethacrylate. The proton forms a salt with the amino group and this results in the anionic dye residue being held to the polymer by an ionic bond.[57]

$[Dye]^- H^+ = 2:1$ Chromium complex azo dye
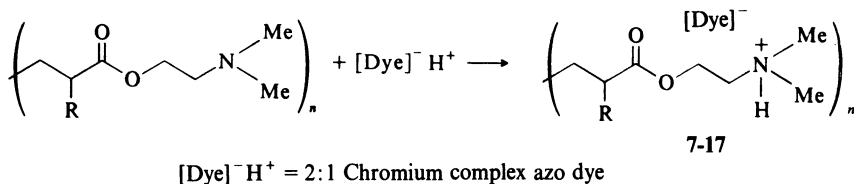
There are many examples of the second type where polymers are chemically modified to produce polymeric CCAs. These include nitration,[58] acylation,[59] and quaternization.[60]

7.5.2.5. Mode of Action

It is not really known how CCAs work. Indeed, the subject has been treated as a "black art." However, the following tentative ideas may have some relevance. The process described is for negative CCAs but applies equally well to positive CCAs.

Triboelectric effects are a surface phenomenon. The charging process of the developer probably involves transfer of the CCA counter-ion at the surface of the toner to the surface of the carrier during contact between the particles (Fig. 7.20a). The toner particles would then become negatively charged because of the CCA anions and the carrier positively charged because of the protons. This mechanism also explains why certain 2:1 chromium (III) or cobalt (III) complex azo dyes that have a proton as the counter-ion are particularly effective CCAs: (1) A proton, being the smallest counter-ion, is highly mobile; and (2) the single negative charge in the dye anion is delocalized over an extremely large pi-system, resulting in an easy removal of the proton.

The presence of aggregates of the CCA at the surface of the toner (probably associated with the carbon black) means that the toner will always
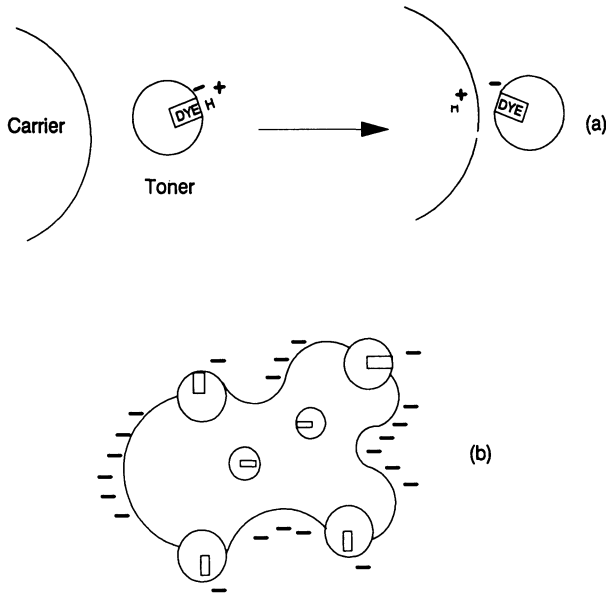
Figure 7.20. Mode of action of CCAs. **a**: Charging process. **b**: Toner action.

have a certain minimum level of negative charge. Repeated contact of the toner and carrier particles will cause further negative charge buildup at the surface of the toner devoid of CCA (it should be remembered that the resins used are chosen because they charge triboelectrically), but this will be limited by the centers of negative charge due to the CCA (repulsion of like charges). CCAs not at the surface of the toner would have no effect (Fig. 7.20b).[46]

This simple picture does explain how a CCA could prevent the charge on a toner particle from being too low or too high. Some evidence that CCAs moderate the charge in this way is that removal of the CCA from the surface of the toner (by leaching with brine containing a dispersing agent) causes a dramatic drop in the triboelectric charge of the toner.[46]

Research on CCAs, especially noncolored CCAs, is still ongoing. Two events are driving this research. One is the move away from chromium-based CCAs because of the fear of forming free chromium VI, a reportedly carcinogenic chemical. Indeed, Canon and Aunyx have contested a law suit on the safety of chromium containing CCAs. The second event is the emergence of color copiers. The colored toners in these machines require different CCAs than those normally used in conventional black toners. For example, they must be either noncolored or have a similar color to the yellow,

magenta, and cyan colorants used in colored toners. Organotin[61] and organoiron[62] complexes are among those being studied.

7.5.3. Colored Toners

At present, color copying is in its infancy. Colored toners probably account for less than 1% of the total toner market but this situation is expected to change within the next few years.[63] Two factors will fuel the increased use of colored toners: (1) the increasing use of color in the graphic arts and Computer Aided Design and Computer Aided Modelling (CAD/ CAM); and (2) the increasing number of primary publications using color. The colored toners will not be restricted solely to photocopying, but will also be used in electrostatic printing (see *Chapter 10, Section 2*) and the newer technologies such as photoactive pigment electrophotoresis (see *Section 7.6*). However, the swing toward colored copying will never be as large as that which occurred in conventional photography (>90% of total film sales are now for colored films rather than black and white),[64] since one of the major uses of photocopying is the copying of documents, books, journals, etc., which employ predominantly black print.

The colorants used in colored toners may be either dyes or pigments. Both dyes and pigments have been patented for use in colored toners but the commercial colored toners generally use pigments. Pigments are preferred because they display higher fastness to light and heat than dyes. One of the practical advantages of this characteristic is that the colored pigment does not bleed during the final heat fusion step of the toner to the paper. In contrast, dyes bleed from the toner resin, especially at the fusion step, which results in a loss of resolution of the copy.[65]

An advantage that dyes possess over pigments is that they dissolve in the toner resins to give highly colored, transparent toner particles. For high quality color copying it is essential that the toner particles be as transparent as possible, since many of the colors of a copy are made up by a combination of two or more of the three primary colors overlaid upon each other.[65] For example, a black is obtained by having the cyan toner particles on top of the magenta toner particles, which, in turn, are on top of the yellow toner particles (Fig. 7.5i). If the toner particles are opaque, then only the color of the top toner particles would be observed, in this case cyan. Indeed, the main reason for the sequence of operations shown in Fig. 7.5 is that the yellow pigment is the least transparent and is therefore deposited first, whereas the cyan pigment is the most transparent and is therefore deposited last.[65]

Typically, the yellow pigments used in colored toners are benzidine disazos such as CI Pigment Yellow 12 (**7-18**)[66] or, less commonly, monoazo yellows such as CI Pigment Yellow 1 (**7-19**).[67] The magenta pigments are
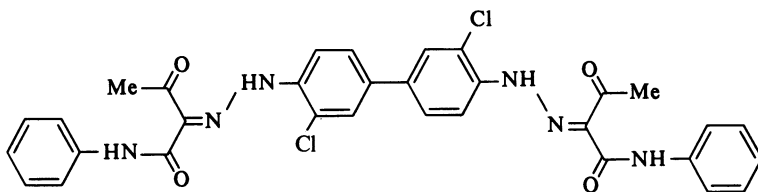
7-18
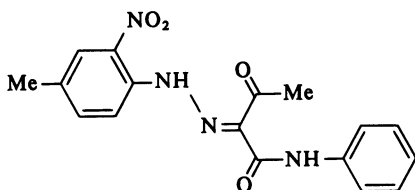
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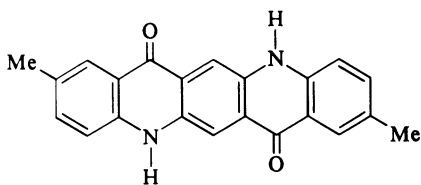
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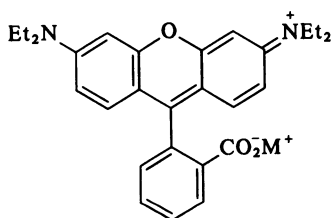
Phosphotungstomolybdic lake
7-21
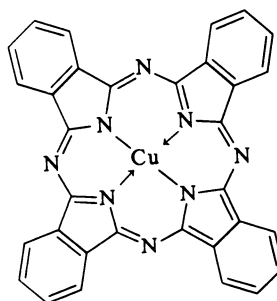
7-22
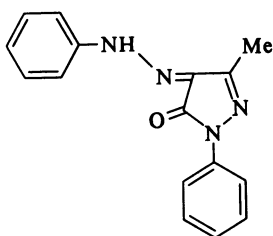
7-23

normally quinacridones such as CI Pigment Red 122 (**7-20**)[66,68] or, less commonly, Rhodamine lakes such as CI Pigment Violet 1 (**7-21**).[69] The cyan pigments are invariably copper phthalocyanines such as CI Pigment Blue 15:1 (**7-22**).[66,70]

Most of the dyes used in colored toners belong to the same chemical classes as the pigments. Thus, the yellow dyes tend to be azos, such as the azopyrazolone CI Solvent Yellow 16 (**7-23**)[71] and the azopyridone (**7-24**),[72]

or azamethines such as CI Disperse Yellow 164.[73] The magentas tend to be Rhodamine bases such as CI Solvent Red 49 (**7-25**)[74] or anthrapyridones such as CI Solvent Red 52 (**7-26**).[75] The cyans are again copper phthalocyanines such as CI Solvent Blue 25 (**7-27**[66,76] and **7-28**[77]). Anthraquinones, such as CI Solvent Blue 111 (**7-29**),[78] are also used as cyans.

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7-25

7-26

CuPc$+$SO$_2$NHC$_{18}$H$_{37})_4$
7-27

7-28

7-29
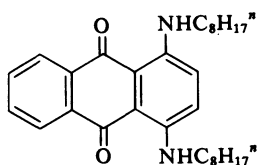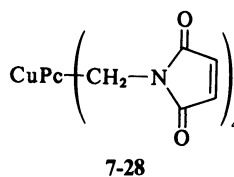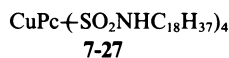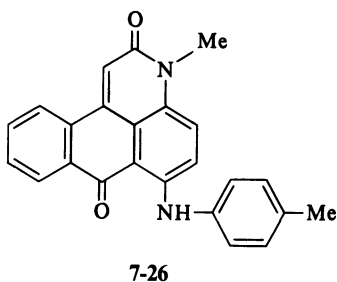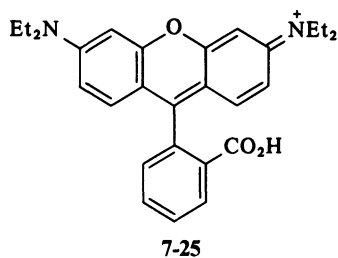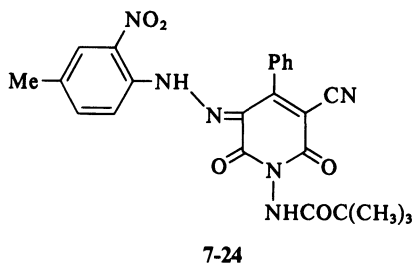
The fact that the yellow, magenta, and cyan dyes and pigments belong to different chemical classes poses another problem: that of triboelectric charge control. Different chemical classes of colorants display different triboelectric charging properties, from strongly positive through neutral to strongly negative[79] (Fig. 7.21). Nigrosine dyes impart the highest positive charge to a toner and 2:1 azo chromium dye complexes impart the highest negative charge, which is why these dyes are used as positive and negative CCAs, respectively (*Section 7.5.2*). CCAs are required to regulate the
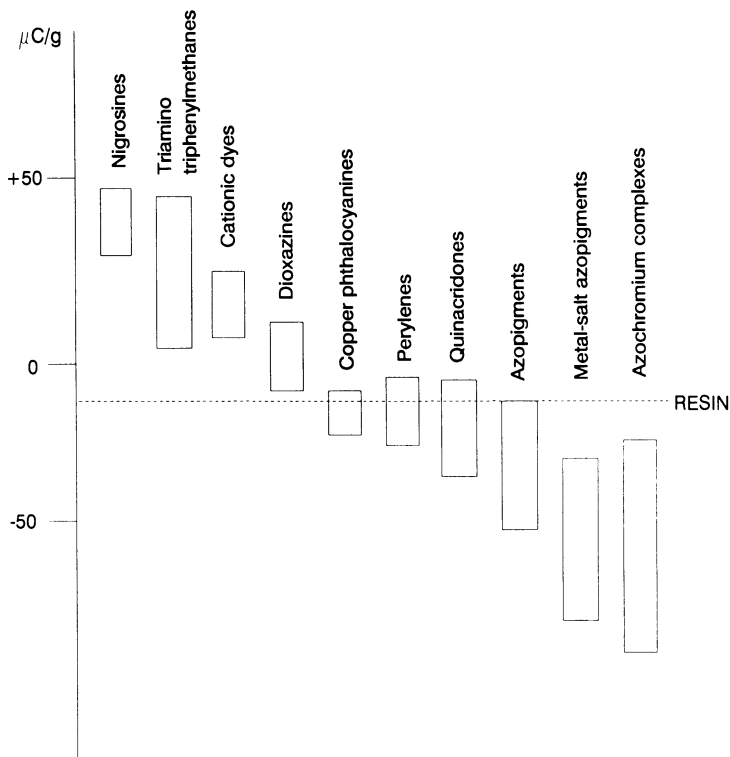
Figure 7.21. Effect of the incorporated pigments on the triboelectric charge of the test toners. *Broken line* indicates the charge of the pure resin.

electrostatic charge on the colored toner particles but, as stressed in *Section 7.5.2*, these now have to be *noncolored* so as not to interfere with the bright yellow, magenta, and cyan colors of the colorants.

Canon and Xerox are the two major companies that were the first on the market with colored copiers and, as might be expected, it is these two companies that hold the most patents on colored toners. Other companies with patents in this area include Ricoh,[71,80] Hitachi Chemical,[69] Sumitomo,[81] Eastman–Kodak,[82] and Oce.[83] Most of these companies have also introduced color copiers into the marketplace.

Because of the problems outlined above, plus the major problem of the slowness of the process arising from the fact that three or four passes are required (it currently takes about 12 sec for a full-color copy of an A4 size document), it is unlikely that the electrophotographic process outlined above will ever dominate the market for full-color copying. However, the related technology of PAPE (see *Section 7.6*) and Mead's CYCOLOR process (see *Chapter 8, Section 4*) could play a major role in full-color copying.

7.6. PHOTOACTIVE PIGMENT ELECTROPHORESIS

PAPE is closely related to conventional electrophotography. The phenomenon was discovered by workers at the Xerox Corporation in the late 1960s[84,85] and has been studied thoroughly since, mainly by Xerox. PAPE has attracted considerable attention because, in theory, it is ideally suited to one-pass full-color photocopying.

7.6.1. Basic Process

The PAPE process combines the principles of photoactive pigment particles, conventional liquid electrophotography, and electrophoresis. It
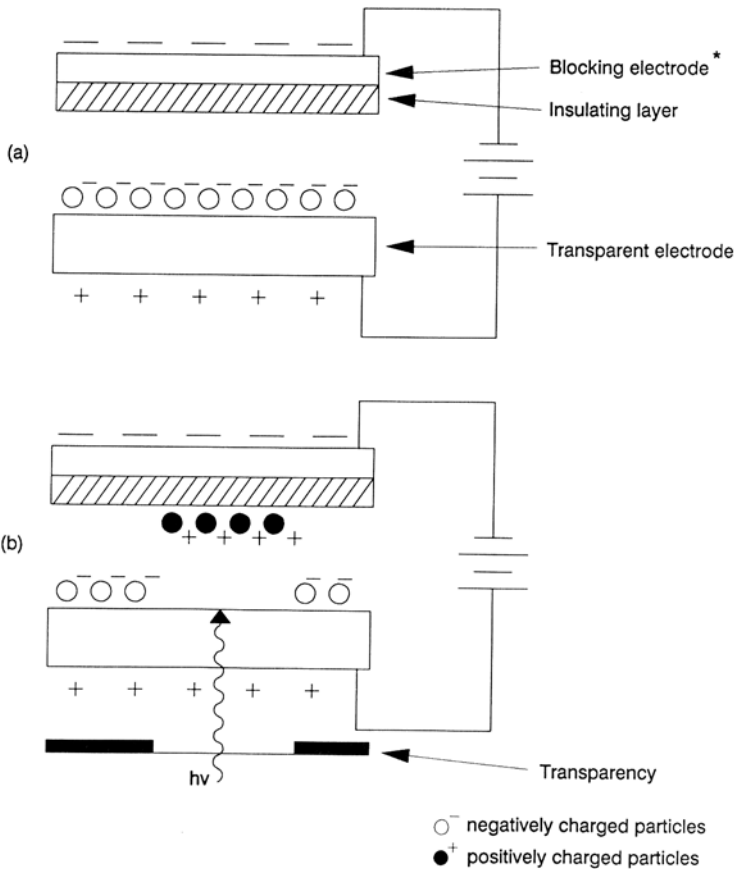
Figure 7.22. Principle of PAPE. *The blocking electrode has an insulating layer to prevent particle oscillation by continual charge exchange at the same electrode.[84]

depends upon the fact that the photoactive pigment particles, when dispersed in a highly insulating liquid, undergo a reversal of electric charge upon irradiation with light.

A simplified version of the apparatus for PAPE is shown in Fig. 7.22. It consists of a dispersion of a finely divided photoactive pigment in an insulating liquid which is sandwiched between two electrodes, a transparent electrode, and a blocking electrode. In the earlier work the transparent electrode (also called the injecting electrode) was NESA glass (glass coated with a thin layer of tin oxide) and the blocking electrode was baryta paper.[85] In later work, polyester film (e.g. Mylar) was used as the transparent electrode and a chromium-plated aluminum drum as the blocking electrode.[86]

The pigment particles in such a situation acquire an electrical charge, shown as negative in Fig. 7.22a, because of the contact potential generated between the solid and the liquid.[84] An electrical field is applied across the electrodes such that the transparent electrode is positively charged and the blocking electrode is negatively charged. In this situation the negatively charged pigment particles are attracted to the positively charged transparent electrode as shown in Fig. 7.22a. Light is now shone through an image (e.g. a transparency) onto the transparent electrode. In those regions where the light passes through the image and the transparent electrode, it hits the pigment particles and causes a reversal of the charge on the particles from negative to positive. These positively charged particles are repelled from the positively charged transparent electrode and migrate to the negatively charged blocking electrode. Those particles not hit by light remain at the transparent electrode forming a positive image of the original. A negative image is formed on the blocking electrode (Fig. 7.22b).

7.6.2. Full-Color Process

As mentioned earlier, the main attraction of PAPE is its potential for producing one-pass full-color photocopying. Full-color copying by conventional electrophotography requires at least three passes (*Section 7.2.3*). To achieve one-pass full-color copying requires the use of three photoactive pigments, namely yellow, magenta, and cyan. Ideally, the pigments should have sharp absorption curves so that each pigment is only sensitive to the radiation of its complementary color. For instance, the yellow pigment should only be sensitive to blue radiation, the magenta pigment to only green radiation, and the cyan pigment to only red radiation (Fig. 7.23).

Pigments used for PAPE should have the correct spectral color (e.g. yellow, magenta, and cyan) and be photosensitive. Typical of the early pigments used by Xerox are CI Pigment Yellow 24 (Flavanthrone) **(7-30)**
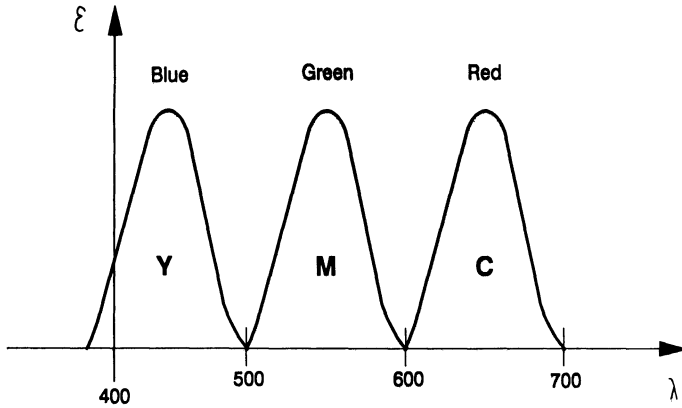
Figure 7.23. Ideal absorption curves. Y, yellow pigment; M, magenta pigment; C, cyan pigment.

and CI Vat Yellow 2 (**7-31**), CI Pigment Red 48:2 (**7-32**), and CI Pigment Red 122 (**7-20**), and CI Pigment Blue 16 (**7-33**), the alpha form of metal-free phthalocyanine.[84,85]

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7-31

7-32

7-33
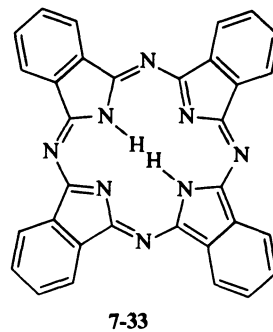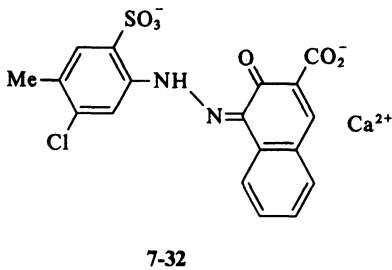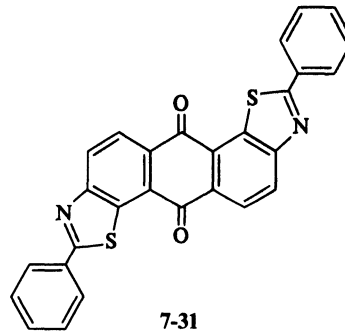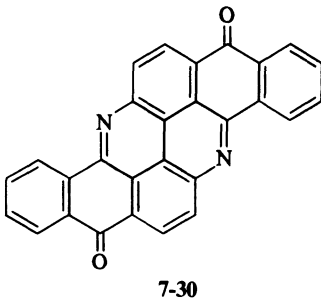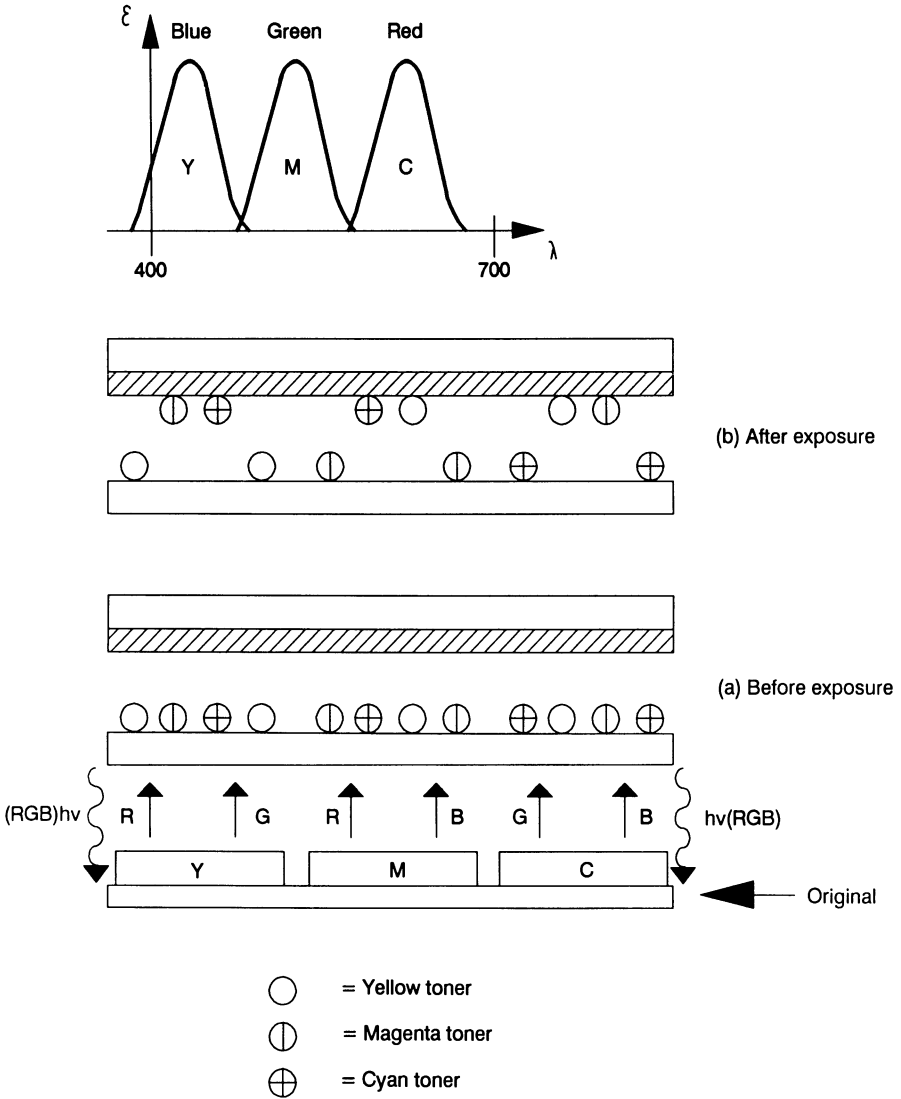
Figure 7.24. Full-color copying using PAPE.

A suitable yellow, magenta, and cyan trichromat of pigments is dispersed in a highly insulating liquid, typically a petroleum fraction such as Sohio Odorless Solvent 3440,[85] and the dispersion sandwiched between the transparent electrode and the blocking electrode. The yellow areas of the original absorb the blue light and reflect the red and green light (Fig. 7.24a). The red and green light are absorbed by the cyan and magenta particles, respectively, causing them to undergo a reversal of electrical charge and

migrate to the blocking electrode. This leaves a yellow image on the transparent electrode corresponding to the yellow image on the original, i.e. a positive image (Fig. 7.24b).

In the same way, the magenta image areas absorb the green light and reflect the red and blue light (Fig. 7.24a). The red and blue light are absorbed by the cyan and yellow pigment particles causing them to migrate to the blocking electrode. The magenta particles remain on the transparent electrode forming a positive image (Fig. 7.24b).

Finally, the cyan image areas absorb the red light and reflect the green and blue (Fig. 7.24a). This is absorbed by the magenta and yellow pigment particles, respectively, causing them to migrate. A positive cyan image remains on the transparent electrode (Fig. 7.24b). All these processes occur simultaneously so that a full-color copy of the original is produced after one exposure of the original to white light.

7.6.3. Problems of Photoactive Pigment Electrophoresis

Although PAPE is fine in theory, there are a number of practical problems. One of these concerns available organic pigments. Organic pigments do not exhibit the ideal narrow absorption curves depicted in Fig. 7.23. They have broader curves which overlap each other (Fig. 7.25). Consequently, the photosensitivity of the yellow, magenta, and cyan pigments is not as specific as desired.

A second problem area is particle interactions. These interactions result in the agglomeration of the yellow, magenta, and cyan particles and hinder
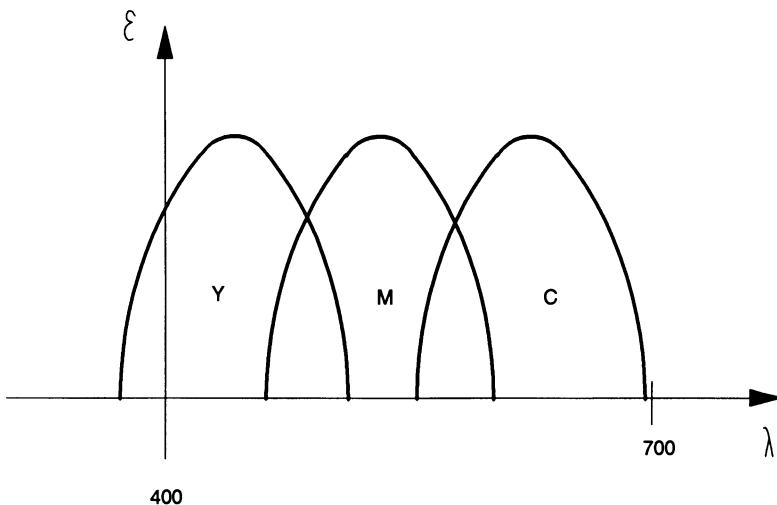
Figure 7.25. Typical absorption curves of yellow (Y), magenta (M), and cyan (C) pigments.

single particle migration. For example, some magenta and cyan particles may migrate along with the yellow particles.

A third problem is that the particles deposited on the blocking electrode can impair the migration of further particles. This can be overcome by repeated cleaning and further exposure steps,[85] but this reduces the optical density of the positive image on the transparent electrode and defeats the objective of PAPE, namely a one-pass full-color copying system.

A fourth problem involves the transfer and fixing of the image from the transparent electrode to the final (paper) substrate. As discussed in *Section 7.5.1*, toners in conventional electrophotography consist of pigment dispersed in a low melting point resin which is heat-fused to the final paper substrate. Most work on PAPE has centered on using pure pigments since these tend to produce the best results. However, if this was to be the case in practice, then an after-treatment step would be required after the transfer step to fix the image on to the paper.

Another problem is the difficulty of replenishing the bath in line with what is removed. As the ratio of colored toner in the bath depends on the balance of color in each document copied, it is very difficult to continually keep the system "in balance."

Finally, PAPE uses a solvent-based developer and therefore suffers from the same disadvantage of liquid toners in electrophotography, namely having solvent as effluent during the fixation stage.

Ways of circumventing these problems have been described. For example, Luebbe and Maltz[87] used the fluorescent dye Rhodamine 6GP to improve the photosensitivity of a red pigment in poly-*N*-vinylcarbazole. Croucher *et al.*[86] used a composite particle comprising a colorant and a photoactive pigment dispersed in a polymeric binder; the particle also contains steric stablizers to minimize particle–particle interactions (Fig. 7.26).
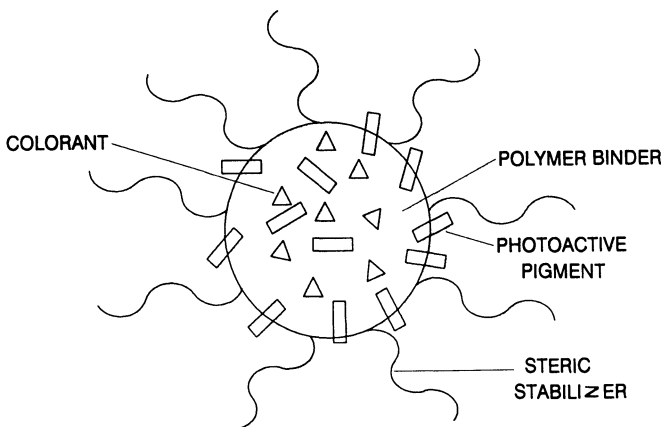
Figure 7.26. Illustration of an ideal PAPE developer.

7.6.4. Correlation with Organic Photoconductors

It is not yet fully understood why certain pigments are photoactive and others are not. However, the phenomenon is obviously closely related to that of OPCs and it may be that the best OPCs make the best photoactive pigments. In this case, it may be necessary to optimize the colors of the charge generating materials to produce acceptable yellow, magenta, and cyan colors. Indeed, this optimization appears to be happening to some extent. For example, the three pigments preferred by Xerox are the vanadyloxy phthalocyanine cyan (**7-34**), the azo magenta (**7-32**), and the quinone yellow (**7-35**).[88] Vanadyloxy phthalocyanine is a highly effective charge generating material for OPCs (*Section 7.4.3*) and has spectral characteristics for a cyan that are superior to the alpha form metal-free phthalocyanine (**7-33**) used previously. According to Xerox the preferred magenta pigment is still (**7-32**), although magenta charge generating materials of the perylene tetracarboxydiimide type such as **7-36** must also be strong contenders. Finally, the preferred yellow is the brominated naphthoquinone furandione (**7-35**). Yellow charge generating materials are not used so there is no direct comparison of the performance of **7-35** in PAPE with its performance in OPCs. However, CI Pigment Yellow 96 was deliberately brominated to improve its spectral characteristics.[89]
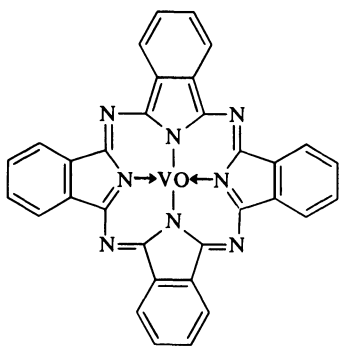
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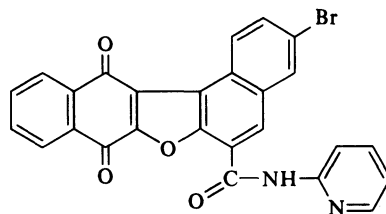
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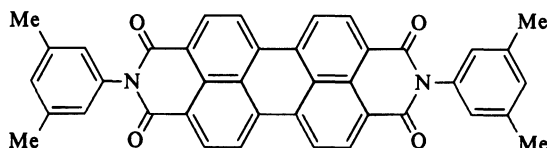
7-36

New photoactive pigments are still being patented. For example, Ciba-Geigy[90] has patented isoindoline yellow pigments (**7-37**) and Eastman Kodak[91] has patented aluminum phthalocyanine (**7-38**).

R¹, R², R³, R⁴ substituted isoindole structure labeled:

7-37

Aluminum phthalocyanine structure labeled:

7-38

R = H or Cl
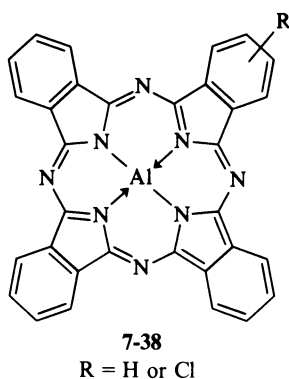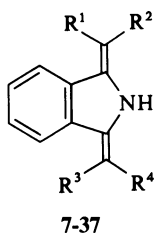
To date, a one-pass full-color copying system based upon PAPE has not reached commercial reality, presumably because of the problems outlined earlier.[92] As our understanding of photoactive pigments increases, these problems should not be insurmountable. However, even if a one pass full-color copying system remains elusive, PAPE technology could still have a role to play in monochromatic color imaging.

7.7. SPECIAL EFFECTS

This section deals briefly with some of the more important specialized uses of electrophotographic chemicals. The four areas selected are (1) non-photocopiable documents, (2) photomicrolithography, (3) prepress proofing, and (4) transfer printing toners.

7.7.1. Nonphotocopiable Documents

The unauthorized leaking of highly confidential information has become a serious problem, especially in the case of confidential government information. The widespread use of photocopiers makes the "mole's" job that much easier. A further problem on the horizon is the introduction of full-color copiers and color printers using electronic scanners. Such copiers and printers will be welcomed especially by forgers, since they will make the counterfeiting of items such as currency, cheques, tickets, and passports that much easier. Consequently, ways of preventing, or at least severely inhibiting, the copying of all these items are being sought.

The photocopying process depends upon the *selective reflection* of white light from the document to be copied. The print, normally black, absorbs the radiation, and the background, normally white, reflects it. Any non-photocopiable document must eliminate (or severely reduce) this selective

reflection of radiation as far as the copier is concerned but still maintain the contrast as far as the eye is concerned. Basically, there are two ways to achieve this: (1) make the background nonreflecting, or (2) make the print as reflective as the background.

Most of the reported work has been done on the first approach, aimed particularly at preventing copying using selenium-based copiers. As was described above (*Section 7.4*), selenium has no spectral sensitivity beyond 600 nm. Matching the absorption characteristics of the paper to the spectral response of the photoconductor produces a copy that is black, since no radiation of the appropriate wavelength reaches the photoconductor. In practice, this means incorporating dyes that absorb all the radiation from 400 to 600 nm: this produces a deep red or maroon paper. However, colorants that absorb outside the sensitivity of the selenium photoconductor (400–600 nm) but still inside the visible spectrum (i.e. in the red region at 600–700 nm) will be detected by the eye. Thus, black or blue colors, both of which absorb strongly in this region, provide sufficient contrast on the red background to be detected by the eye but not by the copier (Fig. 7.27).

Gardner has pioneered the work in this area.[93] Indeed, the work has been successful in preventing the copying of documents using selenium-based copiers and Gardner has formed a company, Nocopi, to market his products.[94]

This approach of a nonreflective background is not ideal (a) because it uses colored rather than the normal white paper, (b) because reading such paper is tiring to the eye and, more importantly (c) because many modern
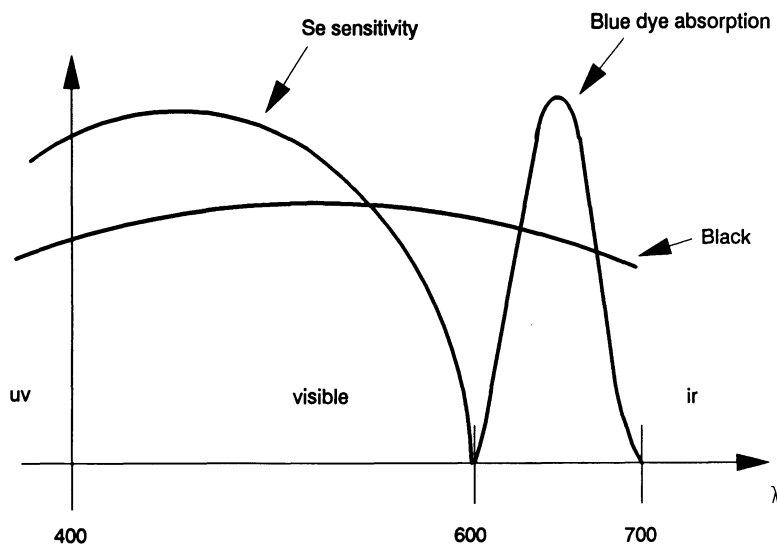
Figure 7.27. Selenium sensitivity in relation to absorption curves of blue and black colorants.

photoconductors, such as arsenic triselenide and especially the OPCs, do not present such windows of spectral insensitivity that selenium photoconductors present.

A slightly different approach involves using photochromic compounds.[95] In theory, these noncolored compounds should become colored on exposure to the UV radiation present in the white light of a photocopier. In practice, the amount of UV radiation in modern copiers is insufficient to produce the color change. Otherwise, the mechanism of copy prevention is as described above for the permanently colored papers.

The second approach to producing a nonphotocopiable document is to make the print as reflective as the background. This could be achieved by using fluorescent inks (e.g. red) providing that the fluorescence, which occurs at longer wavelengths than the absorption, still falls within the spectral sensitivity of the photoconductor. In theory, this approach should be applicable to most photoconductors. Figure 7.28 illustrates the principle. Thus, a highly fluorescent red dye selectively absorbs some of the white light radiation: normally this would produce a photocopy. However, if the dye has a high quantum efficiency and re-emits the absorbed radiation as fluorescence, then, as far as the copier is concerned, all the radiation has been reflected back on to the photoconductor and no copy should be produced. As discussed earlier (*Section 7.4*), colored print which absorbs outside the spectral sensitivity range of a photoconductor will not be copied.

An alternative method of copy prevention which would be very effective requires the compliance of photocopier manufacturers. The method involves

Figure 7.28. Fluorescence and photocopiability.

using ordinary white paper that contains a strip of metal or, better still, an invisible infrared absorbing chemical (see *Chapter 11*). Each copier would scan the document with a solid state semiconductor laser prior to copying. If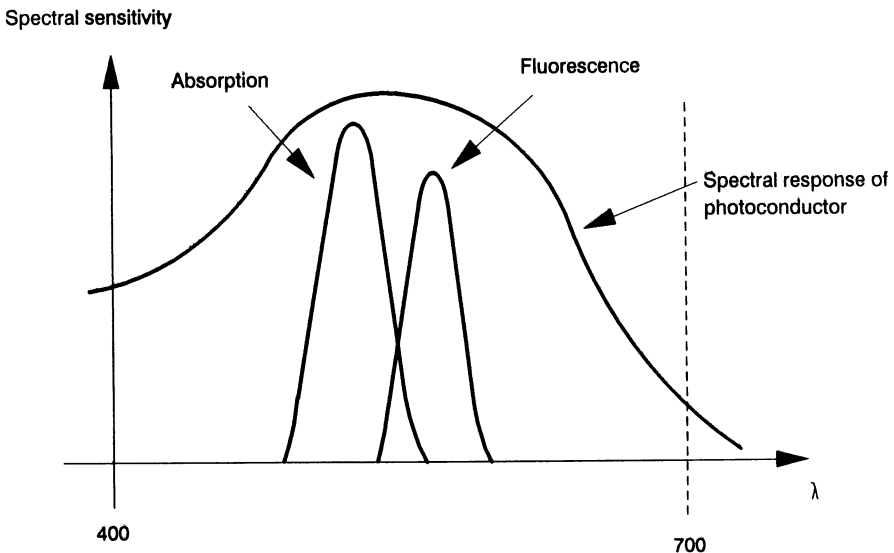 the infrared absorbing chemical was detected, the copier would default and refuse to function.[96] This approach is attractive since (a) it would function with any copier (or laser printer) and (b) it allows the use of white paper. However, as stated above, it would require all manufacturers to cooperate by incorporating an infrared sensing device in their machines.

7.7.2. Photomicrolithography

Photomicrolithography is the process whereby electrophotography is used to produce lithographic printing plates. Traditionally, lithographic printing plates are produced using photoresists. These may be positive working or negative working and require exposure to strong UV radiation through a photographic transparency followed by a chemical etching to form the final plate.[97] This process is costly in time, materials, and money. With photomicrolithography, the paper original is inserted directly into the machine and the finished lithographic plate emerges 3–4 minutes later.[98]

In photomicrolithography an OPC coating is applied evenly to an aluminum lithographic plate. The red charge generation material, dibromo-anthanthrone,[99] which has good sensitivity to white light, and zinc oxide, which has good sensitivity to near UV radiation,[99,100] are typical charge generating materials (*Section 7.4*). Other charge generating materials with different sensitivities, such as phthalocyanines, may also be used.[101] The binder resin normally contains carboxy groups to make it alkali soluble so that the OPC coating on the nonprinted areas after exposure and development can be dissolved to expose the lithographic aluminum.[98,102]

The process to produce an offset lithographic printing plate from a paper original comprises five major steps, as depicted in Fig. 7.29. The first three steps—charging, exposure, and development with a toner—are exactly the same as for photocopying (*Section 7.2.1*). At this stage there is a visible image of the original document on the OPC-coated aluminum plate (Fig. 7.29). The toner particles are then fused, usually by infrared radiation, onto the OPC coating. The thickness of the toner mask formed, which is resistant toward the coat-removing solvent, is typically 3–4 μ. In the final stage, the OPC coating in the areas not protected by the fused toner is removed with an alkaline solvent to expose the surface of the aluminum sheet.

Dry two-component toners are normally used in photomicrolithography. The toners differ from conventional photocopying toners in having a smaller particle size (typically 6–7 μ compared with 15–20 μ) and having good resistance to the alkaline coat-removing solvent. The fusing temperature also has to be right and this is achieved by choosing polymers with glass
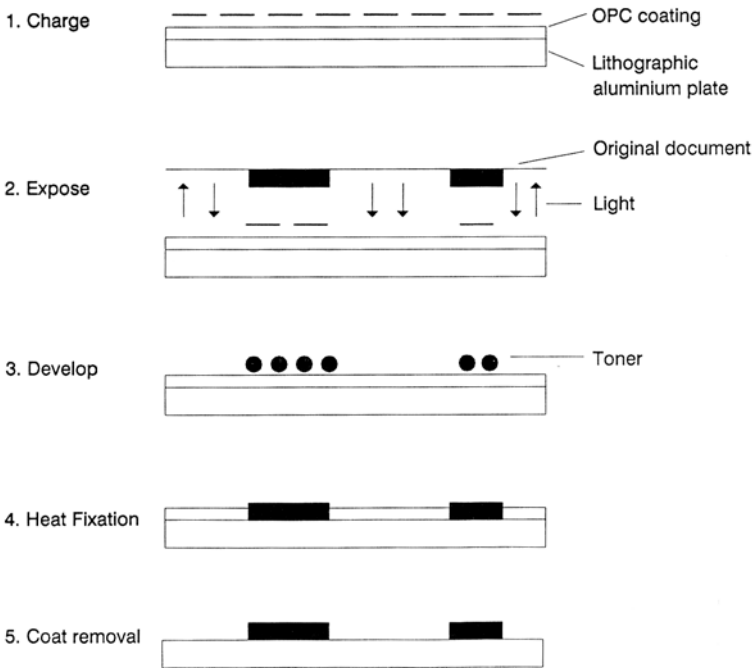
Figure 7.29. Steps in photomicrolithography.

transition temperatures in the range 50–120°C. In practice, styrene-acrylic copolymers are used with the molecular structure modified to achieve the desired properties.

At least two companies have commercial products. Hoechst has a system that uses ELFASOL plates and which already produces around 12 million newspapers per day,[98] and Polychrome/DaiNippon Ink and Chemicals has the Laser AZ-94K platemaker.[103] The importance of this technology has yet to be determined.

7.7.3. Prepress Proofing

Prepress proofing[103,104] is vital to practically all printing, as it provides an opportunity for the printer and the customer to view a sample of the printing before the entire job has been run. In this way, changes can be made before the job goes to press, ensuring that expensive press time, paper, and ink will not be wasted if adjustments are required.

Color proofing is a very important and critical step in the process of color reproduction, as color proofs are made at different stages and for diverse uses in the process. For example, color proofs are required for cus-

tomer approval, usually before the production run: compatability proofs are generated for magazines and other periodicals that contain advertisements, which may be submitted to the printer as color transparencies, color photographic prints, or art work on board. Proofs of the supplied films in the printer's colors and materials are absolutely necessary in these cases to make sure that all the subjects are compatible, since they must all print from the same plate on the same press and with the same paper and inks. Finally, color proofs are used for quality control checks by the printer to assess the efficiency of the manufacturing processes.

Color proofing processes are either on-press or off-press systems. On-press systems involve all the normal stages, such as making plates and running several prints. This system, which for many years was the only way to make proofs, is not discussed further. The off-press systems are shown in Table 7.4. Only the more recent color electronic prepress system (CEPS),[104] is considered. These systems first display digitized data as a soft copy on a screen from which a hard copy can be produced. One major advantage of a digitized soft copy is that it can be transmitted electronically anywhere in the world and identical hard copies produced wherever they are needed.

The first digital hard copy proofing systems introduced in 1982 all used photographic paper to achieve the required quality. However, the newer systems are based on toners and, to a lesser extent, on dye diffusion thermal transfer technology (see *Chapter 8*, *Section 6*), for example, Dai Nippon Printing's prototype $100,000 machine. The technologies employing toners may be conventional ones, such as Coulter's ACP electrophotographic process, or new technologies, such as DX Imaging's Electrostatic Master Print process. Most of these systems use liquid toners because of their higher

Table 7.4. Prepress Technologies and Systems

System	"Player"
Overlay	3M Color Key
	Enco Naps/Paps Proof
	DuPont Cromacheck
Single sheet	Agfa-Gevaert Gevaproof
	3M Transfer-Key and Matchprint
	DuPont Cromalin
Digital (soft)	Hazeltine Electronic
	Toppan CP 525 MK11
Digital (hard)	Hell CFPR 403
	Polaroid/MacDonald-Dettwler High Speed
	Tektronix 4692 Ink Jet
	Iris 2044 Ink Jet
	DNP Digital (Thermal D2T2)

resolution, including modified Landa technology. The colorants used appear to be similar to those used in conventional toners.

7.7.4. Transfer Printing Toners

This topic combines the technologies of electrophotography and thermal transfer printing (see *Chapter 8, Section 6*). In transfer printing toners the conventional colorant, such as carbon black or the dyes and pigments used in colored toners, is replaced by a heat sublimable dye. Otherwise, the toners are essentially the same as the standard toners discussed in *Section 7.5.1*. The process is also the same. Therefore, many colored copies (usually monochrome, e.g. red) of an original can be produced quickly, inexpensively, and in high quality on, for example, thermal transfer paper. The image can then be transferred by the application of heat, typically 210°C for 30 sec, from the transfer paper to a final substrate such as polyester or polyester-cotton, although more unusual substrates such as anodized aluminum may also be used. The thermal transfer step is the same as for the conventional transfer printing of textiles. The advantage of the process lies in its simplicity: anything that can be photocopied can be reproduced in a variety of colors on a final substrate: the only equipment required is a photocopier and a hot iron (Fig. 7.30).

The majority of companies active in the area use conventional textile transfer printing disperse dyes. These are usually low molecular weight azo or anthraquinone dyes devoid of water solubilizing groups. Typical dyes are the azo yellow (**7-23**),[105] the anthraquinone red (**7-39**),[106] and the anthraquinone blue (**7-40**).

7-39

7-40
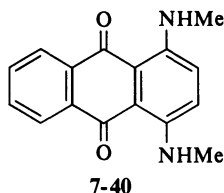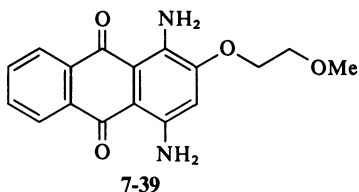
The resins used must be thermally stable to withstand the final heat transfer step and therefore they may differ from the conventional styrene-acrylic or polyester resins used in conventional toners.

The toners may be part of the standard dry two-component developer described in *Section 7.5.1*. This approach has been patented by Coates Bros.[107] Liquid toners may also be used, as in the patents by Ricoh[108] and Toppan Printing.[109] However, most transfer printing toner patents are of the monocomponent magnetic type. These include Coates Bros.,[110] Subligraphics,[106,111] Du Pont,[112] Hitachi Metal,[113] and International Toner Specialities.[114]
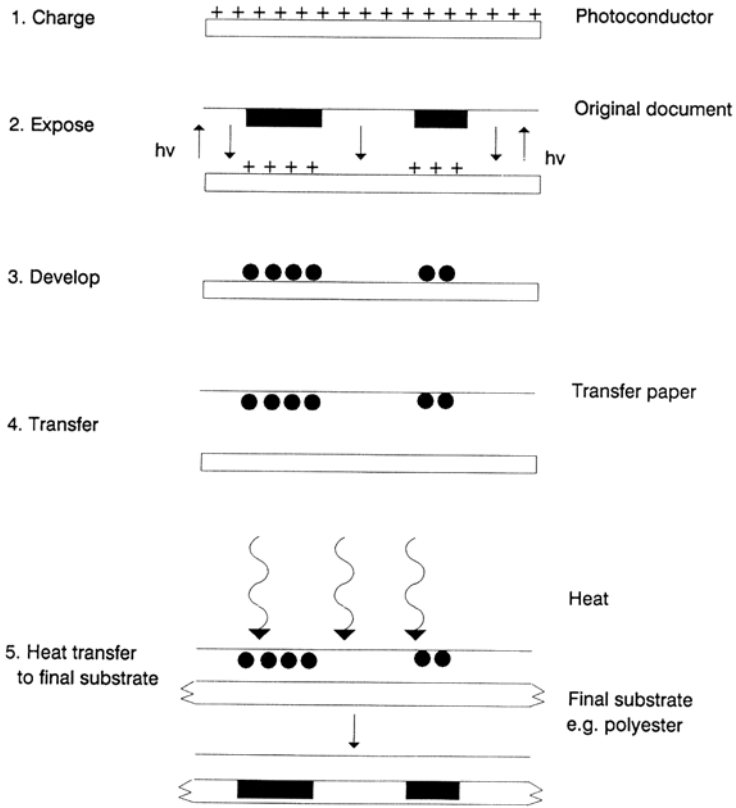
Figure 7.30. Producing an image using transfer printing toners.
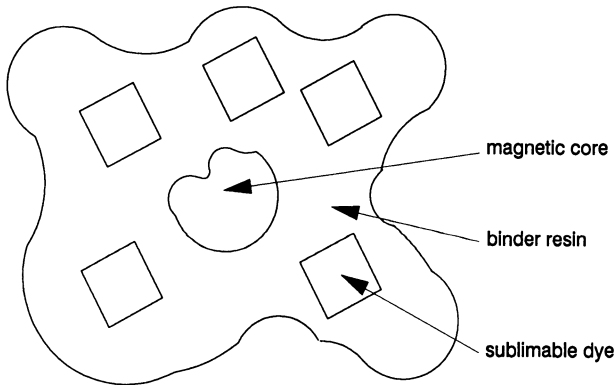

Figure 7.31. Monocomponent magnetic transfer printing toner.

The construction of a typical monocomponent magnetic transfer printing toner is shown in Fig. 7.31. The core consists of a magnetic material such as iron, steel, or magnetite and this is coated with a resin containing the heat sublimable dye and optionally other additives such as surfactants or charge control agents.

Matsushita[115] provides a variation on the above theme, using sublimable color formers (see *Chapter 8, Section 6.5*) instead of sublimable dyes in the transfer printing toners. An acidic substrate is needed to develop the colored image.

7.8. SUMMARY

Electrophotography, perhaps more familiar as photocopying and laser/LED printing, is by far the biggest of all the reprographics technologies. The two key chemical components are the photoconductor and the toner.

Photoconductors may be either inorganic, such as selenium, or organic. For a variety of reasons the trend is toward OPCs and greater than 50% of all commercial copiers and printers now use OPCs. OPCs are predominantly dual layer systems comprising a colored charge generation layer and a non-colored charge transport layer. Charge generating materials, which are normally pigments, are used in the charge generating layer and electron-rich molecules with low ionization potentials are used in the charge transport layer. Both types need to have high purity.

Toners may be of the liquid type or, more usually, the dry type. The key ingredients are the colorant and the CCA. The colorant is predominantly carbon black but with the emergence of full color copiers, yellow, magenta, and cyan dyes or especially pigments are required. CCAs control the electrostatic charge on the toner particles. Negatively charged and positively charged toners are required depending upon the application. Dyes provide the best CCAs and are used in black toners where the color is masked by the carbon black. Metal complex azo dyes, especially chromium and cobalt, provide the best negative CCAs. Nigrosine dyes provide the best positive CCAs. For colored toners, noncolored CCAs are needed.

PAPE is a related technology to photocopying and laser/LED printing. Its main attraction is its potential for a one-pass full-color copying system. As yet, this potential has not been realized commercially.

There are several specialist effects in electrophotography such as non-photocopiable documents, photomicrolithography, prepress proofing, and transfer printing toners. Nonphotocopiable documents is an area that is becoming increasingly important. The variety of photoconductors and machines make it extremely difficult to prevent universal copying. The two basic approaches are to make the background as nonreflective as the print and to make the print as reflective as the background. The best way to

prevent the copying or printing of confidential documents requires the compliance of machine manufacturers. By incorporating an infrared sensor in the machine, any confidential document containing an invisible infrared absorber would automatically cause the machine to abort. Photomicrolithography is an inexpensive way of producing offset litho plates for short runs. Prepress proofing, especially electronic prepress proofing, is an important area which demands high quality and where toner-based technologies are playing a major role. Transfer printing toners offer an easy way of taking an original image and reproducing it on a textile substrate.

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8

Thermography

8.1. INTRODUCTION

Thermography, or thermal printing, is that branch of reprographics which uses heat as the energy source. The heat is normally supplied directly from thermal heads or a heated stylus. However, it can also be supplied indirectly from electrical energy, an example of which is the resistive ribbon technology developed by IBM (now termed electrothermal printing), and from lasers.

Thermal printing can be divided conveniently into two main areas: direct thermal printing and thermal transfer printing. Thermal transfer printing can be subdivided further into thermal wax transfer and dye diffusion thermal transfer (D2T2) (Fig. 8.1).

As seen from Fig. 8.1, thermal printing originated in 1953 when specially coated thermally sensitive paper, upon treating with a heating element or stylus, produced readable marks.[1] Thermal printing technology developed somewhat slowly over the next 20 years until the introduction of the Thermal Transfer process by Nippon Telegraph and Telephone in 1975.[1] This revolutionary new technique enabled printing to occur on plain paper, eliminated the fading problem associated with the direct thermal process (color formers), and made full-color imaging possible. More recently, D2T2 and electrothermal printing (IBM resistive ribbon) have appeared[1,2] (Fig. 8.1).

Pressure-sensitive printing and the new Mead Photocapsule (CYCOLOR) process are also included in this discussion of thermography, since these technologies and especially the chemicals employed are closely related to those in thermal printing. As a rough guide, direct thermal printing and pressure-sensitive printing represent the lower cost/lower quality end of thermography whereas dye D2T2, one of the newest technologies, represents the high quality end. Thermal wax transfer printing represents the middle quality area.

THERMAL PRINTING

Transfer

Direct
(1953)

Wax
(1975)

D2T2
(ca 1981)

Mead
Photocapsule
Process
(ca 1984)

Pressure
Sensitive

Electrothermal
(ca 1984)
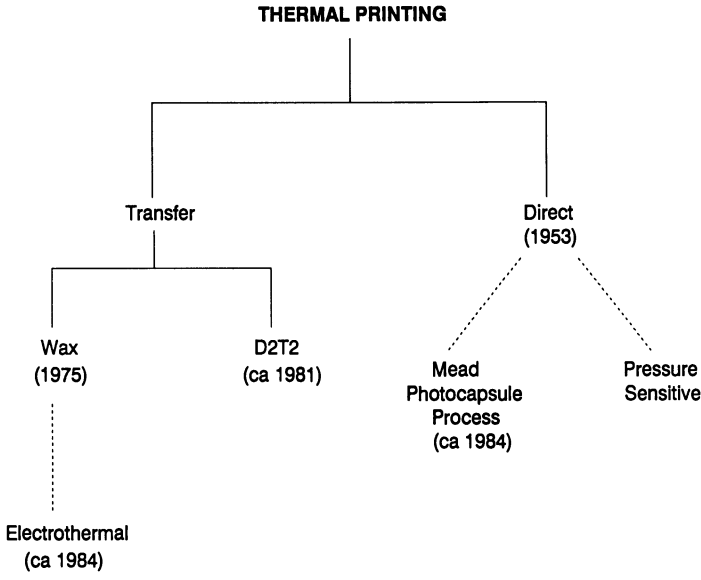
Figure 8.1. Subdivisions of thermal printing.

8.2. DIRECT THERMAL PRINTING

Very simply, direct thermal printing[3,4] is the process whereby an image is produced on thermal paper by using an array of thermal heads. Wherever a heated thermal head touches the thermal paper a dot of color is produced. By the correct positioning of the thermal heads, the desired pattern (text or graphics) is produced. Therefore, an understanding of direct thermal printing can be reduced to an understanding of the construction and operation of thermal paper.

A cross-sectional view of a typical thermal paper is shown in Fig. 8.2. It consists of a base layer upon which is a thermally sensitive layer. The

Hot
stylus

Colored area

Thermal sensitive layer

Base paper
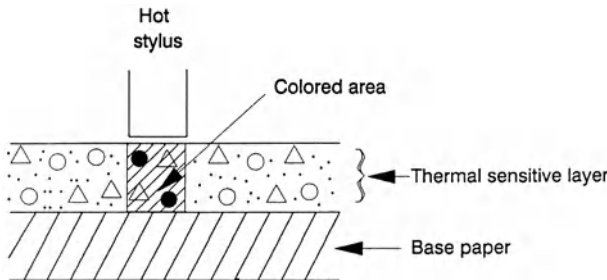
Figure 8.2. Cross-section of a typical thermal paper. *Circles,* color former; *triangles,* developer (bisphenol A).

thermally sensitive layer contains a color former and a developer dispersed in a binder. Heat from a thermal head causes localized melting so that the color former and developer are brought into contact: this produces the color.

The color formers used in thermal paper are essentially colorless organic compounds that develop an intense color when brought into contact with an acid. Black is the most important color in thermal printing, and the most widely used color formers for producing a black are the fluorans of structure (**8-1**). Contact with acid generates the intense black color of the chromogen proper, a cationic dye (**8-2**) of the xanthene (fluoran) type containing a delocalized positive charge.

8-1 Colorless   8-2 Black

(a) R = R' = Et

(b) R = Me, R' = —⟨ H ⟩

(c) R = Et, R' = —⟨ ⟩—Me
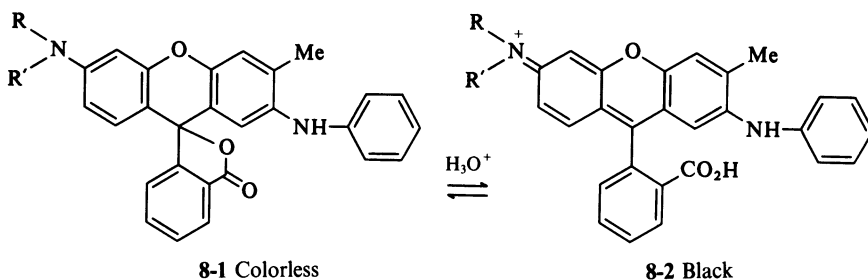
These color formers are known as "one-dye blacks" since the black color is produced from just one dye. Another way of producing black is to use a number of color formers of colors other than black which, when mixed together, produce a black color. For example, a mixture of the blue color former (**8-3**) with the orange color former (**8-4**) generates a black color. Obviously, color formers (**8-3**) and (**8-4**) can be used alone to produce blue and orange colors, respectively, if these are desired, and color formers of

8-3 Colorless   Blue

8-4 Colorless   Orange

8-5   Red
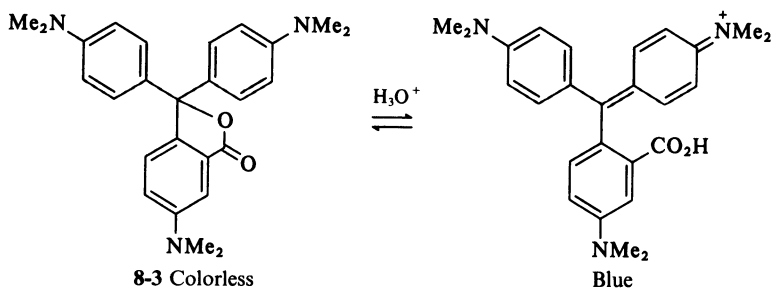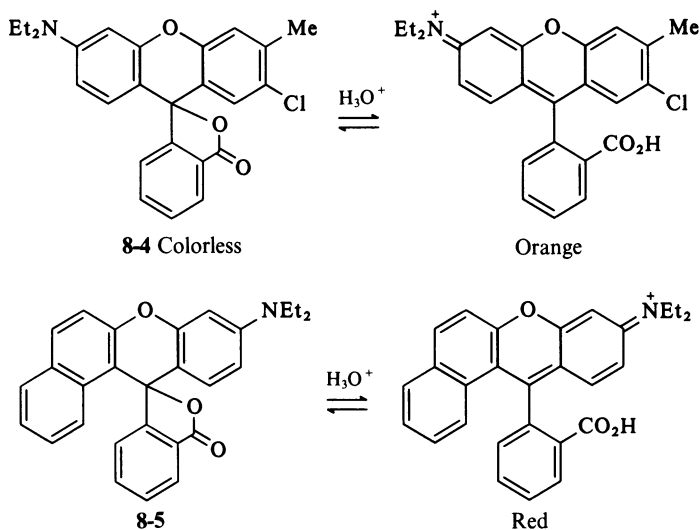
other colors are available. For example, the red color former (**8-5**). The blue color former (**8-3**), which is known as Crystal Violet Lactone, is very widely used in pressure-sensitive paper (see *Section 8.3*).

The developers are usually solid acidic compounds, especially phenols. The most widely used developer is bisphenol A (**8-6**). It is inexpensive and readily available, both desirable attributes since the developer is used in greater amounts than the color former. However, its coloring sensitivity is on the low side. In other words, larger energy inputs are required to give high optical densities (Fig. 8.3).

8-6
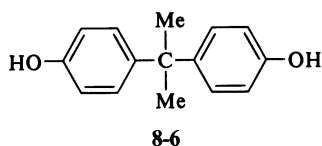
Two approaches have been adopted to overcome the problem. The first is to use developers with increased sensitivity. The best of these is benzyl parabens (**8-7**), which has excellent sensitivity. However, it is much more

HO—CO_2CH_2—

8-7

MeO_2C—CO_2Me

8-8

Cl
—$NHCOCH_2CH_3$

8-9
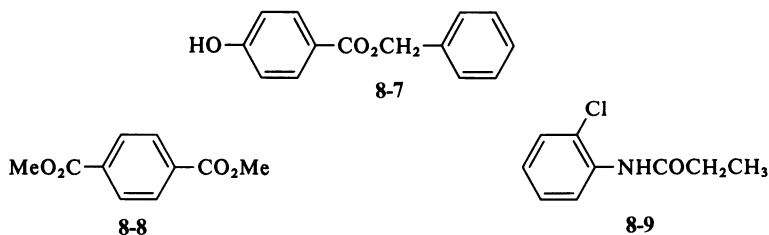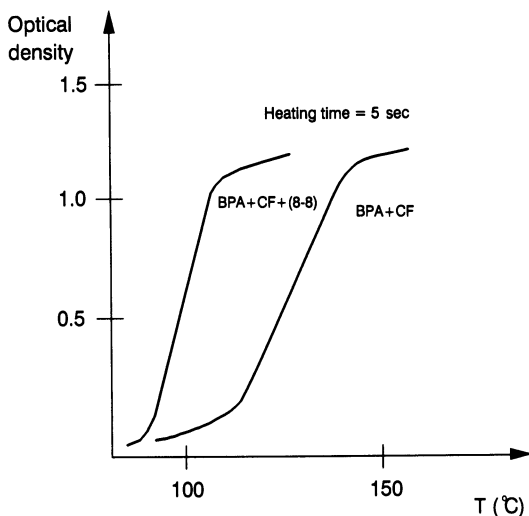
Figure 8.3. Improved sensitivity imparted by dimethyl terephthalate (**8-8**). BPA, bisphenol A; CF, color former.

expensive than bisphenol A. The second approach is to incorporate a "sensitizer" to improve the sensitivity of bisphenol A. Two typical sensitizers are dimethyl terephthalate (**8-8**) and the amide (**8-9**). The improved sensitivity imparted by (**8-8**) is shown in Fig. 8.3.

The function of a binder is to provide a matrix for the color former and developer and to bind the thermally sensitive layer to the base paper. Various polymers are used as binders. Some of the more common binders are polyvinyl alcohol, polyvinyl pyrrolidone, hydroxyethyl cellulose, and carboxymethyl cellulose.

The requirements of thermal paper are as follows:

1. The color-generating reaction temperature is near to 70°C.
2. High optical densities are obtained with the minimum energy, i.e. the coloring sensitivity is high.
3. The paper is stable to storage under various conditions and does not discolor prematurely (i.e. fog).
4. The image, once formed, is durable to various agents such as light, water, and grease.

To meet these requirements, other additives are used in the thermally sensitive layer. These include agents to improve the wet fastness, light fastness, fastness to oils and plasticizers, fogging inhibitors, and antistick agents. Examples of chemicals used to improve the wet fastness include epoxides, polyacrylamides, carboxy-modified polyvinyl alcohol, and sulfones. Selected ultraviolet absorbers are used to improve the light fastness. Typical examples

are the hydroxybenzophenone (**8-10**) and the benzotriazole (**8-11**). A mixture of triethanolamine and (**8-12**) has been claimed to be a fogging inhibitor.
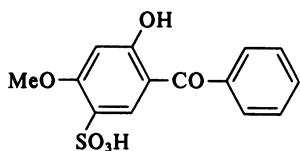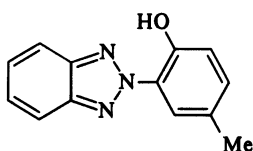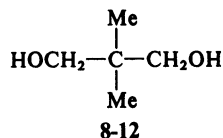
8-10　　　　　　　　　8-11　　　　　　　　　8-12

Antistick agents, which are added to prevent the paper from sticking to the hot thermal heads, fall into three types. The first are the well-known slip agents such as zinc stearate. The second are the fluorinated polymers and the third are fine inorganic particulate matter such as calcium carbonate, silicates, and talc.

Thermal paper is used for facsimile printers, calculator and microcomputer printers, teleprinters, and analytical apparatus recorders, and for printing tickets in automatic ticket dispensers. It is also used in supermarkets to print point-of-sale labels.

At present, the current worldwide production of thermal paper is modest: it is estimated at 60,000 tonnes for 1985, which consumes about 900 tonnes of color former. However, it is a rapidly growing market, as witnessed by the 1000% increase in sales from 1980 to 1985. The current rate of growth of thermal paper is estimated at 40% per annum.

Thermal paper is manufactured mainly in Japan and the United States. The major Japanese manufacturers are Jujo Paper, Mitsubishi Paper, Kanzaki Paper, and Tomoegawa Paper. In the United States, the major manufacturers are Appleton, Nashua, 3M, Labelon, and Graphic Control.

With the advent of less expensive, compact, more powerful lasers, it is hardly surprising that more and more patents are appearing in which lasers replace thermal heads as the energy source. Kanzaki Paper of Japan holds several such patents.[5] One of these (US 4529,992A), uses lasers emitting at different wavelengths in the near infrared (800–2000 nm), each laser interacting with a color former of a specified color so that a multicolored image is produced.

The attractions of lasers are many. They include much faster printing speeds, lower energy consumption, better resolution, and a noncontact method. A possible arrangement of a thermal paper suitable for laser thermal printing is shown in Fig. 8.4. Essentially, the color former and developer are separated by a thin waxy layer. The waxy layer contains an infrared absorber which converts the laser energy into sufficient thermal energy to melt the wax. This allows direct contact between the color former and the developer so that color is generated.

Color former

Waxy layer + Infrared absorber

Developer

Paper base

Laser radiation

Color former and developer

Color former reacts with
developer to form color
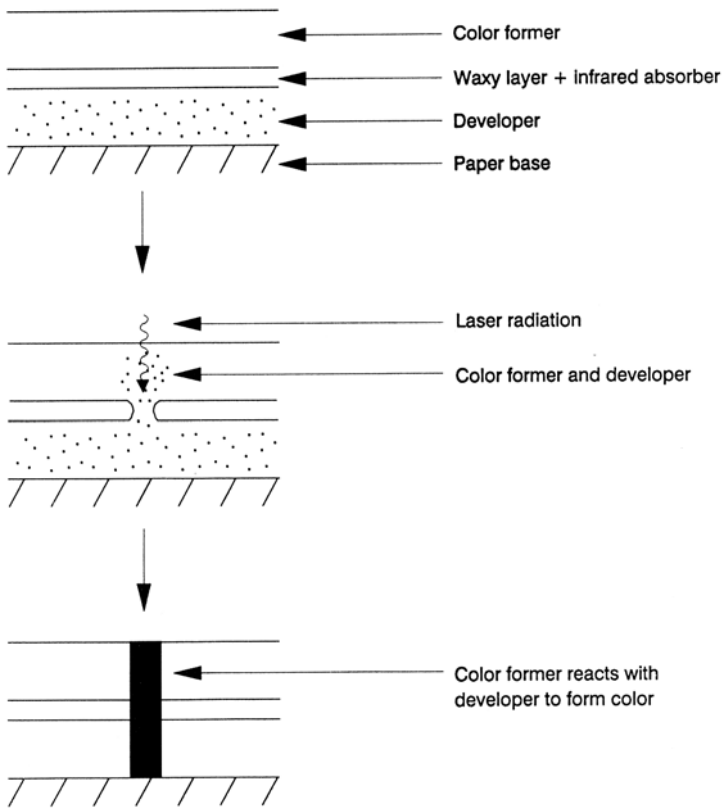
Figure 8.4. Principle of direct laser thermal printing.

8.3. PRESSURE-SENSITIVE PRINTING

Pressure-sensitive printing[3,4] is closely related to direct thermal printing. Both use color formers and developers to generate the color. The major difference lies in the method of bringing these chemicals into contact. Direct thermal printing uses heat. In pressure-sensitive printing the color formers are dissolved in a solvent and the solution is contained in microcapsules. These are coated on the paper. This coated sheet is placed upon a second sheet of paper containing a coating of the developer on the top side of the paper so that the two coatings of color former capsules and developer are in contact (Fig. 8.5). Application of pressure, in the form of a pen, typewriter, or impact printer, ruptures the microcapsules. This releases the color former solution which immediately contacts the developer and generates the color (Fig. 8.5).
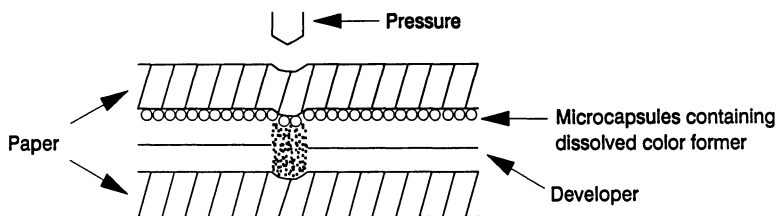
Figure 8.5. Principle of pressure-sensitive printing.

The color formers used in pressure-sensitive, or carbonless paper, as it is commonly known, are generally the same as those used in direct thermal printing (*Section 8*.2). The important colors are blue and black, black being predominant in the United States whereas both blue and black are used in Europe and Japan. However, the general trend is toward black. Blues are obtained from phthalide color formers such as Crystal Violet Lactone (**8-3**) and acyl leucophenothiazines such as Benzoyl Leuco Methylene Blue (**8-13**). Blacks are obtained either from the fluorans (**8-1**) used in thermal printing (one-dye blacks) or from mixtures of color formers. The constitution of these mixed blacks is influenced by several factors, including the shade of black required, the developer to be used (see below) and the properties required.

8-13 Colorless
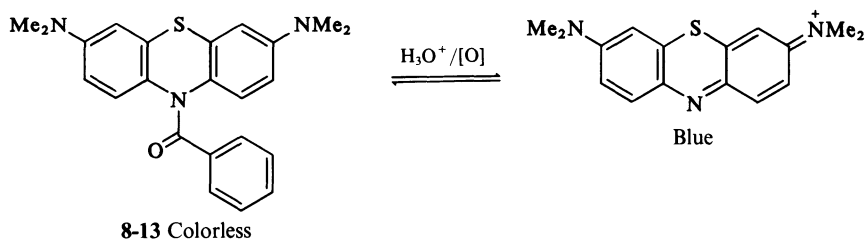
The mixed blacks may or may not contain a black color former as one component. A typical mixed black contains the black color former (**8-1a**), the blue color former Crystal Violet Lactone (**8-3**), and the green color former (**8-14**). The green color former (**8-14**), known as Fuji Green, is widely used as a component of mixed blacks.

8-14   Green
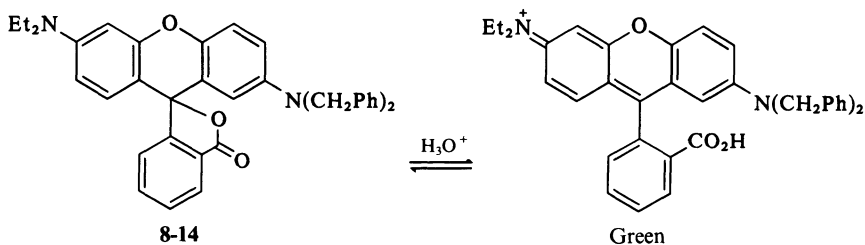
A mixed black devoid of a black color former typically contains the blue color former Benzoyl Leuco Methylene Blue (**8-13**), the green color former Fuji Green (**8-14**), the red color former (**8-15**), and the orange color former (**8-16**).

8-15   Red

8-16   Orange
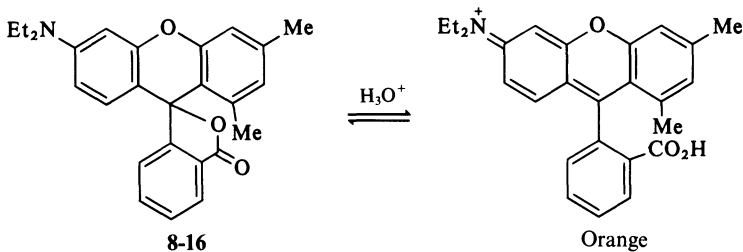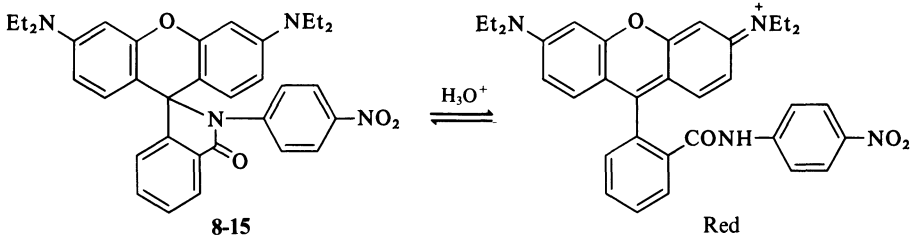
In general, the one-dye blacks exhibit better light fastness than the mixed blacks but the latter have better capsule oil solubility.

Mixtures are also used for blue color formers. The reason for this is to optimize the performance of the paper by utilizing the different properties of individual color formers. For example, Crystal Violet Lactone (**8-3**) gives a very fast coloring reaction with the developer but the blue dye produced has poor light fastness. In contrast, the leuco color former (**8-17**) is slower

8-17   [O]
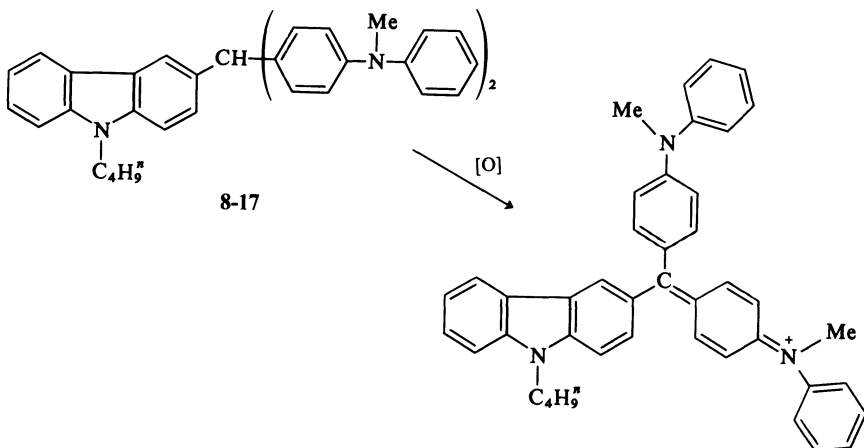
to develop a blue color but the blue dye formed has better light fastness than the blue from Crystal Violet Lactone.[4] Therefore, the most common blues are a mixture of two color formers, one of which gives a fast coloring reaction and one which has good light fastness.

The developers used in pressure-sensitive printing are different from the phenolic developers used in direct thermal printing. They fall into three categories: (1) clay, (2) resin, and (3) metal salt of an organic carboxylic acid.

Clay developers adsorb the color former solution from a ruptured capsule extremely rapidly and therefore the coloring speed is fast. They are also inexpensive. The major deficiency of clay developers is that color formers generally exhibit a lower level of light fastness than they do with resins or carboxylate salts. Activated clay (acid-treated montmorillonite) is an example of a clay developer.

Resin developers actually dissolve the color former and this results in improved wet fastness and light fastness. However, the speed of color formation is slower than with clay and the papers are more inclined to discolor (observed as yellowing). Also, resin developers are more expensive than clay developers. A typical resin is the condensate of formaldehyde and 4-phenylphenol (**8-18**).

$$\text{HCHO} \ + \ \text{（benzene ring）—（benzene ring）—OH} \ \longrightarrow \ \text{Resin}$$

8-18
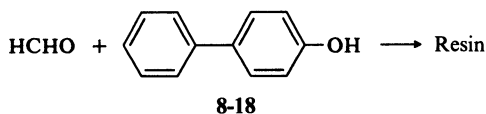
The most widely used metal carboxylate developer is a zinc salicylate (**8-19**). These are the best technically, combining fast coloring speed with high wet and light fastness. However, they are more expensive than resins and clays.

8-19
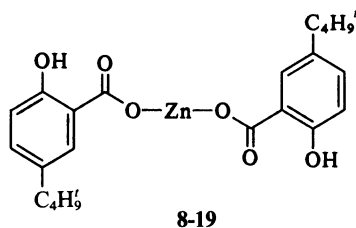
Resin developers predominate in the United States whereas clay developers predominate in Europe. In Japan, clays and zinc salicylates are used.

There are various methods of encapsulation. The two most widely used methods are gelatin coacervation and interfacial polycondensation. Gelatin coacervation involves emulsifying the oil (color former dissolved in the solvent) in warm gelatin followed by crash cooling, usually by the addition of

ice water. This results in microcapsules composed of a gelatin skin and an oil core. Formaldehyde is then added to harden the gelatin. Interfacial polycondensation is a more recent method. It uses synthetic materials such as polyamides and polyurethanes rather than the natural materials of the gelatin coacervation method. With polyamides, the oil containing dissolved terephthaloyl chloride is emulsified in an aqueous phase, and a diamine, such as ethylene diamine, is added. The polyamide is formed at the interface of the oil and water, effectively encapsulating the oil droplets (Scheme 8.1).

ClOC—⟨benzene⟩—COCl + H₂N⌄⌃NH₂ + ⟨Oil droplet⟩ —→

Oil droplet

Oil ⌄⟨○⟩⌄ Polyamide $\left(-\overset{\overset{\displaystyle O}{\|}}{C}-\text{⟨benzene⟩}-\overset{\overset{\displaystyle O}{\|}}{C}-NH⌄⌃NH-\right)_n$

Microcapsule
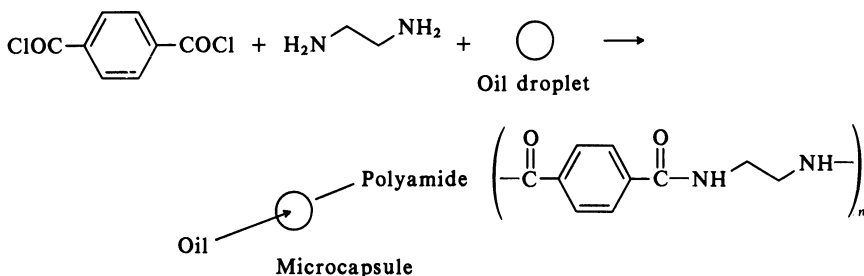
Scheme 8.1. Principle of interfacial polycondensation.

The choice of solvent for dissolving the color former to produce the oil depends upon several factors such as odor, cost, and effectiveness as a solvent. Chlorinated paraffins are used but the major solvents are alkylated aromatic hydrocarbons such as (**8-20**) and especially isopropyl biphenyl (**8-21**), and partially hydrogenated terphenyls.

8-20 ⟨naphthalene⟩—^{i}Pr   **8-21** ⟨biphenyl⟩—^{i}Pr
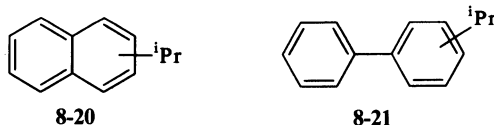
The world market for carbonless paper is currently greater than that for thermal paper, but the growth rate is much lower. It is estimated that 1.3 million tonnes per annum of carbonless paper is produced using 2000 tonnes of color former. The principle manufacturers are shown in Table 8.1.

One future trend in carbonless papers could be to make them machine readable, preferably by an optical sensing system. The standard near infrared readers are semiconductor lasers at 780 nm and light emitting diodes (LEDs) at 900 nm: these are used with silicon detectors having a peak sensitivity at 850–950 nm. The current generation of color formers cannot be detected at these wavelengths, since even the absorption spectra of the blacks do not extend much beyond the limit of the visible spectrum (approximately 700 nm). Two approaches are possible. One is to use novel color formers

Table 8.1. Major Manufacturers Worldwide of Pressure-Sensitive Copying Paper

Country	Manufacturer
Japan	Jujo, Kanzaki, Mitsubishi, Fuji Film, Toppan Moore
United States	Appleton, Mead, Moore, Nashua, 3M
West Germany	Feldmuhle, Zanders, Kohler, Renker
United Kingdom	Wiggins Teape, DRG, Reed
Italy	Binda
Spain	Sarrio
Finland	Ahlstrom
Yugoslavia	Aero
Netherlands	Moore

that absorb in the infrared. Typical infrared color formers are of the Yamamoto type or the Appleton type. The Yamamoto compounds[6] (**8-22**) are infrared absorbers because of the increased delocalization caused by the enforced planarity induced by the bridging link between the two aryl rings. Indeed, (**8-22**) is essentially a bridged Crystal Violet Lactone (**8-3**). Because of the extra conjugation arising from the Michlers Ethylene moeity (**8-23**) the Appleton compounds[7] (**8-24**) are infrared absorbers.

8-22 Colorless λ_{max} 625 and 850 nm (in a thermal paper)
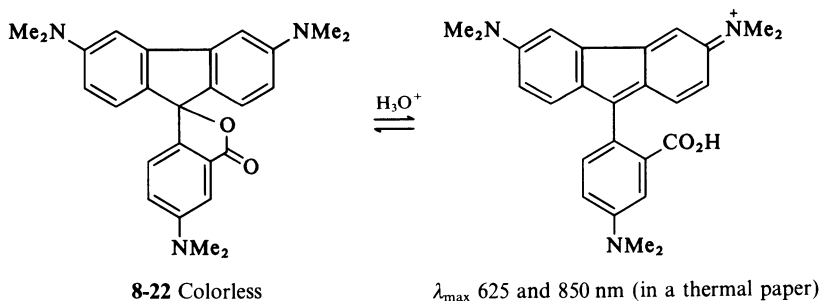
An alternative approach is to use a mixture of existing color formers with an infrared absorber (see *Chapter 11*). Ideally, a noncolored infrared absorber is required in order to preserve the whiteness of the paper. However, no suitable noncolored infrared absorbers are currently available. Therefore, pressure-sensitive papers based on this approach will be more colored, i.e. less white, than those based on infrared color formers. Time will tell which approach, if any, succeeds.

8.4. MEAD PHOTOCAPSULE (CYCOLOR) PROCESS

The technologies of direct thermal printing and the related pressure-sensitive printing are used predominately for producing monochrome prints

8-23

8-23

8-24

Green/black with near infrared absorption (λ_{max} 680 and 875 nm)

(black and to a lesser extent blue). However, the advent of the Mead photo-capsule process,[8-11] known as CYCOLOR, has extended color former technology into producing full-color images.

Mead's photocapsule process is a new technology which combines the known technologies of microencapsulation and photopolymerization. It

Figure 8.6. Carbonless capsule cutaway. Center contains solvent and color precursor.

extends the technology of pressure-sensitive papers (carbonless papers) to enable the production of full-color hard copies from electronic information.

As discussed in *Section 8.3*, in pressure-sensitive printing a colorless dye precursor, a color former, is dissolved in a hydrocarbon solvent and the solution is contained within a microcapsule (Fig. 8.6). These microcapsules are in contact with an acidic resin. When pressure is applied to the paper in the form of writing or typing, the capsule wall is ruptured and the solution spills onto the acidic resin (Fig. 8.7). The acid immediately converts the colorless color former into a colored dye, thus producing a legible copy.

The Mead photocapsule process, like the carbonless paper process, uses a noncolored dye precursor, namely a color former. However, instead of a solvent in the microcapsules there is a liquid monomer and a photoinitiator which solidify (polymerize) when exposed to radiation of the appropriate wavelength (Fig. 8.8). This is currently ultraviolet or blue light. When the radiation strikes the microcapsules, it penetrates the outer walls and causes the monomer to polymerize and solidify. In those microcapsules not struck by radiation, the liquid core remains fluid.

Upon the application of pressure to the selectively exposed sheet with, for example, a roller, the soft unexposed microcapsules rupture. They form an image, exactly as in carbonless paper, by spilling their contents onto an acidic developer layer. In contrast, the exposed capsules are now essentially solid spheres and therefore do not rupture under pressure. Hence, no image is formed in these areas (Fig. 8.9).
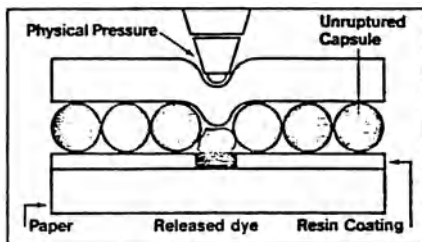
Figure 8.7. Ruptured carbonless capsule releases dye on resin layer to produce blue or black image.
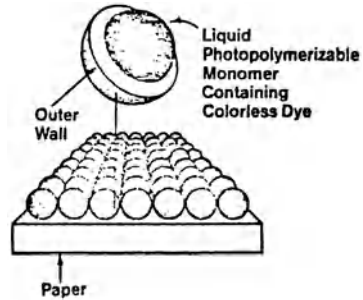
Figure 8.8. New Mead imaging chemistry. A liquid photopolymerizable monomer is used instead of a solvent in the microcapsules.

To produce a colored image the paper is coated with three different microcapsules, each containing one of three color formers, viz. a yellow, magenta, or cyan. By combining these three primary colors, any color can be generated, thereby allowing the production of full-color prints.

Each "colored" microcapsule is sensitive to a specific narrow band of radiation in the blue to ultraviolet range, i.e. from 300 to 500 nm (Fig. 8.10).
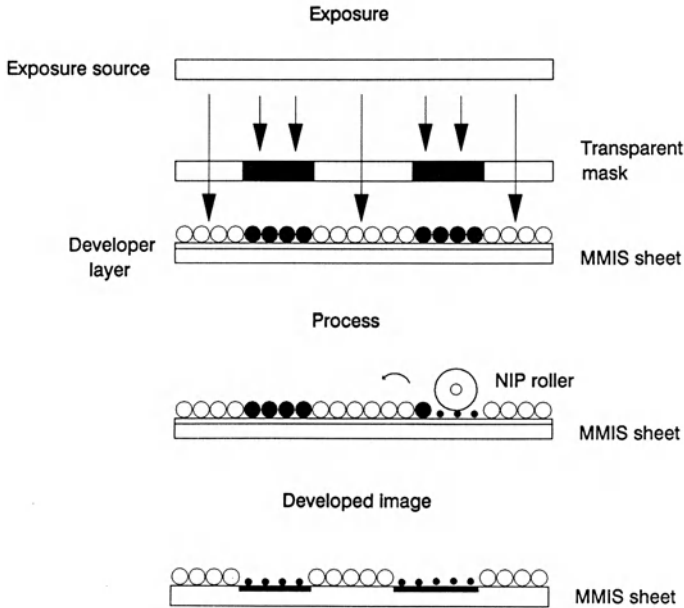
Figure 8.9. Principle of the Mead photocapsule imaging process. *Open circle*, exposed microcapsule; *solid circles*, unexposed microcapsule. NIP, nonimpact printing; MMIS, Mead microcapsule imaging sheet.
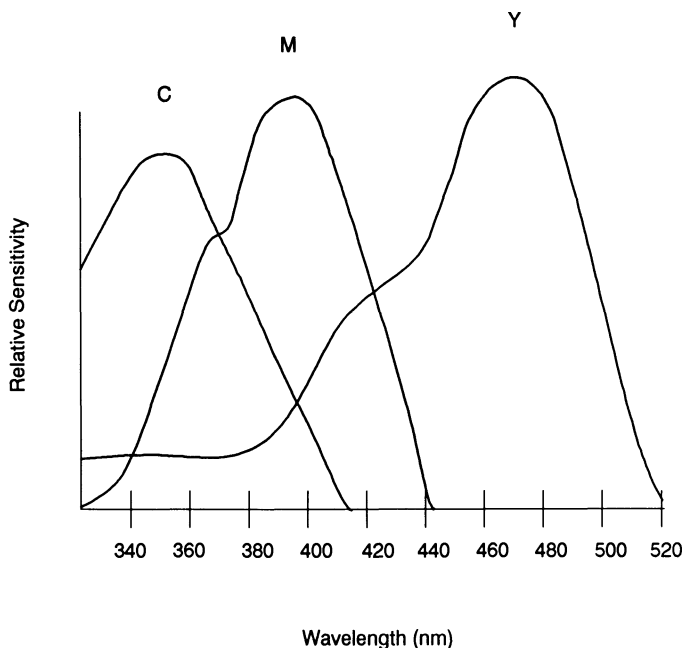
Figure 8.10. Spectral sensitivity of microcapsules containing cyan (C), magenta (M), and yellow (Y) dye precursors.

The wavelengths of light striking the sheet determine which color capsules will be exposed and polymerized. Thus, ultraviolet radiation at 350 nm polymerizes the cyan capsules, ultraviolet radiation at 385 nm polymerizes the magenta capsules, and blue light at 470 nm polymerizes the yellow capsules (Figs. 8.10 and 8.11). Application of pressure after each of these exposure steps would produce the colors red, green, and blue, respectively (Fig. 8.11).

A further important feature of the Mead photocapsule process is the ability to produce continuous tones (gray scales). This is because the level of exposure determines the amount of polymerization: this increases from zero to full polymerization with increasing time of exposure. Thus, on development (i.e. application of pressure), a gray scale of color is obtained from high optical density through medium optical density to low optical density (Fig. 8.12). Having explained the process, we will describe briefly the chemicals used in the construction of the capsules.

The material used for the wall of the microcapsules must be transparent to the exposure radiation, viz. near ultraviolet and blue, otherwise the photopolymerization would not take place. Although many resins and polymers
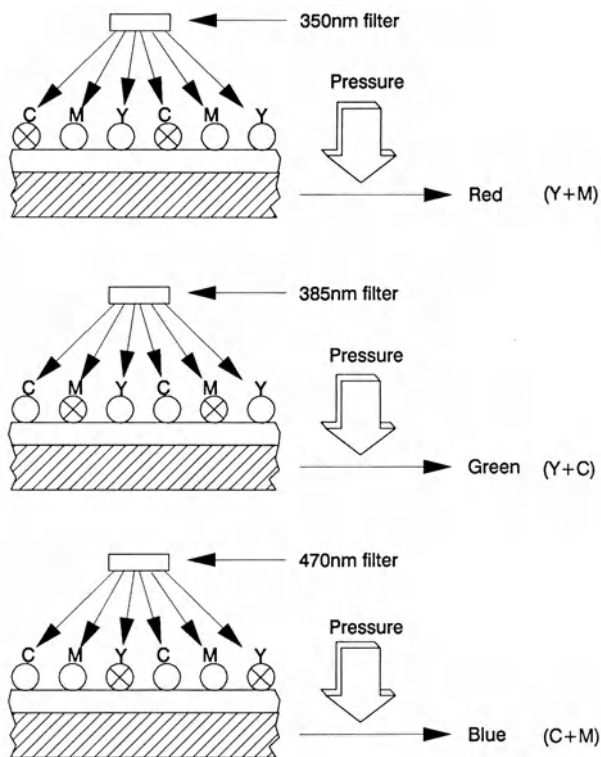
Figure 8.11. Color generation with the Mead photocapsule process. C, cyan; M, magenta; Y, yellow.

can be used, the two preferred materials are a urea-resorcinol-formaldehyde resin and gelatin.[12]

The liquid monomers are unsaturated organic molecules containing at least one and preferably two or more terminal ethylene groups per molecule. For example, unsaturated acid esters of polyhydric alcohols, such as tri-methylol propane triacrylate (TMPTA),[12] have been used.

Examples of photoinitiators include diarylketones, quinones, and benzoin alkyl ethers. It is often advantageous to use a combination of photo-initiators. For example, for ultraviolet sensitivity a desirable combination is Michlers ketone (**8-25**) and benzoin methyl ether (**8-26**) in a ratio of 2:5.

The phthalides (**8-27** and **8-28**) are typical examples of yellow color formers. Magenta color formers are of the phthalide type (**8-5** and **8-29**)
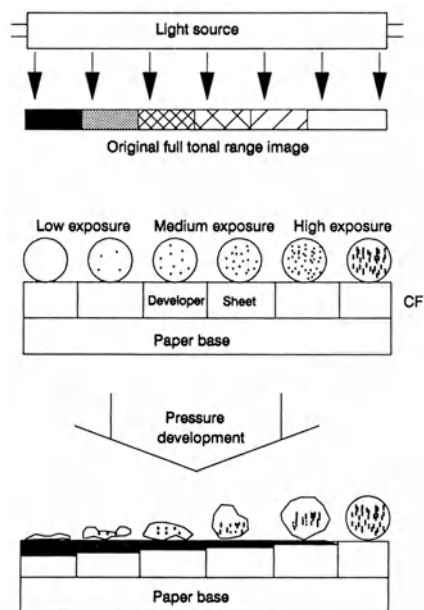
Figure 8.12. Production of continuous tones with the Mead photocapsule process. CF, color former.

8-25

8-26

8-27

8-28
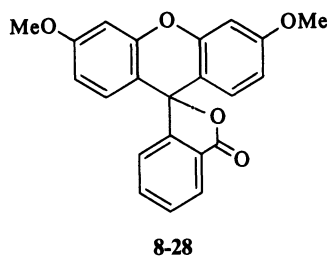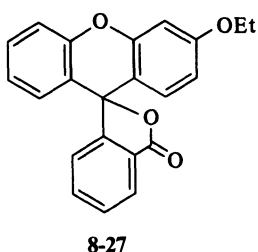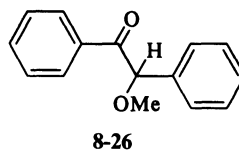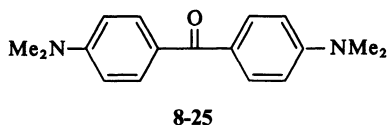
and the spiropyran type (**8-30**). Typical cyan color formers are the thiazine Benzoyl Leuco Methylene Blue (**8-13**), the oxazines (**8-31** and **8-32**), and the diphenylmethane leucauramine (**8-33**).[13]

These are the conventional color formers used in both thermal printing (*Section 8.2*) and pressure-sensitive printing (*Section 8.3*). The acylated leuco

8-5

8-29

8-30

8-13

8-31

8-32

8-33
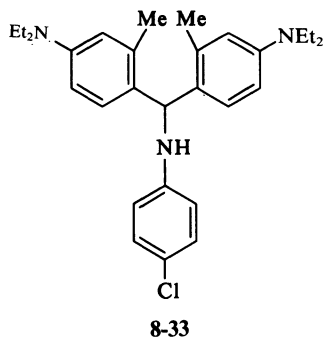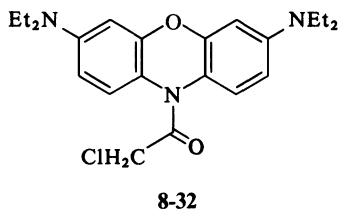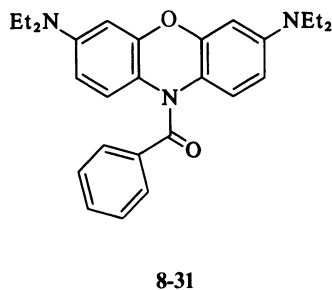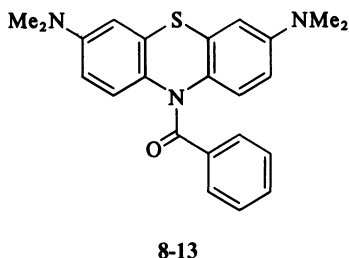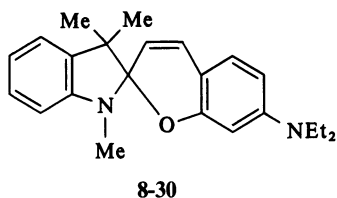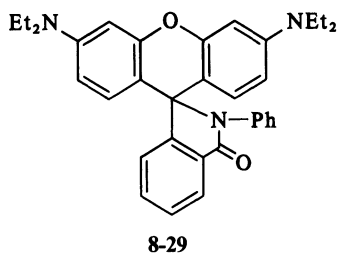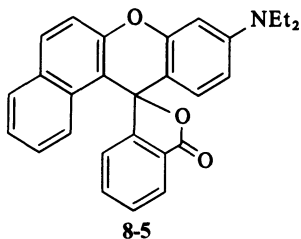
dyes such as (**8-13** and **8-32**) are also used in electrochromic printing (see *Chapter 6*). The acidic resins and clays used as developers are also the same type as those used in thermal and pressure-sensitive printing. Consequently, the final image will suffer the same problems as those in thermal and pressure-sensitive printing. In particular, it will have relatively poor fastness to light. Consequently, the method is not suited to producing docu-

Table 8.2. Comparison of the Imaging Processes

Property	Units	Silver halide	Diazo	Electro- photography	Mead photocapsule
Speed	Ergs/cm^2	0.1–100	10^4–10^8	20–100	100–1000
Spectral sensitivity	Nanometers	Full spectrum	300–450	300–850	320–500
Resolution	Line pairs/mm	100–1000	5000	25–100	50–100
Color image quality	—	Excellent	Good	Fair–Good	Good
Maximum density					
Paper	—	2.0	1.8	1.5	1.0–1.7
Film	—	4.0	2.0	2.0	(To be determined)
Continuous tone	—	Yes	No	No	Yes
Processing	—	Complex	Complex	Complex	Simple
Fixing required	—	Yes	No	Yes	No
Shelf life	Years	2	0.5	Unlimited	1.5+
Print cost					
Black and white	$8\frac{1}{2} \times 11$	\$0.2	\$0.02	\$0.05	\$0.4
Color	$8\frac{1}{2} \times 11$	\$2.0	—	\$0.25	\$0.25

ments for archival storage. However, the Mead photocapsule process has several advantages such as high resolution, low cost copies, and high printing speed. Overall, it compares favorably with other technologies capable of producing full-color hard copies (Table 8.2).

The Mead photocapsule process is particularly well suited to computer color output. For instance, a computer system would output three different signals to a signal convertor, each corresponding to a different color, namely yellow, magenta, and cyan. The signal convertor would control a modulated light source of the three different wavelengths of light: a cathode ray tube, fluorescent tube, and a liquid crystal device or a laser used as the light source. However, in order to become more universally applicable and compete for potentially lucrative markets such as color copying, it is imperative that photoinitiators sensitive to red, green, and blue light be developed (see *Chapter 7, Section 2.3*). No doubt such photoinitiators will be formulated.

How successful Mead's photocapsule or CYCOLOR process will be remains to be seen, but Mead's own commitment to the technology is substantial. Not only have they formed a separate company, Mead Imaging, but they are building new premises to house the research group.

The following discussion concerns thermal transfer printing. As mentioned earlier, thermal transfer printing can be subdivided into thermal wax transfer, a middle quality technology, and the more recent dye diffusion, D2T2, a high quality technology.

8.5. THERMAL WAX TRANSFER

Thermal wax transfer printing utilizes a transfer ribbon consisting of a hot-melt ink coated onto a thin substrate (film). Monochrome ribbon is usually black and color ribbon consists of sequential panels of yellow, magenta, and cyan. Color ribbon also contains a machine-readable coding scheme which allows the printer to determine the color at the imaging head at any point in time.[1]

The thermal wax transfer imaging process consists of passing the ribbon past the thermal heads (pixels) to cause the hot-melt ink to transfer from the ribbon to a receiver sheet such as plain paper or transparencies (Fig. 8.13). The pattern with which the individual thermal heads are heated determines the shape of the image which is created. Monochrome output is created by a single pass of the paper and ribbon by the thermal heads. Color output is created using three passes to combine yellow, magenta, and cyan.[1,2] The prints have an acceptable appearance and excellent archival properties.[2] However, thermal wax transfer printing has two deficiencies:

1. Some of the transferred wax plus colorant resides on the surface of the receiver sheet; this causes the prints to have poor rub fastness, i.e. susceptible to smudging.
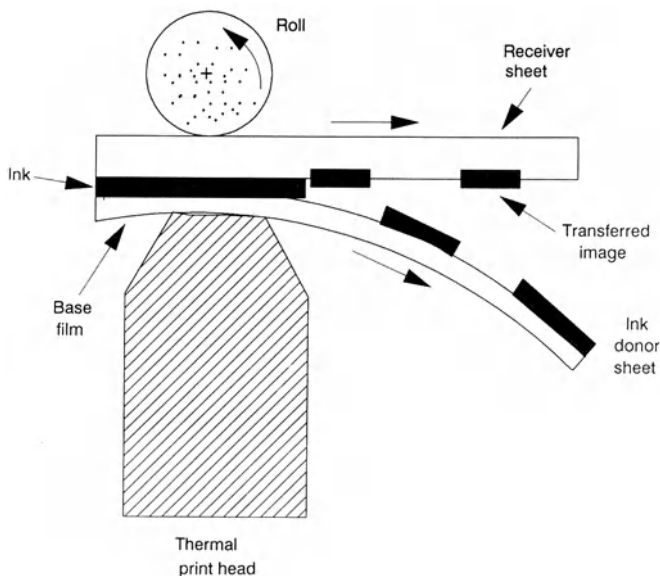
Figure 8.13. Thermal wax transfer printing process.

2. It is difficult to produce a good gray scale since the transfer is gener-
ally an "all-or-nothing" transfer.[2]

Despite these deficiencies thermal wax transfer printing offers a reliable,
inexpensive way of producing either monochrome or full-color output.[14,15]

8.5.1. Color Sheet

As seen from Fig. 8.13, the color sheet consists of a base film or substrate
coated on one side with a color coat. The color sheet substrate can be one
of a number of heat-resistant plastic films that have good thermal conduc-
tivity and are available in thin film[16,17] ($<20\ \mu$). Paper, especially condenser
paper, is also suitable.[2] Table 8.3 shows the properties of various materials.
In practice, the most commonly used material is 6 μ polyester although 3.5 μ
polyester is also beginning to be used.[1,14] Six micron polyester is readily
available, reasonably cost effective, smooth (unlike paper), and has good
thermal conductivity and high tensile strength (cf. paper). A heat-resistant
backcoat is generally not needed since the transfer temperatures are below
the softening point of polyester (ca. 200°C).

Colorants for thermal wax transfer printing must be thermally stable,
especially nonbleeding so as not to lose resolution during the thermal transfer
step, have good light fastness, and be compatible with the waxes employed.
Also, they must be nontoxic. Pigments satisfy these criteria best and indeed
the colorants used are predominantly pigments. Black is the major color and
this is usually carbon black although nigrosine is also mentioned in patents.[17]
The yellow pigments are generally azos, the magenta pigments either azos
or quinacridones, and the cyan pigments phthalocyanines. Representative
pigments are CI Pigment Yellow 12 (8-34), CI Pigment Red 51:1 (8-35, azo)
or CI Pigment Red 122 (8-36, quinacridone), and CI Pigment Blue 15:1
(8-37). The pigments are used in amounts of 1%–20%, typically
5%–10%.[17]
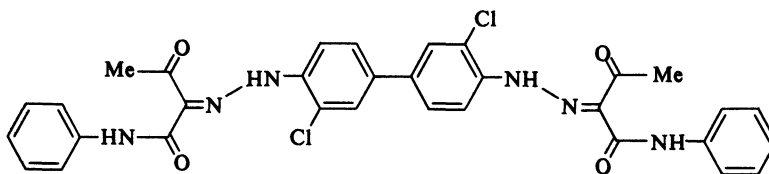
8-34

As already mentioned pigments are used in preference to dyes because
of their good fastness properties, especially nonbleeding in the hot wax. The
disadvantage of pigments is their lack of transparency, which impairs faithful
reproduction of full-color images. This effect is particularly evident in over-

Table 8.3. Characteristics of Various Types of Bases

Base	Heat resistance (°C)	Thermal conductivity $(cm^{-1} sec^{-1} K^{-1}) \times 10^{-3}$	Specific heat $(g^{-1} K^{-1})$	Density (g/cm^3)	Thickness (μm)	Tensile strength (kg/mm^2)
Polyester	~200	1.4	1.3	1.4	4 → 12	23 (25 μm)
Polyimide	>400	1.8 (200°C)	1.1	1.4	7 → 12.5	12 (200°C)
Nylon	~180	2.7	1.7	1.1	15	6.5
Moisture-proof cellophane/ordinary cellophane	400~500	—	—	1.4	20	~3
Condenser paper	~400	~0.6	~1.2	~0.8 → 1.2	7 → 20	~6
White raw paper	~400	~0.6	~1.2	~0.8 → 1.2	20	~6

8-35

8-36

8-37
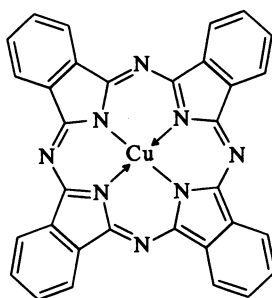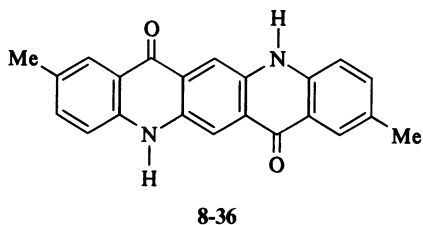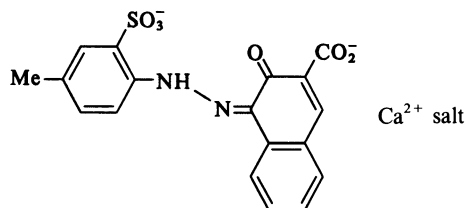
head transparencies. For example, the yellows appear good on paper when viewed by reflected light but are very poor on overhead transparencies when viewed by transmitted light. In this case, the yellows are seen as muddy browns. Dyes, on the other hand, have excellent transparency but are prone to bleeding. There is, therefore, scope for an improved colorant that has the transparency (and tinctorial strength) of dyes and the fastness properties, especially nonbleeding, of pigments.

Many waxes and binders are quoted in patents but a typical formulation comprises a solid wax (at 25°C), an easily meltable wax, and a binder.[17] The solid wax is normally a paraffin and is generally the major component. Typical solid waxes are carnauba wax, montan wax, beeswax, and ceresine wax. Easily meltable waxes are the ester waxes and oxidized waxes.[14,17] Low-molecular-weight polyethylene is also used.[17]

The binders tend to be those employed in conventional systems such as cellulose ethers and esters, acrylic resins, polyvinyl acetate, polystyrene, and styrene–butadiene copolymers.[17]

Additives may be materials to improve the thermal conductivity, such as black pigments (e.g. acetylene black, lamp black, graphite, or aniline black) or metal powders (e.g. aluminum, copper, tin, or zinc). Other additives may be extender pigments, such as magnesium or calcium carbonate, clay, kaolin, and silicic acid anhydride (Aerosil).[17] Release agents such as silicones or siloxanes[18,19] and terpenes[20] have also been mentioned in the patent literature.

The coating is either a hot-melt coating or a solvent coating. Little information is available on this aspect of the process.

Important properties of thermal wax transfer ribbon are melting point, viscosity of the molten ink, and hardness of the ink coating. The inks must be formulated in such a way that they are hard at normal temperatures and conditions but exhibit a low enough melting point to effect speedy transfer with minimal energy. Most inks melt in the range 50–100°C,[17] typically 65–68°C.[14] An ideal ink has a low viscosity at its melting point to minimize paper smear. Normally, viscosities are in the range 20–1000 cP, for example, 60 cP at 55°C.[21] As mentioned above, it is desirable that the transfer ink layers are hard, since soft layers are easily soiled. A penetration value of 0.1–50, according to Japanese Industrial Standard K2530,[17] is a desirable level of hardness for the ink layer.

8.5.2. Receiver Sheet

The receiver sheet is normally plain paper or transparencies for overhead projectors. Much better transfer occurs on smooth "plain" paper, i.e. Bekk smoothness greater than 100 sec, and work is ongoing to improve the transfer to "ordinary" plain paper.[22] Currently, these give lower print optical densities and poorer print definition.

8.5.3. Patent Activity

Thermal wax transfer is a relatively young technology and this is reflected by the growth in patent activity (Fig. 8.14). Prior to 1983, the number of patents in any year was a single-digit figure. However, from 1983 onward, the patents increased enormously, with 79 being published in 1985. As expected, Japanese companies dominate the patenting with giants such as Ricoh (34), Konishiroku (30), Canon (19), Mitsubishi (15), and Fuji-Xerox (8) leading the way. It is interesting that of the 28 patents on colorants, only one[23] was on dyes. The remainder were on pigments.

8.5.4. Electrothermal Printing

Ricoh, Fuji-Xerox, Matsushita, and Suwa Seikosha have patents on electrothermal printing. This process differs from thermal wax transfer printing in that a stylus supplies electrical energy to a resistive base film, thereby generating the thermal energy to transfer the ink. The ink is essentially the same as for thermal wax transfer; it is just the energy source that is different. IBM appears to be the leaders in black electrothermal printing (IBM Quietwriter) whereas Seiko Epson is active in colored electrothermal printing.
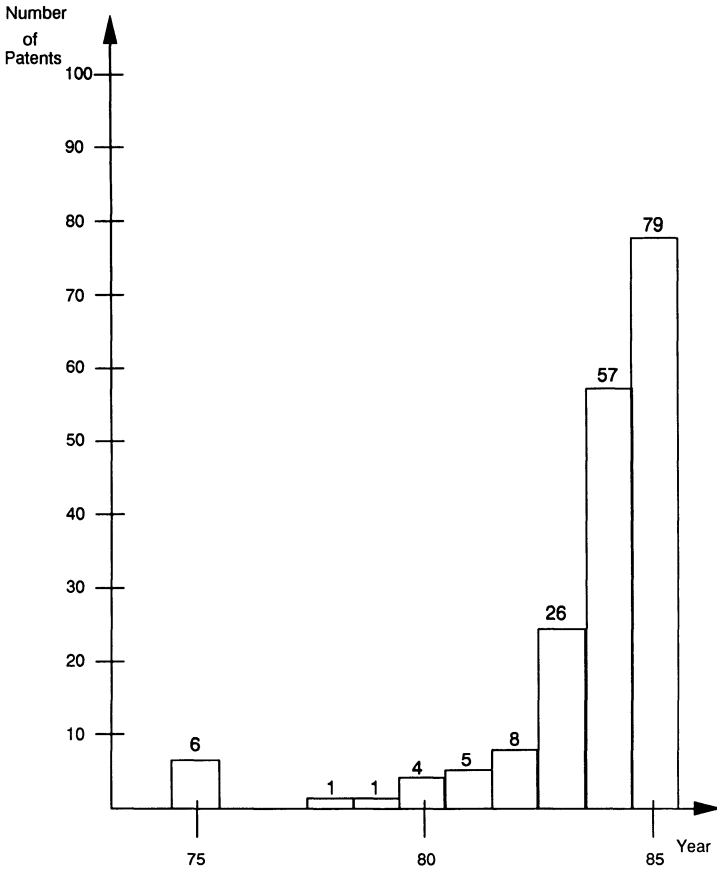
Figure 8.14. Patent activity in thermal wax transfer printing.

8.5.5. Laser Transfer

As is the case with direct thermal printing, it is possible to use lasers rather than thermal heads as the energy source. Indeed, there is a patent from Tomoegawa Paper[24] that describes laser-driven thermal wax transfer. Interestingly, it is used for the laser fabrication of lithographic printing plates.

8.6. DYE DIFFUSION THERMAL TRANSFER

The ultimate aim of all the full-color hard copy reprographics technologies is to capture the lucrative silver halide photographic market, estimated at 20 billion dollars per annum. The quality of silver halide photography is

high, so the technology that captures this market must also be capable of producing high quality images. In addition to quality, low cost (equal to or less than silver halide photography) and high speed are also desirable attributes. As yet, none of the reprographics technologies fulfill all these requirements. However, in the intense battle between the major technologies of inkjet, electrophotography, and thermography, it is D2T2 that is most successful in capturing the silver halide photographic market. There are a number of reasons for this:

1. D2T2 is unique among the technologies in being able to produce continuous tones (i.e. a gray scale) easily and without loss of resolution.
2. D2T2 can produce the high optical densities (up to 2.5) required for high quality printing. Again, none of the competing technologies can achieve this.
3. The plastic substrate used for the finished print is very similar in appearance and handling to current photographic prints.
4. The fastness properties, especially to light, heat, and rubbing, are good.
5. Finally, but most importantly, D2T2 can undergo a step change in technology, namely the replacement of thermal heads with lasers as the energy source. This development, which will probably require infrared absorbers to convert the laser energy into heat (see *Chapter 11*), will result in a dramatic improvement in printing speed, print resolution, and energy costs. Ink jet, for example, cannot undergo such a step change in technology. In contrast, electrophotography has already undergone such a step change and the resulting impact of laser printers in page printing is there for all to see.

8.6.1. Electronic Photography

For over 100 years photography, both black and white and color, has been based on silver halide technology. It is, therefore, a mature and well-understood technology and has attained such a high quality that it is the standard by which all other color hard copy technologies are judged. However, silver halide photography has some limitations. One of these is cost. A silver halide film, once inserted into a camera, has to be processed completely, irrespective of whether only one or all of the exposures have been used. This can be a nuisance. Furthermore, "bad" pictures (e.g. blurred or poorly composed) are also developed, even if not printed, because there is no way of ascertaining the quality of the exposure prior to processing the exposed film. A second, and arguably more serious limitation, is inconvenience. Until the advent of "instant photography" (e.g. Polaroid), there

was a considerable time delay involved between taking the pictures and actually viewing them. This is because the exposed film has to be sent off for processing (developing and printing). The Polaroid process has overcome this particular drawback but at a cost—the prints are of poorer quality.

In the current electronic age of computers, videos, and televisions, it is hardly surprising that electronic photography is arriving. The basic concept is extremely attractive. In electronic photography, an electronic camera replaces the conventional silver halide camera and a magnetic disc replaces the silver halide film. The magnetic disc will allow up to a maximum of 50 pictures to be taken. At any stage, i.e. whether 1, 10, or 50 pictures have been taken, the disc can be placed into a printer which is attached to a television set, and each picture can be viewed on the television screen. If the picture is satisfactory and a color hard copy print (i.e. "photograph") is required, a button is pressed and, after approximately one minute, out pops a color "photograph."

Electronic photography has several attractions. The two most important ones are that it makes photography potentially very inexpensive, and it is a clean, dry, instant process capable of producing high quality prints.

It is potentially inexpensive because the user pays only for the pictures that actually print out as a color hard copy. Defective photographs or those that are deemed unsatisfactory after viewing on the television screen, cost absolutely nothing if they are not printed out. Like a video tape, the disc is reusable simply by placing it back in the electronic camera. Indeed, once the camera and disc have been purchased, these can, in theory, be used for ever. The only cost incurred is the purchase of the cassette that inserts into the printer to produce the color hard copy prints.

The electronic camera used in electronic photography is in fact a "still video camera." Not surprisingly, therefore, color hard copy prints can be taken from any video by freezing (pausing) it at any point and printing the still image.

A further advantage of electronic photography is the ability to electronically manipulate the picture once it is on the television screen. For instance, the colors can be altered, objects added or removed, and the picture enlarged or reduced. This obviously has many attractions, a major one being greater control over the quality of the photograph.

Widespread use and the eventual domination of electronic photography is still some way off, partly because of the expense and relatively poor quality of today's electronic cameras. However, improvements in this area coupled with imminent introduction of high definition television will undoubtedly lead to electronic photography being the dominant photographic technology in the future. Indeed, it has been postulated that electronic photography will have replaced silver halide photography by the year 2000.[25]

8.6.2. History and Development

The thermal transfer printing of textiles, especially polyester, has been known for many years. In this process, sublimable disperse dyes are printed on thin paper in the pattern required for the final image. The printed paper is then placed in contact with the textile substrate to be printed. Application of heat, either from a hot iron or a hot press, is applied to the paper. This causes the printed pattern to transfer from the paper support by a process of sublimation and color the polyester textile substrate[26] (Fig. 8.15). Typically, temperatures of 200°C for 30 sec are needed to effect the process.

In concept, D2T2 appears to be an extension of textile transfer printing so that by increasing the temperature to 400°C the dye transfer takes place in milliseconds rather than 30 sec. However, in practice it is more complex than this because the process involved is a melt-state diffusion process rather than the sublimation process associated with textile transfer printing. By using an array of thermal heads to print dots and a trichromat ribbon of yellow, magenta, and cyan dyes, full-color prints can be produced using a three-pass system. The amount of dye transferred is directly proportional to
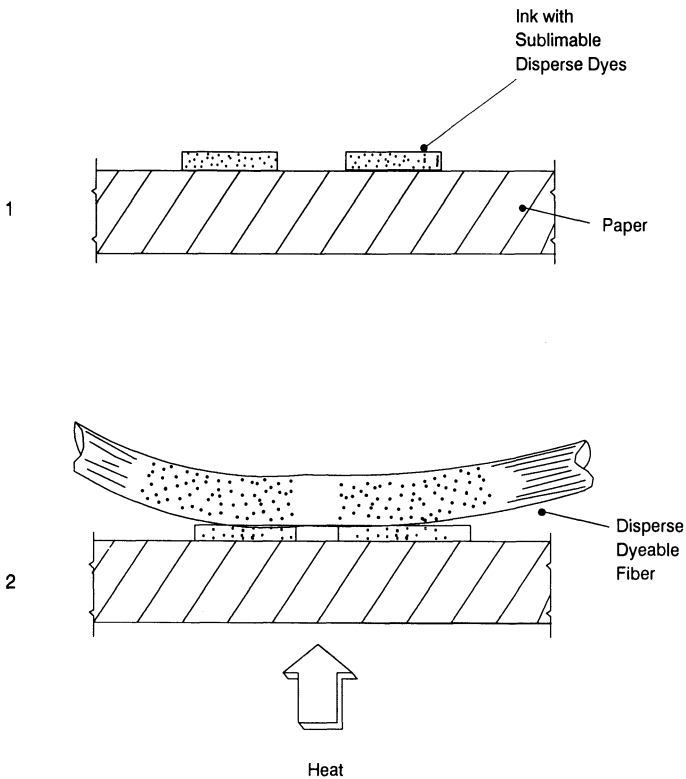
Figure 8.15. Heat transfer printing process.

the quantity of heat supplied, so that continuous tones can be produced easily without any loss in resolution. As noted above, this is one of the major advantages of D2T2 over competing technologies.

Sony is the company credited with inventing D2T2. They have the first recorded patents on the subject, with the first patents filed in 1981,[27] and were the first into the marketplace with the Mavica electronic camera and the Mavigraph printer.[28] However, the products had a number of teething problems. Other companies have also launched products, notably Hitachi and Kodak. Indeed, judging by the intense patent activity, most of the major Japanese companies, as well as some American and European companies, are actively engaged in the D2T2 technology. Some companies, such as Kodak, produce an integrated product of electronic hardware and consumables, whereas other companies produce either hardware (e.g. Hitachi) or consumables [e.g. Dai Nippon Printing (DNP) and ICI].

8.6.3. Dye Diffusion Thermal Transfer Process

As is the case for thermal wax transfer printing (*Section 8.5*), D2T2 also uses a yellow, magenta, cyan trichromat color sheet and a receiver sheet. However, in D2T2 the colorants are dyes rather than pigments and the receiver sheet is normally white plastic rather than plain paper or overhead transparencies.
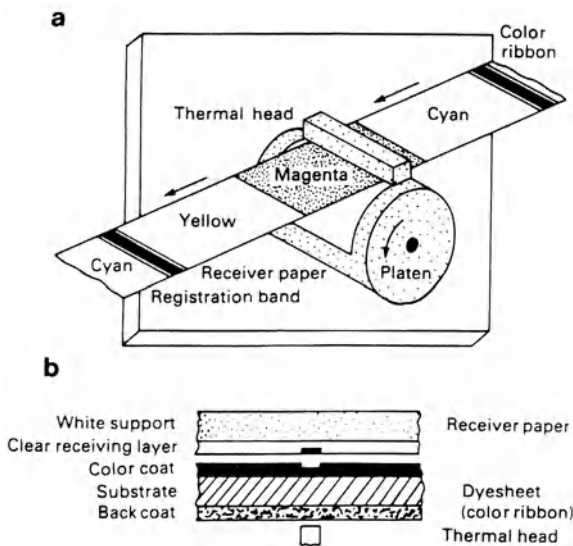
Figure 8.16. The D2T2 process. (a) Overall view. (b) Cross-sectional view.

A cross-sectional view of a dyesheet and a receiver sheet is shown in Fig. 8.16. The base substrate for the dyesheet is either condenser paper or, more usually, 6 μ polyester film. The latter is preferred because of its greater smoothness and strength (Table 8.3). However, a heat-resistant backcoat is needed since polyester softens at 200–250°C and the thermal heads reach temperatures up to 400°C. The backcoat also serves a further purpose in producing good quality prints since it has the correct frictional properties to control the friction between the dyesheet and the thermal head.[29]

The color coat is applied to the opposite side of the polyester to the backcoat (Fig. 8.16). It is normally applied as a solution of the dye plus binder in a solvent, followed by evaporation of the solvent. However, it can also be applied as a dispersion. Either process leaves an amorphous layer of dye plus binder. In some cases, a subcoat is applied between the color coat and polyester film to (a) assist adhesion to the polyester film and (b) prevent diffusion of dye into the polyester film. This is usually an acrylic polymer.[30]

The receiver sheet is normally about 150 μ thick. It can be paper-based and coated with plastics or it can be based on a white pigmented plastic. In either case, the surface that receives the dye is coated with a clear, thin receiving layer. This is normally a (co)polyester or polycarbonate, probably because the dyes used in D2T2 tend to be disperse dyes used for the dyeing of polyester textiles (*Section 8.6.5*). The receiver sheet is discussed in more detail in *Section 8.6.6*.

8.6.4. Dyesheet

The substrate is usually polyester, which is available as a 6 μ film (e.g. 6 μ grade MYLAR from DuPont and 6 μ grade MELINEX from ICI), is relatively cheap, has high tensile strength (cf. paper), is smooth, and has good thermal conductivity (Table 8.3). Its only drawbacks are that it softens below the operating conditions and that it is receptive to the dyes used. Other materials are known such as polyimides which have high melting points (>400°C), but they are expensive and are not generally available as thin films.

The backcoat should be thermally stable to 400°C and above. It also controls the frictional properties of the dyesheet. Polyurethanes are typical backcoats.[31]

The color coat contains binders and dyes. Binders are normally polymers that have some affinity for polyester and help to bind (glue) the dye to the polyester film. Ideally, they should be thermally stable, have little or no affinity for the dye (i.e. be able to release it during the heat transfer step), and provide the inks used for coating with the desired viscosity requirements. Typical binders are polyvinyl butyral[32] and cellulosic derivatives such as

cellulose acetate, cellulose acetate butyrate,[33] ethyl cellulose, ethylhydroxy-ethyl cellulose, and carboxymethyl cellulose.[34]

The dye is the key component of the whole system since it is the component responsible for producing the colored image. In other words, the dyes produce the color that appears in the final print. Consequently, we will consider the dyes in more detail.

8.6.5. Dye Diffusion Thermal Transfer Dyes

Dyes for D2T2 have to satisfy a set of demanding criteria. These are listed in Table 8.4. The color (shade) of the dyes has to be right which is not as simple as it seems. In order to produce high quality prints, the yellow, magenta, and cyan colors need to have well-defined spectral characteristics. This means that they must have the correct hue, brightness, and shape of absorption curves. Also, for the highest quality printing, a separate black is required.

The dyes must possess inherently high tinctorial strength or coloring power. This is necessary to achieve print optical densities up to 2.5, which are required for high quality prints. In practice, this means using dyes with high molar extinction coefficients ($\mathscr{E}_{max}$ values).

The dyes must dissolve in the receiving layer of the receiver sheet and therefore must have solubility in polymers such as polyester. Furthermore, as most dyesheets are prepared by solution coating, the dyes should also be soluble in solvents acceptable to the printing industry. These include aromatic hydrocarbons such as toluene; alcohols such as ethanol, isopropanol, and butanol; ethers such as tetrahydrofuran; and ketones such as methyl-ethylketone and cyclohexanone.

D2T2 dyes must possess high thermal stability to withstand the operating temperatures of the thermal heads, which reach temperatures up

Table 8.4. Dye Diffusion Thermal Transfer Dyes: Properties Required

Color: yellow/magenta/cyan, separate black
Strength: optical density to 2.5
Solubility: $\geq 3\%$ of ambient temperature in acceptable solvents
Thermal stability: to 400°C
Fastness
Light fastness ⎫
Silver halide photography ⎬ Image stability
Heat fastness ⎪
Zero migration or transfer ⎭
Dyesheet stability
Stable under user conditions for at least 18 months
Toxicology: Ames-ve

to 400°C. Although these high temperatures are reached for periods of only milliseconds, conventional textile dyes are not normally subjected to temperatures greater than 200°C. Therefore, this high thermal stability is a new requirement of dyes for D2T2.

The fastness properties of the dyes are extremely important and in many respects the most difficult to achieve. The light fastness, or degree of resistance to fading, has proved especially troublesome in the D2T2 process. For example, many conventional dyes for polyester textiles give excellent light fastness for this application; however, the same dyes in the D2T2 process can give abysmal light fastness. Thus, the red dye (**8-38**) gives a light fastness rating of 6* when used to dye polyester textile fabrics. In contrast, the same dye only exhibits a light fastness rating of 2–3 when used in the D2T2 process![35]

8-38
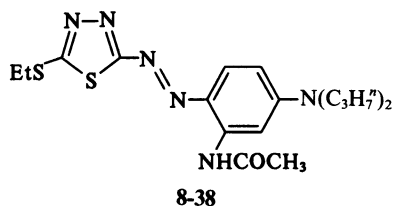
There are several reasons for the dramatic drop in light fastness of dyes in the D2T2 application. First, the dyes are held in a thin layer only several microns thick. This contrasts to the situation in textile fibers where each fiber, which can be several hundred microns thick, is dyed uniformly. Fading of the first few microns in textile fibers has virtually no effect since there are many tens of microns of dyed fiber still remaining. In contrast, fading of the first few microns of dye in a D2T2 print destroys the color completely! Secondly, all the dye in a D2T2 print is near the surface and is therefore easily attacked by singlet oxygen, the main agent responsible for the photofading of dyes. Thirdly, the white background of a D2T2 print reflects light back through the dyed layer, so that the light essentially gets a second chance to attack the dye molecules. Finally, it is well known that white pigments, such as titanium dioxide, promote the photofading of dyes.[38]

The heat fastness of dyes in the D2T2 print is also important. Thus, the dyes must not migrate (diffuse) in the final print if it is inadvertently exposed to heat; for example, by leaving it near a central heating radiator or in a locked car on a hot, sunny day. Any such dye migration would result in a loss of resolution that would manifest itself as "blurring." The heat fastness of dyes highlights an important point. On the one hand, the dyes have to be

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* The rating system is based on the international blue scale of 1–8, with 1 being very poor and 8 excellent. The scale is a logarithmic one, such that light fastness 8 is 2^8, or 256 times better than light fastness 1. (See ref. 37 for a fuller explanation.)

sufficiently mobile to transfer readily under the influence of heat from the dyesheet to the receiver sheet. However, on the other hand, the dyes, once transferred, have to be resistant to heat. With dichotomies such as this there obviously has to be a compromise to achieve both good thermal transfer and good heat fastness in the final print. Indeed, compromise is required in attempting to meet all the criteria with just one dye.

Dyesheet stability is another important factor. For example, the color coat must remain as an amorphous layer for a reasonable period of time (approximately 18 months) to give the product a reasonable shelf life. Any tendency of the dye to crystallize or migrate to the surface will result in printing defects.

Last, but by no means least, is the topical subject of toxicology. Not only must the final product be completely safe to handle by the consumer, but the components (chemicals) used to make the final product must also be safe, since plant operatives handle these chemicals during manufacture, usually on a large scale. Normally acute toxicity data such as LD_{50} values and skin and eye irritation tests are done. However, one of the most important aspects of the chemical is that it must be nonmutagenic and, by implication, noncarcinogenic. In other words, the chemical must not cause cancer. The Ames test, which employs bacteria, is the universally adopted screening test for mutagens, and new chemicals for commercial use should be Ames negative (i.e. not cause mutations in bacteria). The toxicological aspects of dyes and pigments are discussed more fully in *Chapter 12*.

Since the D2T2 process is, in theory, simply an extension of the mature textile transfer printing process, it is hardly surprising that the sublimable disperse dyes used for the latter process were the first types of dyes to be evaluated for D2T2. Three of the leading yellow, red, and blue dyes for textile transfer printing are CI Disperse Yellow 54 (**8-39**), CI Disperse Red 60 (**8-40**), and CI Disperse Blue 3 (**8-41**). Indeed, these dyes along with other dyes used for textile transfer printing were the first to be used in D2T2.[39]
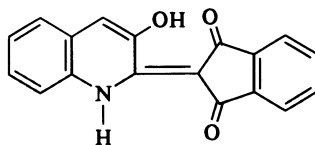
8-39
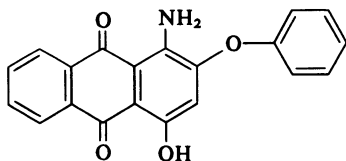
8-40
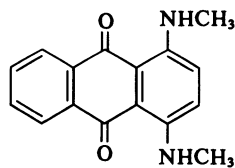
8-41

More recently, it has been discovered that the process is not one of sublimation but is rather a melt-state diffusion of the dyes—hence the name dye diffusion thermal transfer.[40] This has opened up the possibility of using dyes that are nonsublimable but which are capable of melt-state diffusion.

The types of dyes evaluated and actually used in D2T2 will now be discussed. For convenience, this is done by considering each of the three primary subtractive colors of yellow, magenta, and cyan.

8.6.5.1. Yellow Dyes

In many respects yellow is the easiest of the three colors to satisfy. A number of chemical classes produce yellow dyes of the disperse or solvent type needed for D2T2 and most of these have been evaluated.

The quinophthalones, which provide the leading textile transfer printing dye, have been patented by Mitsubishi[41] and Matsushita.[42] These dyes of general formula (**8-42**) provide bright, strong yellow dyes which can give good light fastness providing the right substituents are used (e.g. R = OH). The drawbacks of this class are the lack of synthetic flexibility to allow fine-tuning of color, properties, etc., and the poor solubility of the dyes in most solvents. This makes solution-coated dyesheets difficult to produce.
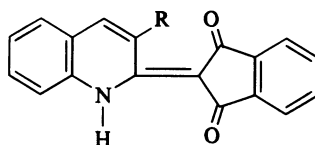
8-42   R = H, OH

Another class of dye used for textile transfer printing is azophenols.[43] CI Disperse Yellow 3 (**8-43**) is a typical dye of this class. These dyes tend to be relatively dull and have poor light fastness in the D2T2 application.[35]
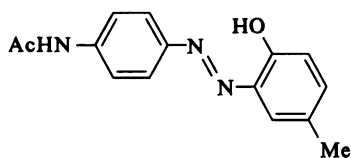
8-43

Azopyrazolones are used as photographic dyes[44] and it is not surprising therefore that this class has also been evaluated for D2T2.[45] Azopyrazolone is a misnomer, since it has been established that these dyes exist exclusively in the hydrazone tautomeric form.[46] The general formula of the dyes claimed in ref. 45 is **8-44**. Azopyrazolone dyes exhibit poor light fastness in D2T2.
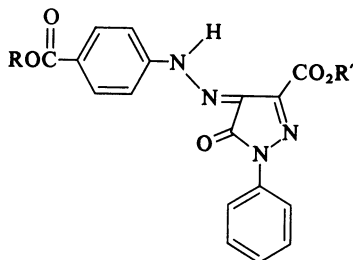
8-44

Methine dyes are a class of dye that has been used extensively both in the conventional coloration of textile fibers[47] and as photographic dyes.[44] They have been patented by a number of companies for application in D2T2. For example, Mitsubishi, Matsushita, and Sumitomo have patented methine dyes based on anilines such as **8-45**,[48] whereas Eastman Kodak[49] have patented dyes based on tetrahydroquinolines such as (**8-46**). The dyes are bright, strong, and display reasonably good light fastness.
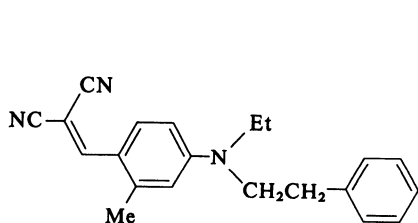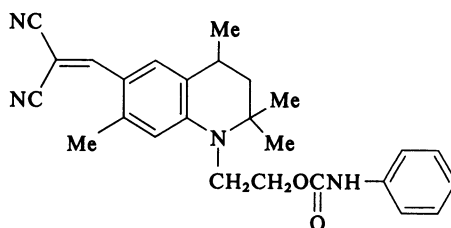
8-45   **8-46**

Azopyridones are another useful class of yellow dyes for D2T2. Like the azopyrazolones they exist exclusively in the hydrazone tautomeric form.[50] As a class azopyridones provide bright, strong yellow dyes which can exhibit good light fastness properties. A feature of all azo dyes is synthetic flexibility: this allows fine-tuning of the various properties (cf. quinophthalones). These features have encouraged a number of companies, including Mitsubishi,[51] Mitsui Toatsu,[52] Sumitomo,[53] and ICI,[35] to evaluate azopyridone dyes for D2T2. Typical dyes are (**8-47**) (Mitsubishi) and (**8-48**) (Mitsui Toatsu).
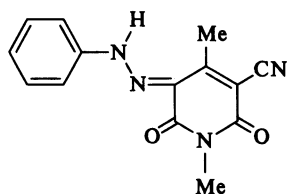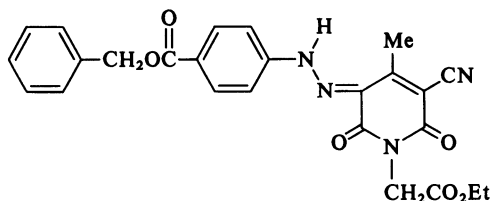
8-47   **8-48**

An unusual approach to D2T2 dyes has been adopted by Matsushita and ICI. These companies have attempted to use the brightest and strongest types of dyes, namely basic (cationic) dyes, in D2T2.

Matsushita uses leuco dyes and an acidic receiver sheet.[54] A leuco dye is a colorless dye precursor which, because of its low polarity, transfers readily with heat. A receiver sheet with acidic sites has to be used to generate the dye proper; in this case a yellow dye (Eq. 8.1).

$$\text{Colorless} \quad\rightleftharpoons\quad \text{Yellow} \tag{8.1}$$
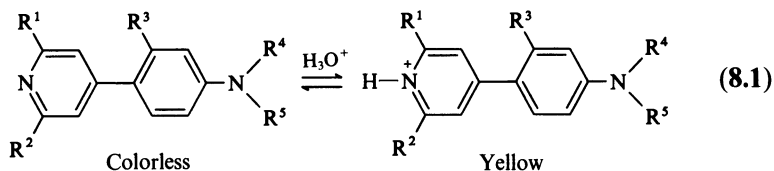
There are two major problems with this approach: (1) that leuco dyes tend to have poor light fastness, and (2) an additional heat treatment step is usually required to develop the color fully.

ICI has taken a slightly different approach.[55] Working with some of the brightest and strongest cationic dyes that are designed for polyacrylonitrile, and which display excellent light fastness on this substrate, ICI has chemically modified the dyes to render them thermally transferable. Dye **8-49** is typical of these modified dyes.

8-49
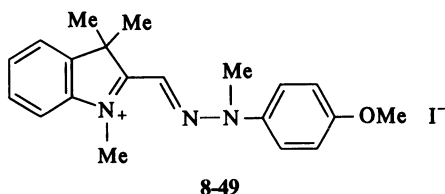
8.6.5.2. Magenta Dyes

As is the case with dyes for silver halide photography, a magenta dye has proved more difficult to achieve than a yellow dye. The leading red dye for textile transfer printing is the anthraquinone dye, CI Disperse Red 60 (**8-40**). The advantages of anthraquinone dyes are ´ rightness and good fastness properties, especially to light. Not surprisingly, CI Disperse Red 60 has been mentioned in a number of D2T2 dye patents.[39] As expected, the dye provides bright red prints which exhibit good light fastness. However, CI Disperse Red 60 has two major defects: (1) it is too yellow in hue to be a true magenta, and (2) it is tinctorially weak—a general feature of anthraquinone dyes.

DNP has attempted to overcome the shade problem by using a mixture of CI Disperse Red 60 with a bluer anthraquinone dye, namely CI Disperse

Violet 26 (**8-50**).[56] This approach is fine provided the two dyes transfer at a similar rate to avoid off-tone buildup and that they exhibit similar fastness properties.
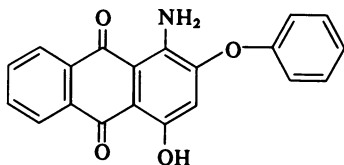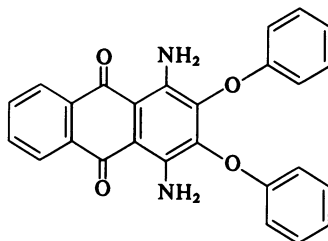
8-40   8-50

ICI has attempted to overcome both the shade and low strength problems of CI Disperse Red 60.[57] In theory, the lack of strength can be overcome by using more dye in the color coat of the dyesheet. In practice, this creates problems of dyesheet stability, such as dye crystallization. By incorporating a small amount of an analogous magenta dye, such as **8-51**, which exhibits high dyesheet stability, relatively large amounts of CI Disperse Red 60 can be used in the color coat. As is the case with DNP, the bluer shade is achieved by adding a bluer anthraquinone magenta dye.
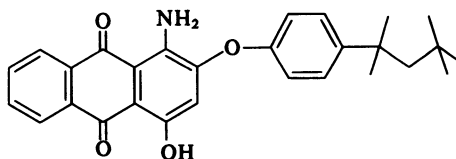
8-51

Azo dyes are by far the most important class of dye[58] and so azo dyes have also been evaluated extensively as D2T2 magenta dyes. Three types of azo dyes have been evaluated: carbocyclic azo dyes, heterocyclic azo dyes, and hydrazone azo dyes.

Carbocyclic azo dyes are based on benzene and naphthalene intermediates with azobenzene (**8-52**) being the backbone of most magenta dyes. Azobenzene itself is essentially colorless. To obtain magenta dyes, ring A normally contains two unsaturated electron-withdrawing groups, the most popular being nitro and cyano, and ring B contains an NN-dialkylamino group para to the azo linkage. Typical carbocyclic azo magenta dyes are represented by the general formula **8-53**,[59] with **8-54** being a typical dye.
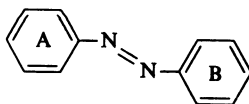
8-52
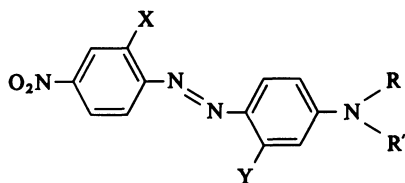
8-53

X = CN, NO$_2$

Y = H, Me, NHAc

R, R′ = C1–C4 alkyl, optionally substituted by electron-withdrawing groups
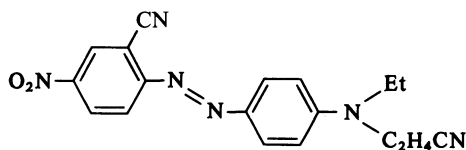
8-54

Carbocyclic azo dyes are the "bread and butter" dyes of the dyestuffs industry. As a class they are tinctorially strong and have good fastness properties. Thus, higher print optical densities can be obtained from the carbocyclic azo dyes than from anthraquinone dyes. However, dullness is a major drawback. Carbocyclic azo dyes are duller than anthraquinone dyes and this could limit their usefulness in D2T2.

Heterocyclic azo dyes are even stronger than the carbocyclic azo dyes and significantly stronger (up to four times) than the anthraquinone dyes. They are also bright—much brighter than carbocyclic azo dyes and, in certain cases, as bright as anthraquinone dyes. Their fastness properties, however, are lower than the anthraquinone dyes, especially to light. Because of these attractive features, a number of companies have patented heterocyclic azo magenta dyes for D2T2. Both Mitsubishi and Mitsui Toatsu have patented 1,3,4-thiadiazoles[60] (e.g. **8-55**). In addition, Mitsubishi has also patented the isomeric 1,2,4-thiadiazoles,[61] (e.g. **8-56**). Both types are claimed to be bright, strong, and have good fastness properties.
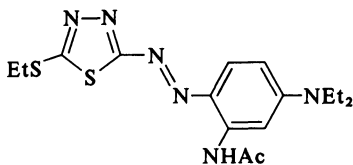
8-55
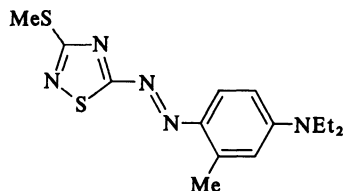
8-56

ICI[62] and Eastman Kodak[36] have both patented isothiazole azo magenta dyes, with **8-57** being a representative dye. ICI has also patented[62] pyrazoles (e.g. **8-58**) and thiophenes (e.g. **8-59**) as magenta dyes for D2T2. It is interesting to note that since a cyano group and a ring nitrogen atom confer similar properties to a molecule, then the cyano isothiazole dyes (**8-57**) should have a similar color, strength, and fastness properties to the 1,2,4-thiadiazole dyes (**8-56**).
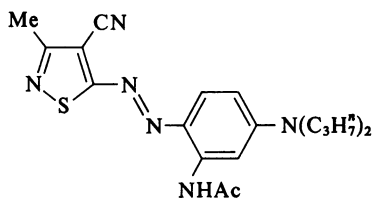
8-57
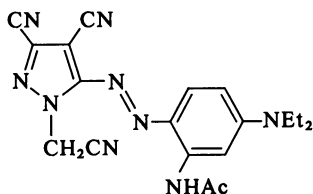
8-58
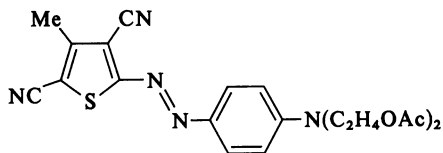
8-59

Dicyanoimidazole dyes (e.g. **8-60**) have also been claimed as magentas for D2T2.[63]
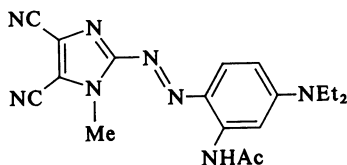
8-60

The third type of azo dyes evaluated as magentas for D2T2 are those that exist in the hydrazone tautomeric form (cf. azopyrazolone and azopyridone yellow dyes). These are the azonaphthol dyes. Indeed, this type of dye is used as a magenta in conventional silver halide photography.[44] The azonaphthol dyes (**8-61**) patented by Mitsubishi[64] are typical.

In addition to the azo and anthraquinone dyes, other dye classes have been evaluated for magenta D2T2 dyes. One of the most interesting is the tricyanovinyl type. Mitsubishi has a number of patents[65] on tricyanovinyl magenta dyes, with Sumitomo[66] and Matsushita[48] also patenting this class of magenta dye. Structure **8-62** depicts a typical dye. Tricyanovinyl magenta dyes are claimed to be bright, strong, and to have good fastness properties.
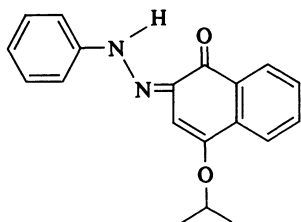
8-61
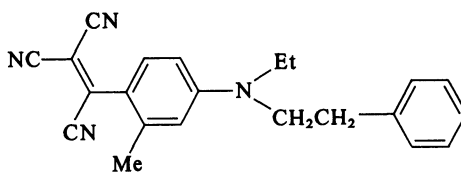
8-62

It is interesting that inserting just one extra cyano group into the methine chromogen causes such a large bathochromic shift from yellow (see *Section 8.6.5.1*) to magenta.

As was the case for the yellow dyes, Matsushita[54] and ICI[55] have patented basic dyes as magentas for D2T2. Matsushita again use a colorless dye precursor (8-63) to generate the magenta dye (8-64) on contact with the acidic receiver sheet. ICI uses a cationic dye having a large polarizable anion (e.g. iodide) to induce covalency and reduce polarity. The triazolium diazahemicyanine dye iodide (8-65) is claimed as a magenta D2T2 dye.
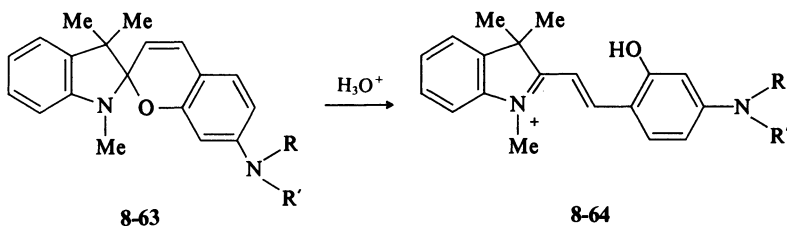
8-63

8-64
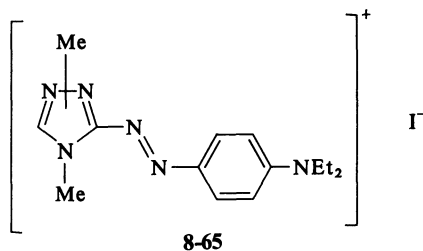
8-65

8.6.5.3. Cyan Dyes

To obtain a satisfactory cyan dye for D2T2 is probably the most difficult task of all. To begin with, very few cyan dyes belonging to the disperse or solvent dye classes are known. The best cyan chromogen is copper phthalocyanine. Unfortunately, the large molecular size of phthalocyanines results in unacceptably low diffusion rates in polyester and therefore precludes their use in D2T2. Consequently, the search for D2T2 cyan dyes has centered upon three areas:

1. Tailoring the major classes of dyes used for the conventional coloration of polyester. These are anthraquinones and monoazos.
2. Examining the dye types used in conventional silver halide photography. These are the indoanilines.
3. Evaluating novel types of dyes. These are the naphthoquinones and heterocyclic disazos.

As mentioned earlier the class of blue dyes used in conventional textile transfer printing is anthraquinone. Anthraquinone blue dyes are bright and can have good properties but, like all anthraquinone dyes, they are tinctorially weak. Nonetheless, anthraquinone dyes have been evaluated extensively by a number of companies in an attempt to produce a cyan D2T2 dye.

1,4-Bisalkylamino anthraquinones provide the greatest number of blue disperse and solvent dyes. Matsushita[67] and Mitsubishi[68] have patented dyes of this type for D2T2. CI Solvent Blue 36 (**8-66**) is a typical dye.

8-66
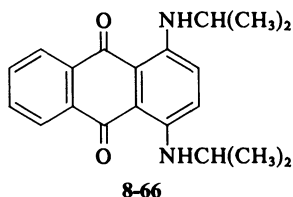
Dyes of this type are really too red to be a true cyan and tend to have only poor-to-moderate light fastness. Indeed, this latter aspect is exacerbated by the fact that 1,4-bisalkylamino anthraquinone dyes fade off-shade (redder).

The introduction of a 2-cyano group into 1,4-bisalkylamino anthraquinones not only gives a greener shade (closer to a cyan) but also improves the light fastness. Indeed, the dye **8-67** is the only textile transfer printing blue dye to possess high light fastness. Not surprisingly, dyes of this type have been patented for D2T2 by both Mitsubishi[69] and Sumitomo.[70]

8-67
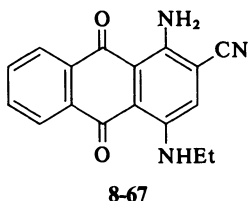
Mitsubishi[71] has also patented dyes of type (**8-68**) in which the electron-withdrawing group is an ester group rather than a cyano group.

O NH$_2$
CO$_2$Me

O NHEt
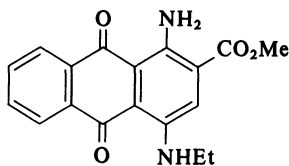
8-68

An alternative approach to greener blue dyes having improved light fastness is to use 1-(alkyl)amino-4-arylamino anthraquinones. Both ICI[34] and DNP[72] have patented these dyes for D2T2. CI Solvent Blue 63 (**8-69**) is a typical dye.

O NHMe

O NH

Me
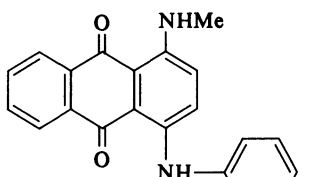
8-69

The only true anthraquinone cyan dyes are the CI Disperse Blue 60 types. These have the general formula **8-70**. Dyes of this type have been patented for D2T2 by DNP.[73]

O NH$_2$ O
N—R
O NH$_2$ O
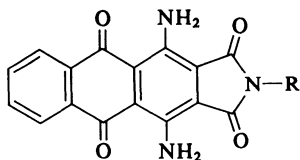
8-70 R = lower alkyl or alkoxyalkyl

A serious disadvantage with anthraquinone dyes is their lack of tinctorial strength which results in low print optical densities. For this reason, monoazo dyes have been evaluated since they are much stronger than anthraquinone dyes.

It is difficult to obtain cyan dyes from carbocyclic azo dyes. To approach this color the dye has to have a multiplicity of both electron-withdrawing groups and electron-donating groups. These tend to make the dye dull and worsen its fastness properties. Because of this, only one patent[74] has appeared on carbocyclic azo cyan dyes (**8-71**) for D2T2.

Heterocyclic azo dyes derived from sulfur and/or sulfur/nitrogen heterocyclic diazo components can produce cyan colors. These dyes are also brighter and stronger than the carbocyclic dyes, so it is not surprising that
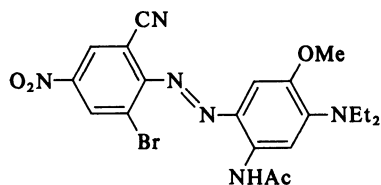
8-71

they have been evaluated more extensively than the carbocyclic dyes. Mitsubishi has been particularly active in this area, filing a number of patents on both thiophene[75] and thiazole[76] azo dyes. ICI[62] has also patented azo thiophene cyan dyes. Structure **8-72** represents a typical thiophene cyan dye and structure **8-73** a typical thiazole dye.
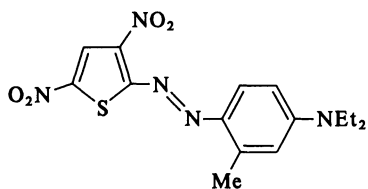
8-72
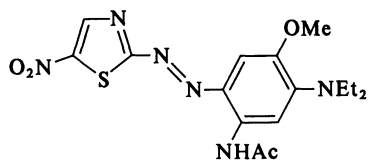
8-73

In general, the thiophene dyes give the better cyan colors. However, both dye types exhibit only moderate light fastness.

The classical cyan dyes used in conventional silver halide photography are indoanilines.[77] These produce true cyan colors. However, their tinctorial strength and light fastness properties are only moderate. Mitsubishi,[78] DNP,[79] and Eastman Kodak[80] have patented indoaniline cyan dyes for D2T2. Typical dyes are **8-74** and **8-75**.
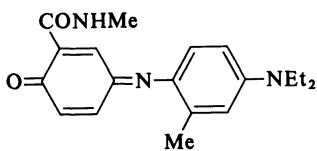
8-74
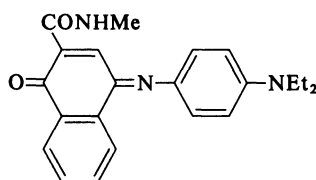
8-75

As mentioned earlier, two novel types of dye have been evaluated in the search for a satisfactory cyan for D2T2. These are naphthoquinones and disazoheterocyclics.

Naphthoquinones are smaller molecular-weight homologues of anthraquinones. Surprisingly, they are more bathochromic (i.e. give greener colors) than anthraquinones. Indeed, they are used to produce infrared absorbers (see *Chapter 11*). Mitsui Toatsu,[81] Matsushita,[82] and Mitsubishi[83] have all patented 1,5-naphthoquinones, typified by **8-76**, as cyan dyes for D2T2. In

addition, Mitsubishi[84] has also patented a mixture of naphthoquinone and anthraquinone cyan dyes.

8-76
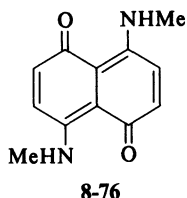
Disazothiophene dyes have been evaluated by ICI.[85] Normally, disazo dyes are dull. Surprisingly, disazo dyes incorporating a thiophene middle component are bright. Not only are they bright, they are also very strong ($\mathscr{E}_{max}$ ca. 70,000, i.e. about five times stronger than anthraquinones) and exhibit good light fastness in D2T2. Dye **8-77** is typical.

8-77
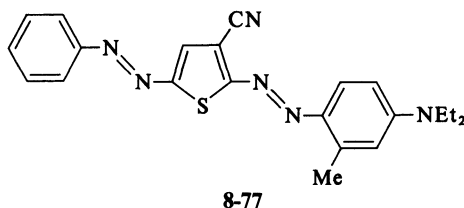
Again, Matsushita[54] and ICI[55] have patented basic dyes for D2T2. Matsushita uses the colorless carbinol dye (**8-78**) which, on contact with an acidic receiver sheet, develops the cationic blue diphenylmethane dye, Michler's Hydrol Blue (**8-79**) (Eq. 8.2). ICI uses the iodide salt of oxazine dyes such as **8-80**.

$$\text{8-78} \qquad\qquad \text{8-79} \qquad\qquad (8.2)$$

8-80
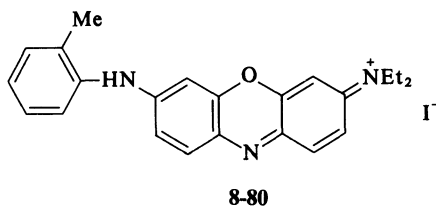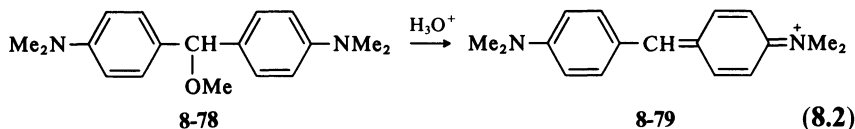
Mitsubishi has patented[86] the use of reactive disperse dyes for D2T2. The concept here is that the dye, once transferred, will form a covalent chemical bond with the receiver sheet, thus anchoring the dye firmly to the receiver sheet. This should give excellent fastness properties both to solvents

and heat. Of course, modified receiver sheets are required containing free hydroxy or amino groups to react with the dye (Eq. 8.3).

$$\boxed{\text{Dye}} - SO_2CH = CH_2 + \boxed{\text{RS}} - OH \ \rightarrow \boxed{\text{RS}} - OCH_2CH_2O_2S - \boxed{\text{Dye}} \qquad \textbf{(8.3)}$$
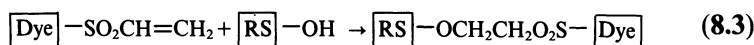
$$\boxed{\text{RS}} = \text{Receiver Sheet}$$

8.6.6. Receiver Sheet

There are three major parts to the receiver sheet, namely the base substrate, the dye receiving layer, and the release agent. The receiver sheet may be prepared by either a coextrusion process or by a solvent coating process. Solvent coating is the process normally employed since it offers much more flexibility both in the actual construction of the receiver sheet and in the use of additives.

The base substrate is normally a white plastic. DNP[87] has claimed a pigmented polypropylene trilaminate whereas Eastman Kodak[88,89] claims white pigmented polyester (MELINEX 990 white base from ICI). Typical thickness is about 150 μ. Plastic-coated paper can also be used.[40]

The receiving layer has to be a clear substance which is receptive to the dyes used in D2T2. Since these are of the solvent and disperse type used for dyeing polyester fiber (*Section 8.6.5*), it is hardly surprising that polyesters are the most commonly used receiving layers. DNP[87] uses a 5-component copolyester (Table 8.5), as described in a Toyoba patent.[90] The bulky neopentyl glycol disrupts the structure of the polymer, thus allowing easier uptake of dyes. In physical terms, it lowers the glass transition temperature (T_g) of the polymer. A mosaic pattern of the receiving layer can also be employed to improve the gloss.[87]

Polycarbonates are also used as a receiving layer. Thus, Eastman Kodak[88] has patented high-molecular-weight (>25,000) polycarbonates of

Table 8.5. Typical Copolyester
Receiving Layers

Chemical	Parts
Terephthalic acid	4
Isophthalic acid	4
Sebacic acid	1
Ethylene glycol	1.2
Neopentyl glycol	1

type **8-81** derived from bisphenol A. Addition of a linear polyester or a poly(caprolactone) to a polycarbonate-based receiving layer is claimed to improve the light fastness.[91]

8-81
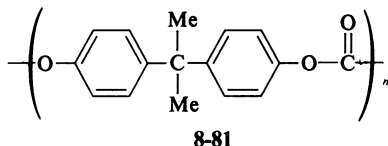
During the printing stage in D2T2 the dyesheet and receiver sheet are held together under pressure and the thermal heads reach temperatures up to 400°C to transfer the dye. Under these conditions the dyesheet and receiver sheet can fuse together so that subsequent separation after printing is impossible. Even if the dyesheet and receiver sheet can be separated after printing, total transfer can occur whereby all the color coat is transferred to a receiver sheet. To avoid these undesirable occurrences, a release agent is added to either the color coat of the dyesheet[92] or, more usually, to the receiver sheet either by a surface coating on the receiving layer or as an integral part of the receiving layer.[93] The chemicals used as release agents are the well-known antistick chemicals used in, for example, nonstick frying pans. Typically, these are fluorinated or phosphated surfactants, silicone oils, and solid waxes.[92,93]

A cross-sectional view of a typical plastic-based receiver sheet is shown in Fig. 8.17.

8.7. SUMMARY

Thermography is one of the three most important nonimpact printing technologies, along with electrophotography and ink jet. It can be subdivided into direct thermal printing and thermal transfer.

Direct thermal printing and the closely related pressure-sensitive printing are based upon color formers. They are both used primarily for monochromatic output (typically blue and black) and represent the low cost, low quality end of thermal printing. The Mead Corporation has extended color former technology into a full-color process, the Mead photocapsule process.

The newer technology of thermal transfer printing can also be subdivided into thermal wax transfer and D2T2. Thermal wax transfer represents a middle quality technology. It uses pigments dispersed in a wax as the color coat and plain paper or overhead transparencies as the receiver sheet. It is essentially an "all-or-nothing" process which makes continuous

Figure 8.17. Cross-section of a typical receiver sheet.
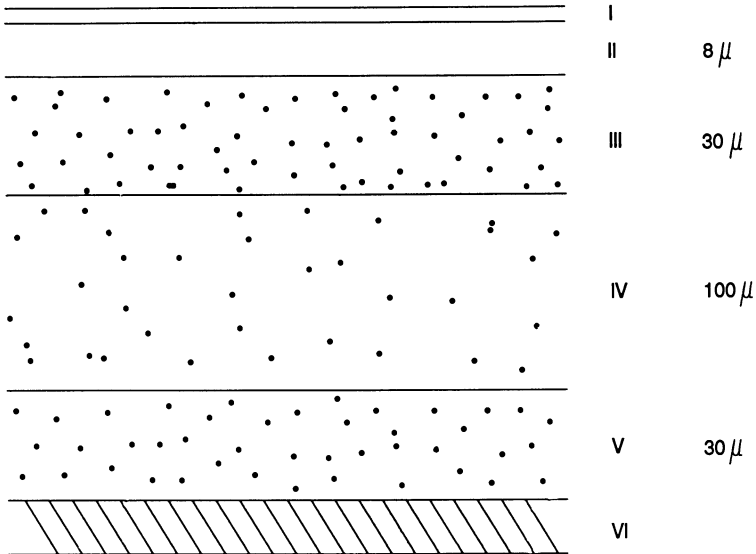
I Very thin silicone layer

II This is the clear receiving layer which is a copolymer consisting of:

Terephthalic acid	4
isophthalic acid	4
sebacic acid	1
ethylene glycol	1.2
neopentyl glycol	1

Layers III,IV and V are the backing sheet which is polypropylene.

III Polypropylene containing calcium carbonate plus a white pigment (titanium dioxide) with little voiding.

IV Polypropylene containing calcium carbonate (less than in III) plus pigment; this layer is voided (biaxially orientated).

V As for layer III.

VI Thin, heat resistant backcoat.

tone production difficult. In contrast, D2T2 uses dyes rather than pigments in the color coat and white plastic-based film, especially polyesters, as the receiver sheet. Good continuous tones and high optical densities can be obtained, which enables high quality prints to be produced. Thus, D2T2 is the favorite to capture the high quality markets, including, eventually, the lucrative silver halide photographic market.

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9

Ink-Jet Printing

9.1. INTRODUCTION

Ink-jet printing simply involves squirting droplets of ink on to a substrate (paper or plastic) to produce an image. It completes the trio of the three major nonimpact printing technologies, along with electrophotography (*Chapter 7*) and thermography (*Chapter 8*).

Ink jet can be divided into two major technology types: continuous and drop-on-demand. Each of these can be subdivided further as shown in Fig. 9.1. How these technologies evolved will now be considered briefly.
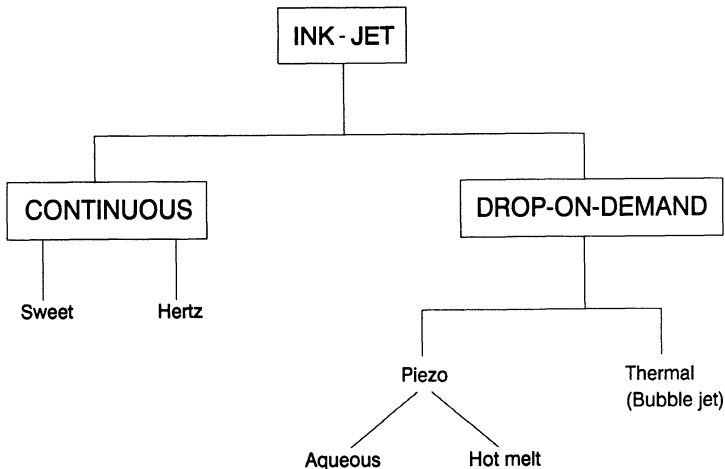
Figure 9.1. Subdivisions of ink-jet printing.

Table 9.1. Patents on Ink-Jet Inks

	1975–76	1977	1978	1979	1980	1981	1982	1983	1984	Total
Japan	1	6	9	13	53	45	133	37	145	442
U.S.	3	4	4	13	17	8	8	7	2	66
Other	1	0	1	0	0	1	2	3	2	10
	5	10	14	26	70	54	143	47	149	518

9.2. HISTORY AND DEVELOPMENT

Ink-jet technology is not new. The first use of ink jets in recording devices dates back as far as 1930 and the first successful product using ink jets was developed by Elmquist in Sweden in 1951.[1] However, it was not until the 1960s, 1970s, and 1980s that the inventions were made upon which today's ink-jet technology is based. It was Sweet in 1964–65 who invented the continuous ink-jet method and this was modified by Hertz in 1967.[1] The second major ink-jet technology of drop-on-demand was invented by Zoltan in 1972.[1] This used a piezoelectric element to eject the ink. The use of heat to eject the ink by bubble formation was discovered independently by Canon and Hewlett-Packard in 1979.[2,3] These two companies cross/licensed the thermal ink-jet technology in 1983.[3] More recently, the hot-melt ink-jet system (also known as solid ink-jet and thermoplastic ink-jet) was discovered by Dataproducts (formerly Exxon),[4] and Howtek.[5] Tektronix are also involved in this technology.[6]

Until 1976 the United States was the undisputed world leader in ink-jet technology.[2] However, since that year the Japanese have dominated the ink-jet area. This is reflected by the numbers of patents on ink-jet (Table 9.1).[2] For example, in 1984 Japanese companies applied for 145 patents while only two patents were issued to American companies. A probable driving force for the intense Japanese activity is the suitability of ink-jet for printing kanji characters. During 1987–1988 there appears to be a resurgence of interest in ink-jet printing in the USA with Hewlett-Packard in thermal ink-jet and Tektronix and Dataproducts in solid ink-jet leading the way. Other American giants such as IBM and Xerox are considering licensing ink-jet technology.

Table 9.2 shows the results of a more detailed patent survey of ink-jet activity from 1980 to 1985.[7] This shows that the majority of patents were on dyes, including dye synthesis, dye mixtures and control of dye impurities.

9.3. TECHNOLOGY

As seen in Fig. 9.1 ink-jet is conveniently divided into two basic types, namely continuous ink-jet and drop-on-demand ink-jet.

Table 9.2. Ink-Jet Patent Activity (1980–1985)

Category	No. of patents	Comments
Dyes	220	Dyes are claimed rather than pigments. 198 Patents specifically mention increased reliability or durability.
Dye synthesis	86	Major classes are azo and phthalocyanine.
Dye mixtures	118	Claim that a mixture of dyes is better than a single dye. Typically mixtures of acid and direct dyes.
Dye purification	27	Methods to minimize (control) levels of impurities such as electrolyte and insolubles.
Solvents/chemicals	104	Most nontoxic, water-soluble materials are covered. The most common solvents are glycols and N-methyl pyrrolidone.
Thermoplastic inks	6	Hot-melt ink-jet.

9.3.1. Continuous Ink-Jet

As the name implies, in continuous ink-jet systems[1,8] a continuous stream of ink droplets is ejected from a nozzle. Some of these are targetted at the paper to form the image while the remainder are collected in a gutter and either recycled or rejected. This selective deflection is achieved by first electrostatically charging some of the ink droplets, then deflecting those that are charged using high voltage electrodes. Obviously, two designs are possible. In the first design, the charged ink droplets are deflected on to the paper to form the image and the uncharged droplets are collected in a gutter. This is the raster scan continuous ink-jet method (Fig. 9.2). In the second design, the uncharged ink droplets form the image and the charged ink
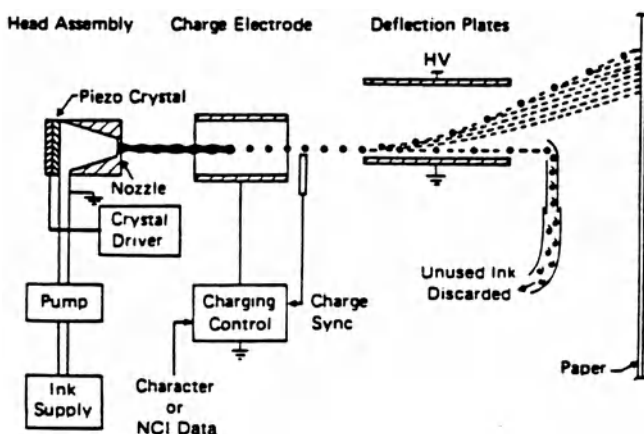
Figure 9.2. Components for a single-nozzle, raster-scan, continuous ink-jet printhead.
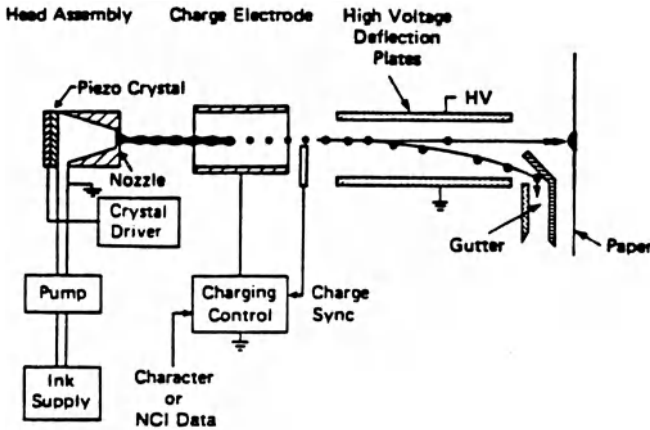
Figure 9.3. Components for a single-nozzle, binary, continuous ink-jet printhead.

droplets are deflected into the gutter. This is the binary continuous ink-jet system (Fig. 9.3). Both the raster scan and binary continuous ink-jet systems are based on the original Sweet technology and are especially suited for monochrome printing. The Hertz technology, whereby a fine mist of irregular-sized ink droplets is formed, uses the binary design of the uncharged droplets forming the image (Fig. 9.4). It is more suited to color printing than the previous two methods. Indeed, it is employed by Iris in their color ink-jet printers.

As seen from Figs. 9.2–9.4, each continuous ink-jet system is characterized by having a common set of components, namely a high pressure pump, a drop charge electrode, and high voltage deflection plates. For more detailed information on the construction and operation of continuous ink-jet systems, consult refs. 1 and 8.
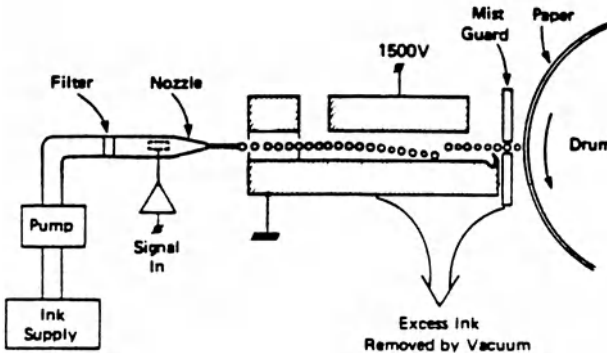
Figure 9.4. Components for a single-nozzle, Hertz, continuous ink-jet printhead.

9.3.2. Drop-on-Demand Ink-Jet

Drop-on-demand, or impulse, ink-jet systems differ in two major respects from continuous ink-jet systems. First, all the ink droplets are used to form the image: none are wasted. Ink droplets are only ejected where a dot is required on the substrate, i.e. they are produced "on demand." Secondly, the droplets are not charged. Hence, there is no deflection involved. Instead, the droplets are "fired" in a straight line to the desired position on the paper (Fig. 9.5). This feature highlights an important point, namely that the printhead in drop-on-demand ink-jet printing should be as close as possible to the substrate surface so that the ink droplets travel as short a distance as possible to produce accurate images. In continuous ink-jet systems the droplets can travel greater distances. Consequently, continuous ink-jet systems are more suited to industrial applications such as the printing of rough, irregular surfaces, such as cardboard boxes. In contrast, drop-on-demand ink-jet systems are suited to printing on plain, smooth substrates where higher quality is required. For example, office output (see *Section 9.6*).

As seen from Fig. 9.1, drop-on-demand ink-jet systems may be subdivided into two broad types, namely piezo and thermal (or bubble jet). The piezo type may be subdivided further into systems using the conventional liquid inks (which may be aqueous based or solvent based), and the more recent hot-melt inks. These are solid at room temperature but on heating they melt to form a fluid ink. This fluid ink is ejected. On hitting the cool substrate it resolidifies. A significant proportion of the solid ink resides on the surface of the paper giving the print an embossed feel. The basic principles are outlined in Fig. 9.6.

It is fascinating the way that three totally different technologies have converged. Electrophotography, thermal and ink-jet began as completely different technologies having very little in common. For example, electrophotography used a pigment dispersed in a resin to produce the image, thermal transfer used a pigment dispersed in a wax and ink-jet used a water-soluble
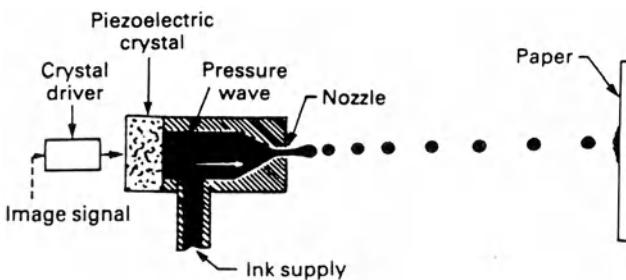
Figure 9.5. Drop-on-demand ink-jet printer.
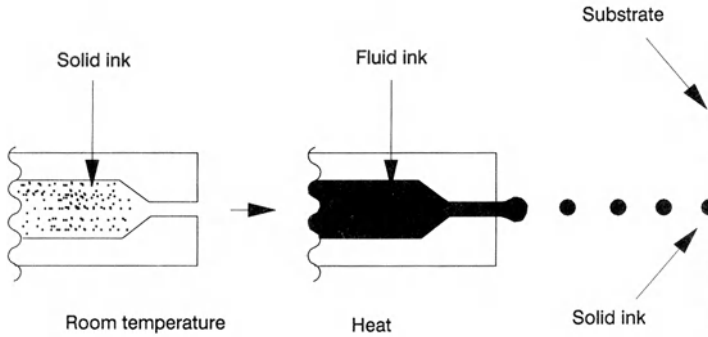
Figure 9.6. Principle of hot-melt ink-jet.

dye dissolved in an aqueous ink. Now, electrophotography, thermal transfer and hot-melt ink-jet all use colorants, usually dyes, dissolved in a resin so that the final image on the substrate is similar both physically and chemically irrespective of which technology was used to produce it. Evidence in favor of this is provided by Dataproducts' solid ink-jet printer which produces prints of at least equal quality to laser printers.[9]

9.4. INK-JET INKS

Basically there are three types of inks: aqueous, solvent, and hot-melt. The most common inks for drop-on-demand ink-jet printers for office quality output are aqueous-based inks whereas solvent-based inks are prevalent for continuous ink-jet printers, especially for industrial labeling. The recently introduced hot-melt inks based on waxes/resins could be a significant force in the future for drop-on-demand ink-jet printers. Before considering these inks individually the general features required of all ink-jet inks is discussed.

9.4.1. General Features

All ink-jet inks have to meet the dual requirements of good print quality and compatibility with the printer (Table 9.3). Good print quality depends upon being able to form controllable droplets and on the printing properties of the ink. Table 9.3 presents the important properties that influence droplet formation, the printing properties required of an ink to produce good quality prints,[8] and the more general properties required of an ink, including compatibility with the printer.[9]

Table 9.3. General Features of Ink-Jet Ink

Physical properties	Printing properties	Functional properties
Viscosity	Good optical density	Machine compatibility
Specific gravity	No feathering	Stable drop formation
Surface tension	Uniform spreading	No particle contamination
Dielectric properties	Fast set time	No nozzle crusting
pH	Good waterfastness	Low corrosion
Color	Good fading resistance	No biological growth
	Good soak resistance	Long shelf life
	Good rub resistance	No long-term health problems
	Good smear resistance	No chemical hazards
	Gloss	
	Able to print on paper	
	variations	

9.4.2. Aqueous Inks

Aqueous-based inks normally contain other solvents in addition to water. Glycols, such as diethylene glycol, and *N*-methylpyrrolidone are the most common cosolvents[10] (Table 9.2). The cosolvents serve several functions. For example, they act as humectants, i.e. they help minimize the evaporation of water and thereby prevent the crystallization or crusting of the dye. Any crusting would block the ink-jet nozzles and prevent the system from operating effectively. Cosolvents also help to control the viscosity and the surface tension of the inks, two very important parameters (Table 9.3). Furthermore, they can improve the solubility of the dye thus producing more stable inks.[10]

One major disadvantage of the use of water in inks is that it is a good growth medium for microorganisms such as bacteria and fungi. If unchecked, these will have disastrous effects, including clogging the filters and nozzles. Consequently, a biocide effective against both bacteria and fungi is normally added to an aqueous ink. In cases where the cosolvent is an alcohol or glycol, this may also serve as the biocide if it is present in sufficient quantity.

Water also has the disadvantage of being a good corrosion promoter, a feature which is accentuated by the presence of certain electrolytes in the dye. Care must therefore be taken to select both a pure dye and a pH that is compatible with the materials used in the ink and in the printer.

Insoluble or particulate matter in the ink presents a serious problem. Obviously, strenuous efforts should be made to avoid introducing such matter in the first place. The major source of such contamination is the dye and only highly purified dyes should be used in the inks (see *Section 9.5*). In some inks chelating agents are added to solubilize metal salts.[11]

Obviously, aqueous-based inks require water-soluble dyes. This aspect is discussed fully in *Section 9.5*.

9.4.3. Solvent Inks

Solvent-based inks are used when a fast drying rate is required and/or when printing on to hydrophobic substrates such as plastics or metals. Ketones such as methylethylketone (MEK) are the most common solvents. However, a major disadvantage with such solvents is flammability. Because of this alcohols, such as ethanol, are also being used since these are less flammable than ketones but are faster drying than water. Solvents also pose more of a toxicity problem than water and some solvents inks are already being banned in certain parts of the United States.

Solvent-based inks predominate in large character industrial labeling of, for example, cardboard boxes and also in the marking of metal and plastic containers and industrial components. The predominant color is black. For solvent-based inks, solvent-soluble dyes are required. These dyes and their requirements are discussed in *Section 9.5*.

9.4.4. Hot-Melt Inks

Hot-melt inks are like wax crayons, being solid at room temperature and fluid when heated. Since this technology is new there is a paucity of information on the types of vehicles used. However, fatty (C_{18}—C_{24}) carboxylic acids and alcohols have been claimed by Exxon,[4] and sulfonamides of structure 9-1 by Tektronix.[6] The preferred melting points appear to be in the range 60–125°C.

9-1   mp 105°C
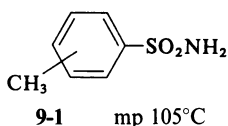
9.4.5. Ink–Paper Interactions

Matching the properties of the ink to the paper substrate is of paramount importance for obtaining good quality prints. Figure 9.7 shows the interrelationships between the paper, ink and printhead.[10] Indeed, the ink–paper interaction is vitally important in determining the quality of the final print. Ideally, an ink should produce good quality prints on all types of paper but this is extremely difficult, if not impossible, to achieve. All papers are different and in order to obtain the optimum print quality from a particular ink and printer it is usually necessary to use a paper designed for that
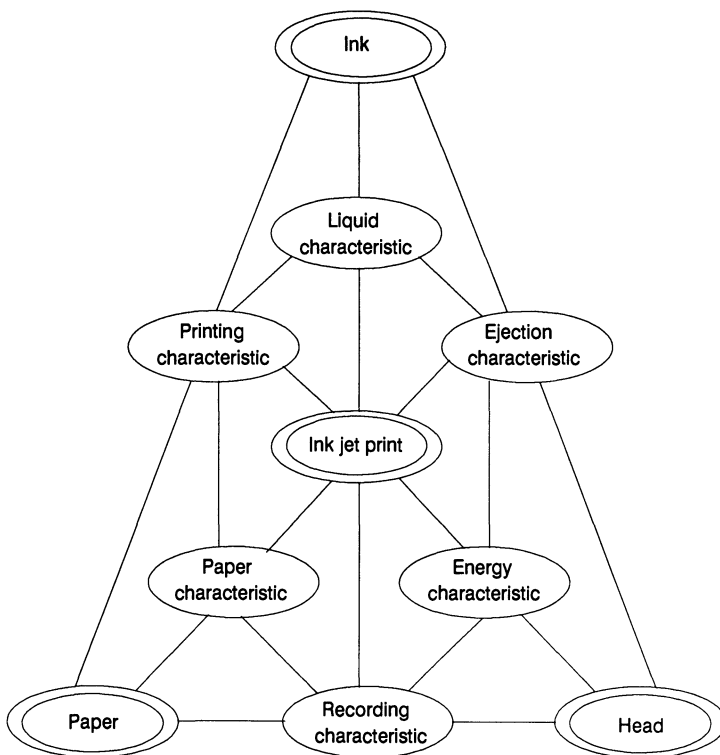
Figure 9.7. Relationship among ink, paper, and head.

system. In general, coated rather than plain papers give the best quality. However, the ideal situation is to be able to print with good quality on any paper. Although this ideal situation has not yet been achieved, rapid progress is being made.

In the early days of ink-jet printing a lot of effort was expended in producing papers specially designed to give optimum quality prints from the available ink-jet printers. As a consequence, many ink-jet printers only gave reasonable print quality on coated papers. The situation is different today: the bulk of the research effort is centered upon improved ink-jet printers and improved ink-jet dyes and inks. The dramatic improvements in all these areas means that high quality prints can now be produced on plain paper.

The nature of the ink largely determines its interaction with the paper. Usually, a compromise has to be reached between high water and smear fastness (see *Section 9.5.6*) on the one hand and print definition on the other hand. In general, solvents aid penetration into the paper and thereby improve the wet and smear fastness but at the expense of print definition:

the print edges are less regular, a phenomenon referred to as feathering. In aqueous inks, the level of cosolvent is usually between 1% and 10%. A detailed account of the factors affecting ink–paper interactions may be found in ref. 8.

9.5. INK-JET COLORANTS

9.5.1. Properties Required

Of the two major classes of colorants, namely dyes and pigments, dyes are used almost exclusively in ink-jet inks, particularly for office applications. The reason is simple. Pigments, being insoluble, have a much greater tendency to clog the nozzles, especially after a machine has been switched off and is then restarted at a later date. The choice of dye depends upon the ink used, whether it is aqueous, solvent, or hot melt, and on the type of printer (thermal or nonthermal). However, irrespective of the solvent system, all ink-jet dyes have to satisfy a number of stringent criteria. These are listed in Table 9.4.

9.5.1.1. Color

Black is by far the predominant color. This is hardly surprising since black is the color of text. However, for full-color printing the three subtractive primary colors of yellow, magenta, and cyan are also required.

Obtaining true yellow, magenta, cyan, and even black colors is not easy. The key parameters are the absorption maxima (peak wavelength) and the shape of the absorption curve, in particular its broadness and the presence (or absence) of unwanted secondary absorptions.[12] Ideally, bright dyes (which have narrow absorption curves) are required in order to produce a comprehensive balanced color gamut. It should always be remembered that

Table 9.4. Properties Required of Ink-Jet Dyes

Color: yellow/magenta/cyan/black
Color strength: high
Solubility: 5–20%
Insolubles: $<0.5 \ \mu m$
Electrolyte/metals (ppm): Cl^-, SO_4^{2-}, Ca^{2+}
Fastness: light, water, smear
Shade: Same on different paper; print definition
Toxicology: Ames −ve
Thermal stability: Kogation[a]

[a] The buildup of insoluble deposits on the heating element (see *Section 9.5.1.9*).
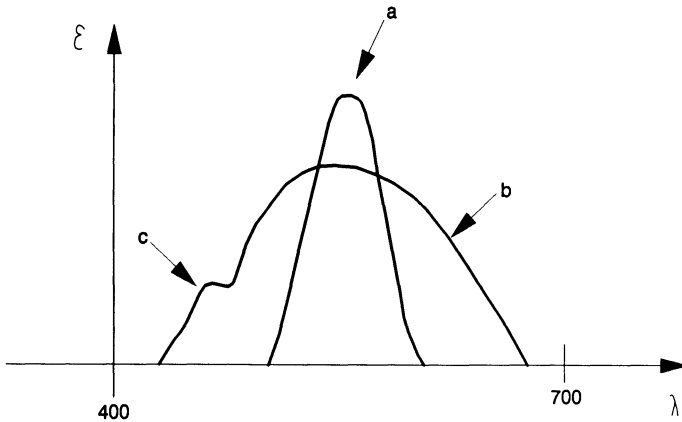
Figure 9.8. Absorption curves of (a) a bright, ideal magenta dye and (b) a duller, nonideal magenta dye having unwanted secondary absorptions (c).

bright dyes can be made duller (e.g. by adding a shading color such as black), but dull dyes cannot be made bright. Figure 9.8 illustrates these principles for a magenta dye.

Obtaining an ideal black shade is not easy. There are many shades of black ranging from reddish blacks to neutral blacks to greenish blacks. The situation is compounded further, since Oriental sensibilities prefer one shade of black (a greenish black) and Western sensibilities prefer a neutral or slightly redder shade of black.

Even after a dye having the correct color has been chosen care must be exercised that the color remains unaffected by changes in ink concentration, ink pH, ink solvents, and ink–paper interactions.[8,13]

9.5.1.2. Color Strength

The color strength of the dye should be as high as possible for several reasons. One reason is to enable prints having high optical densities to be produced. Consider two dyes, A and B. The inherent tinctorial strength of dye A is five times that of dye B. This means that an ink containing only 1% of dye A would give the same print optical density as an ink containing 5% of dye B (providing the molecular weights of A and B are similar). Obviously, this has a number of ramifications. One of these is cost effectiveness. Providing dye A is less than five times the cost of dye B, then it is more cost effective than dye B. Another advantage is the increased flexibility possible in the ink formulation, leaving more scope for additives. Finally, the ink stability is likely to be greater, regarding both dye precipitation and also kogation (see *Section 9.5.1.9*) in thermal ink-jet systems.
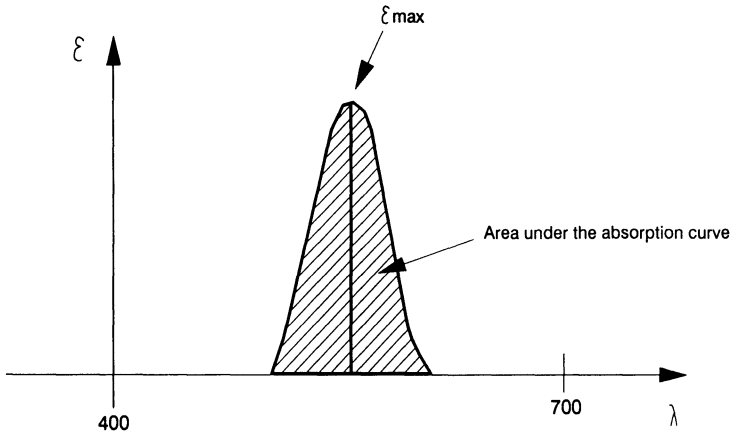
Figure 9.9. Relationship between ε_{max} and tinctorial strength.

The inherent tinctorial strength of a dye is expressed by the area under the absorption curve. The molar extinction coefficient, ε_{max}, which measures the height of the absorption curve, is usually taken as a rough measure of the tinctorial strength (Fig. 9.9). Fluorescence also contributes to the strength of a dye but the overwhelming majority of ink-jet dyes are nonfluorescent.

The formula for calculating ε_{max} from an optical density measurement is given by Eq. (9.1).

$$\varepsilon_{max} = \frac{OD}{c \times l} \tag{9.1}$$

where OD = optical density

c = concentration in moles/liter

l = path length in centimeters

9.5.1.3. Solubility

A dye for ink-jet should have as high a solubility as possible to minimize any tendency for the dye to crystallize and cause problems such as nozzle blockage.

What factors influence the solubility of a dye? These depend upon whether the dye is intended for an aqueous ink, a solvent ink, or a hot-melt ink.

The group that confers the best water solubility on dyes is the sulfonic acid group. Generally, the greater the number of sulfonic acid groups per

molecule, the greater the water solubility. The sulfonic acid group is rarely present as the free acid ($-SO_3H$) but rather as a metal salt ($-SO_3^- M^+$). In conventional dyestuffs the metal is sodium but lithium usually confers enhanced water solubility, and some ink-jet dyes are marketed as lithium salts. Ammonium (NH_4^+) and potassium (K^+) are other favored cations. Carboxylic acid groups, especially in the form of salts, also confer water solubility on dyes.

Dyes having solubility in solvents such as MEK, and also waxes and resins for solid inks, are generally devoid of polar groups such as sulfonic acid. Instead, they normally contain alkyl groups, the length and degree of branching of the alkyl chain having a marked effect on the solvent solubility. Metal complex azo dyes (2:1) are also used, especially blacks. The dye part of the molecule contains a unit negative charge which is delocalized over the entire molecule. This is balanced by a cation (**9-2**), and the nature of the cation affects the solubility, i.e. whether it is H^+, Na^+, or $-N^+R_4$.

$$[\text{Dye}]^- \ \text{Cation}^+$$
$$\textbf{9-2}$$
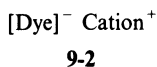
A mixture of dyes of similar structure, especially isomers, often has higher solubility than the individual components.

9.5.1.4. Insolubles

The dyes must be as free from insoluble matter as possible, otherwise the ink-jet nozzles will soon clog up. Freedom from insolubles is achieved by using pure intermediates to synthesize the dye and by subjecting a solution of the dye to a filtration stage. This may be done during manufacture of the dye or on the ink prior to usage (or both).

9.5.1.5. Electrolytes/Metals

Anions and metal cations are normally present in commercial dyes either as a consequence of the preparation or as an added diluent. Anions such as sulfate and especially chloride are undesirable in ink-jet inks due to the corrosion problems they cause to the metal printheads. Certain metal cations, particularly divalent cations such as calcium, need to be removed, since these can precipitate with certain anions such as sulfate and with the dye itself. Normally, the level of electrolyte has to be reduced to the parts per million (ppm) level, less than 100 ppm being typical. This is generally accomplished by dialysis or ultrafiltration.

9.5.1.6. Fastness Properties

Light fastness, wet fastness, and smear fastness are the most important fastness properties required. They are also the most difficult to achieve, particularly with aqueous-based ink systems.

a. Light Fastness. The final printed document must have reasonable light fastness (resistance to fading by light) if it is to serve any useful purpose. However, it is a well-known fact that in general dyes have much poorer fastness to light than pigments.[14] Furthermore, the light fastness that dyes exhibit on paper is lower than the light fastness that they exhibit on textiles. Not surprisingly, it has proved difficult to obtain ink-jet dyes having good light fastness.[8,15] This is demonstrated by the accelerated light fastness testing of the water-soluble dye Patent Blue A. After 40 h exposure in an Atlas fadeometer, all the color had been destroyed[8] (Fig. 9.10).

b. Water Fastness. The final print should be resistant to water so that if the paper gets wet or is rubbed by moist fingers, smudging does not occur. This feature illustrates the extreme difficulties of producing an ideal aqueous ink-jet dye. On the one hand, high water solubility is required for the ink,
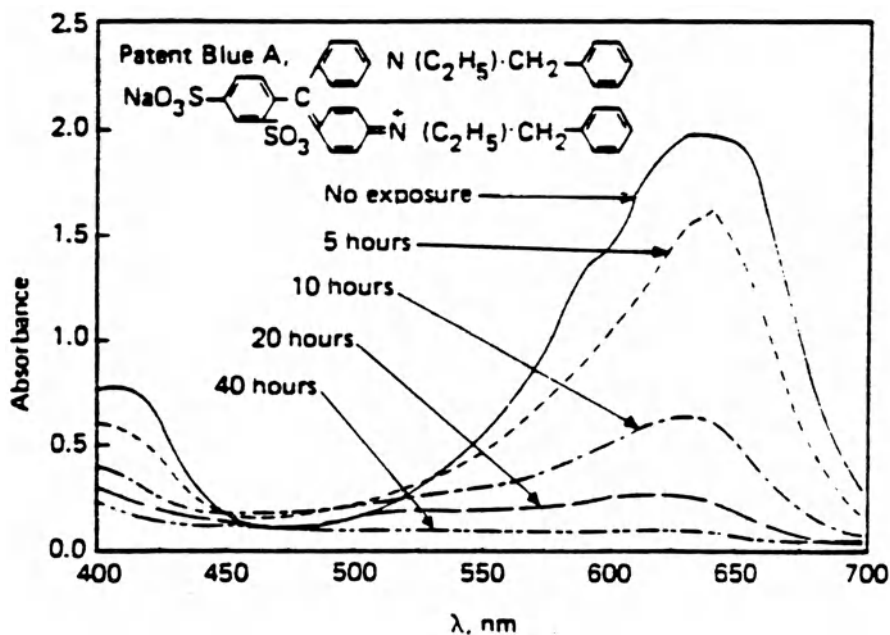
Figure 9.10. Absorption spectra of Patent Blue A ink on paper as a function of exposure time to an Atlas fadeometer.

but on the other hand, water insolubility is required once the dye is on the paper! Usually a compromise position has to be reached to achieve adequate solubility and adequate water fastness.

One of the most promising approaches to achieving high water fastness is by using the concept of differential solubility, i.e. using a dye that has high water solubility in the ink but low water solubility when on the paper.[16] Aqueous-based ink-jet inks are normally slightly alkaline (in the pH range 7.5–10.0) and most papers are slightly acidic (pH 4.5–6.5). By incorporating groups that have pKa's of 6.5 to 8.0 into the dye molecules, it is possible to produce dyes that have high water solubility in an alkaline ink (where the group is ionized and therefore confers extra water solubilizing properties), but which have relatively low water solubility on the acidic paper (where the group is in its less water-soluble, nonionized form). Two prime examples of such groups are carboxy ($-CO_2H$)[15] and hydroxy ($-OH$). The concept is illustrated in Scheme 9.1.
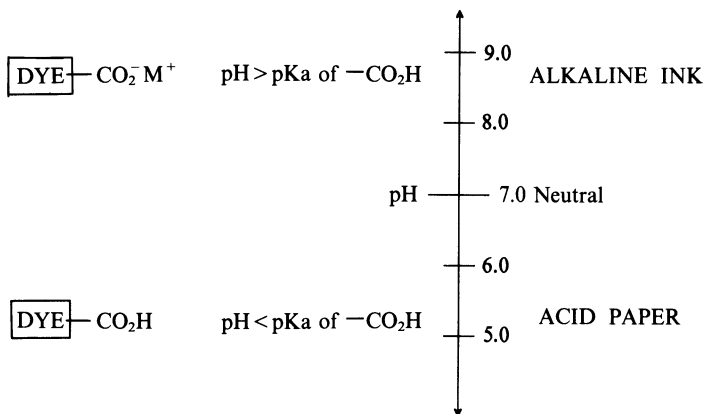
Scheme 9.1. Use of differential solubility to achieve high ink solubility and high water fastness.

The water fastness of dyes in either solvent or wax/resin-based inks are excellent since the dyes used (see *Sections 9.5.3–9.5.6*) are water insoluble.

c. Smear Fastness. This is effectively resistance to smear when using a highlighter pen. Such pens usually contain aqueous alkaline inks and can cause a dye to smear by facilitating the formation of water-soluble species. Again, dyes from solvent or wax/resin inks are less prone to smear than those from aqueous inks.

9.5.1.7. Shade

The shade or hue should appear the same irrespective of the substrate on which it is printed. Again, this can be difficult to achieve since the sub-

strates vary enormously in physical properties. For instance, papers vary in texture, adsorption, additives, and pH, and ideally the dye should be insensitive to these differences.

9.5.1.8. Toxicology

Environmental health and safety has assumed increasing importance in recent years. In the workplace, this applies to safer working practices and, in the chemicals industry, to toxicologically safe chemicals. The toxicological aspects of dyes are dealt with in detail in *Chapter 12*, but one important criterion of dyes is that they should, indeed, must be, noncarcinogenic. In other words, they must not cause cancer in humans. The accepted primary screening test for mutagenicity (in bacteria) is the Ames test, and it is normally required that dyes should be Ames negative, i.e. not cause mutations in bacteria. Therefore, ink-jet dyes should ideally be Ames negative.

9.5.1.9. Thermal Stability

If the dye is required for a thermal ink-jet system such as Canon's Bubble Jet or Hewlett Packard's Think Jet, then the extra parameter of thermal stability or kogation fastness is required. Since the temperatures involved are as high as 300°C, then dyes stable to these conditions are required.

Kogation is derived from the Japanese word *koga* meaning "to char." It refers to the buildup of insoluble deposits on the heating element during operation of a thermal ink jet. Good kogation is when these deposits are absent or very low, whereas poor kogation is when the deposits are substantial. The insoluble deposits act as an insulating barrier. They hinder heat flow from the heater to the ink and cause overheating of the element itself. Poor kogation is caused by two factors. The first is the presence of inorganic impurities such as iron, copper, and silicon. The second is the degradation of the dye itself. Reduction of the inorganic impurities to acceptable levels (usually <50 ppm) eliminates kogation due to the impurities. Solving the second cause of kogation, namely dye degradation, has proved more difficult.

A detailed study of azo dyes by Suga *et al.*[17] has shown some interesting structure/kogation/mutagenicity correlations. The major finding is that dyes having good kogation fastness are generally nonmutagenic (Ames negative) and that dyes having poor kogation fastness are generally mutagenic (Ames positive). Kogation fastness worsens as the number of azo groups and/or primary amino groups increases. Dyes having good kogation fastness satisfy two criteria. First, each fragment of the dye molecule contains a water solubilizing group, usually sulfonic acid. This ensures that the dye itself, plus *any* decomposition fragments, are all water soluble. There is no buildup of
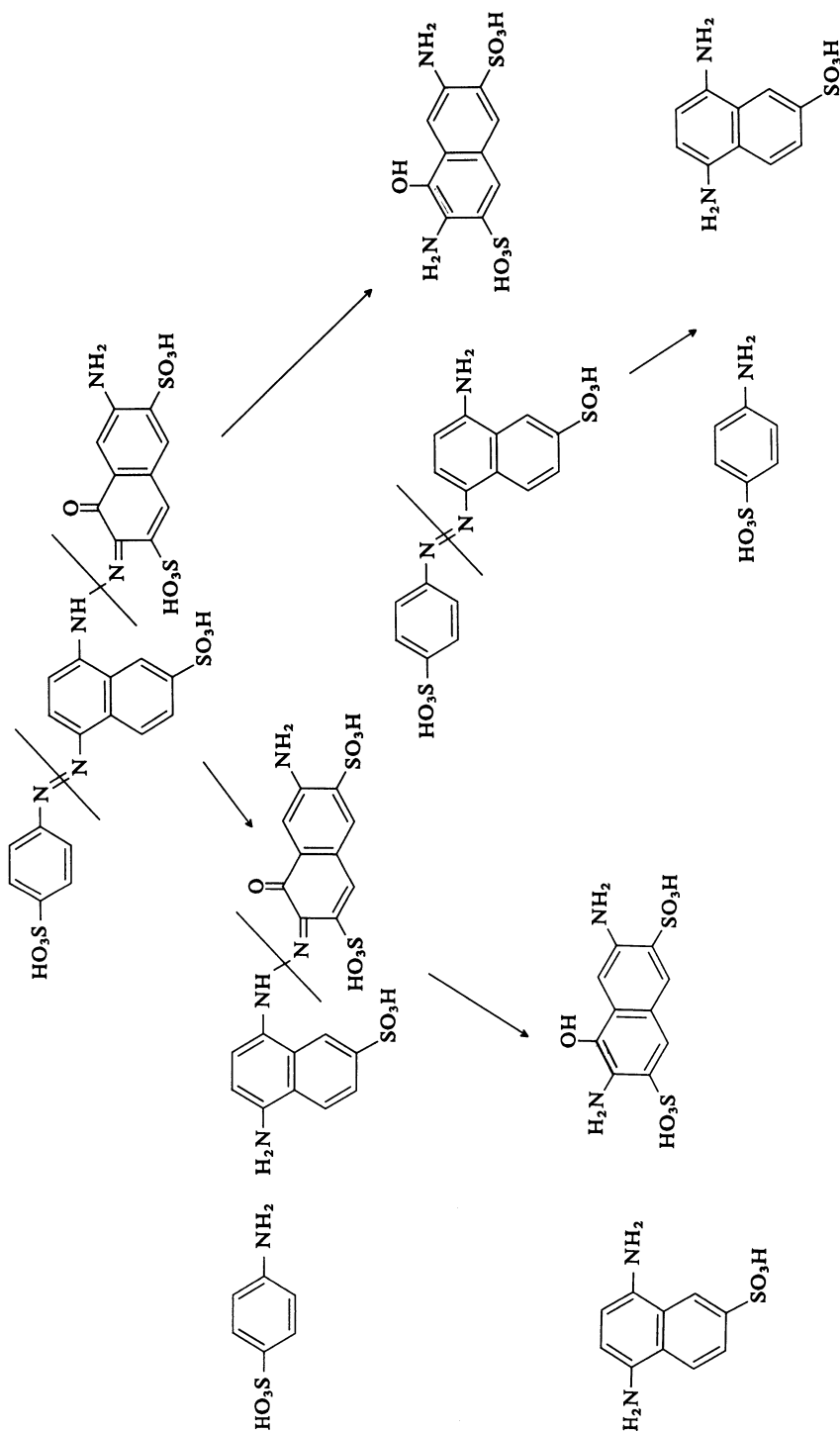
Scheme 9.2. Probable degradation products of CI Food Black 2.

insoluble deposits on the heater. This feature is illustrated in Scheme 9.2. Gregory[18] has shown that the water solubility of the dye and any possible degradation products play a major role in rendering the dye Ames negative. The second criterion is that the dyes should have a minimum of primary amino groups since these are known to trigger mutagenicity.[19] (See *Chapter 12*.)

9.5.2. Dye Types

The dyes used in ink-jet are considered now. In all four shade areas— yellow, magenta, cyan, and black—the dyes fall nicely into two types: dyes for aqueous-based ink-jet systems and dyes for solvent/hot-melt ink-jet systems. Dyes for aqueous ink-jet systems belong to the acid, food, and especially the direct class of dyes. The two main structural types are azo and phthalocyanine. Ink-jet dyes for solvent and hot-melt ink-jet systems are normally of the solvent or disperse type and generally belong to the azo or anthraquinone dye classses.

9.5.3. Black Dyes

Because of the enormous amount of black text, black dyes are by far the most important dyes for ink-jet printers. Water-soluble black dyes for aqueous-based inks are considered first.

9.5.3.1. Water Soluble

All the major water-soluble black ink-jet dyes are polyazos from the acid, food, and especially direct dye classes. In general, existing dyes are used currently but purified to ink-jet standards. Major problems are toxicology (need to be Ames negative), light fastness, and particularly wet fastness and smear fastness. Typical black dyes for nonthermal ink-jet systems are the trisazo dyes CI Direct Black 154 (**9-3**) and CI Direct Black 171 (**9-4**), and especially the tetrakisazo dye CI Direct Black 19 (**9-5**). This tetrakis-

9-3

9-4

9-5
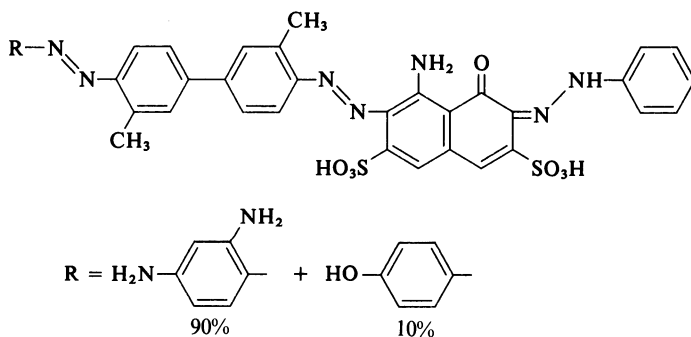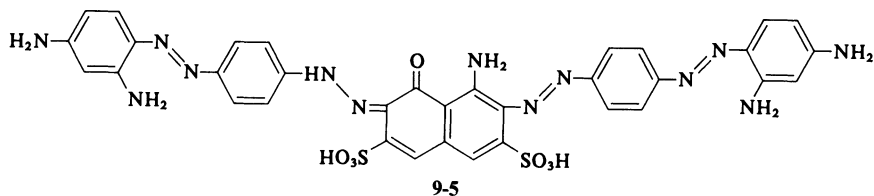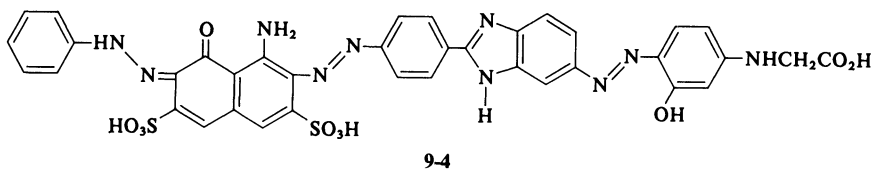
azo dye has good wet fastness combined with reasonable light fastness. A major disadvantage is its mutagenicity. The dye is Ames positive. CI Direct Black 19 is also unsuitable for thermal ink-jet systems since its thermal stability or kogation fastness is insufficient.

The dye currently favored for thermal ink-jet systems such as Canon's Bubble Jet and Hewlett-Packard's Think Jet is CI Food Black 2 (9-6).[10] Being an established food dye it should be safer, and indeed it is nonmutagenic (Ames negative). This disazo dye has good thermal stability (good kogation) but only moderate solubility and poor wet fastness. Making the lithium salt improves the solubility but not the wet fastness. The shade of CI Food Black 2 is also on the blue side, i.e. it is a bluish-black.

9-6
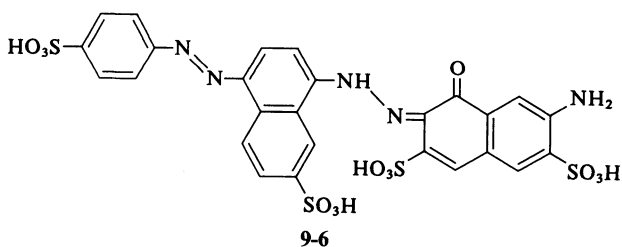
Many analogues of CI Food Black 2 have been made in an attempt to overcome these deficiencies.[20] The carboxylic acid dye (9-7) is typical.

9-7
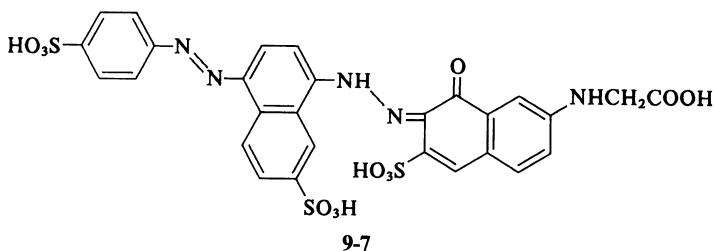
Acid dyes are also being evaluated for aqueous ink-jet systems. Like the food dyes, the acid dyes are generally smaller molecules than the direct dyes. The disazo dye, CI Acid Black 1 (**9-8**), is a representative acid dye.

9-8
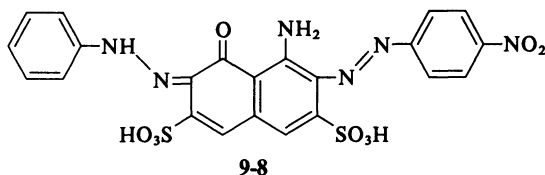
Two dyes that are proving especially valuable for ink-jet printers, both thermal and especially nonthermal, are CI Acid Black 191 and especially CI Direct Black 168. The structures are as yet undisclosed but both are trisazo dyes. The dyes have good light fastness, good solubility, good wet fastness, and good kogation fastness. They are also Ames negative. However, one of
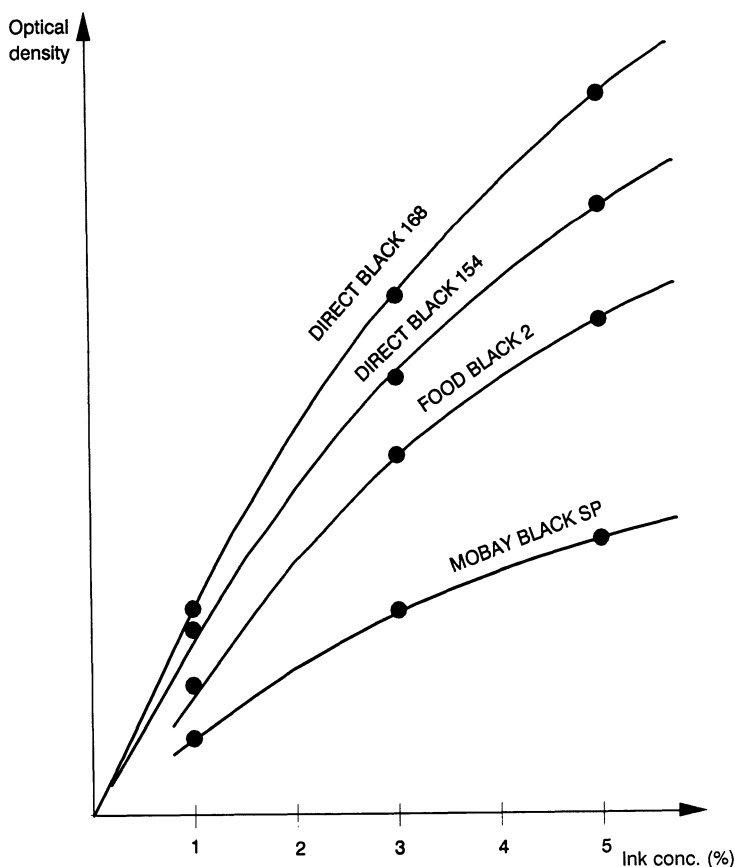
Figure 9.11. Build-up of black dyes in 100% diethylene glycol on plain paper.

Table 9.5. Physical Properties of Direct Black 168 versus Nearest Equivalents for Ink Jet

Dye	Ames status	Ink solubility	Ink stability	Color buildup	Shade	Light fastness	Wet fastness
Direct Black 168 (pure)	−ve	Good	Ongoing	Very good	Neutral to green	Medium	Good
Food Black 2 (pure)	−ve	Good	Good	Good	Blue	Poor	Poor
Direct Black 19 (pure)	+ve	Very poor	?	Good	Blue	Poor	Very good
Direct Black 154 (pure)	−ve	Poor	?	Very good	Neutral to green	Bad	Good
Acid Black 2 (pure)	−ve	Good	?	?	Red	Poor	Medium

the key advantages of these dyes is their inherently high color value which is reflected in high print optical densities. Obviously, this makes them cost effective. Figure 9.11 and Table 9.5 show the relative print optical densities and other important properties of CI Direct Black 168 versus other leading black dyes. Figure 9.12 shows their positions in CieLab color space.

There has also been considerable activity in researching for novel black dyes. One approach adopted has been to covalently link a navy blue dye with an orange dye, using a chlorotriazine as the linking group.[21] The black dye **9-9** is representative of this type.
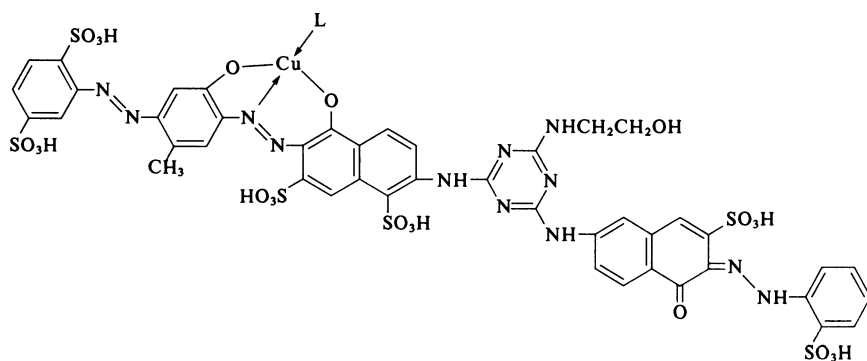
9-9

None of the current dyes is fully satisfactory on plain paper, especially with respect to water fastness and smear fastness, and further research is required to produce better dyes.
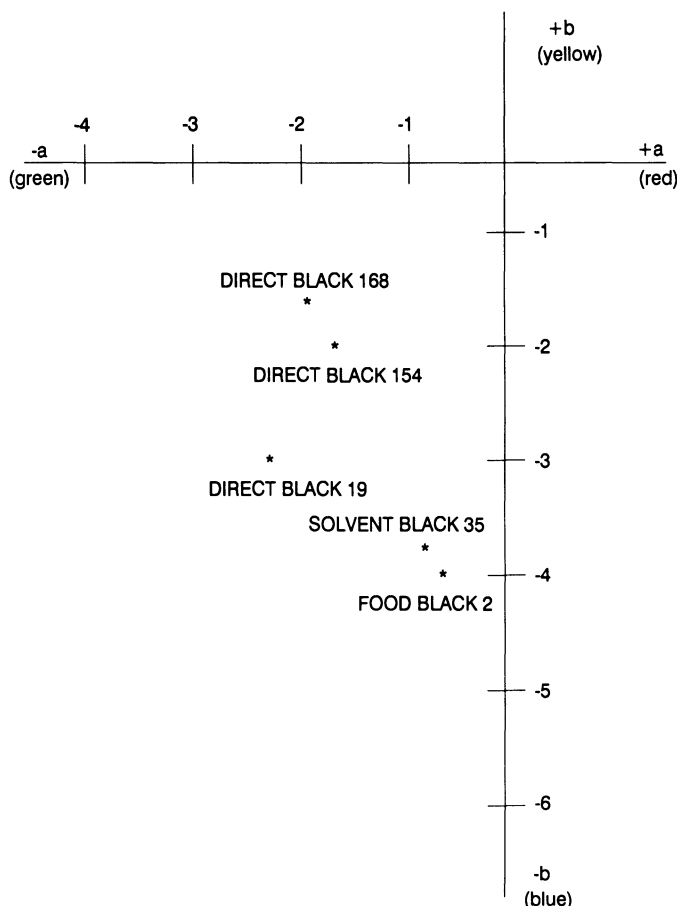
Figure 9.12. Shade descriptions of various ink-jet dye prints at 5% based on the CieLab matrix.

9.5.3.2. Solvent/Resin Soluble

Not surprisingly, these dyes tend to belong to the solvent or, less frequently, disperse dye classes. The most prevalent black dyes are CI Solvent Black 35 and especially CI Solvent Black 29. CI Solvent Black 35 is a 2:1 chromium (III) azo complex dye which is an approximately 50:50 mixture of two isomers (**9-10**). Being a metal complex dye it has good light fastness. It also has good solubility in ketonic solvents such as MEK, although it has poor solubility in alcohols.

CI Solvent Black 29 is a closely related dye which is used extensively in ink-jet systems. In fact, it consists of the same two isomers as in CI Solvent Black 35 but in a different ratio.

9-10
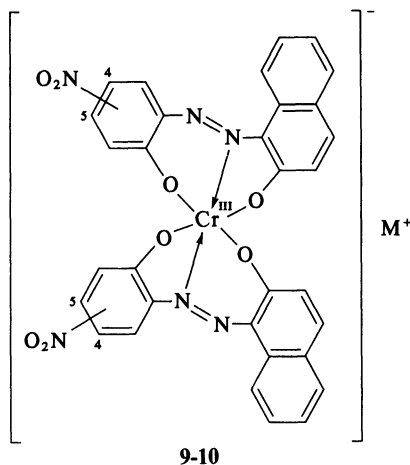
Hot-melt ink-jet printing is a new technology and it is not known which dyes are used, but it is likely that the black dyes are similar to those described above for solvent ink-jet systems.

9.5.4. Yellow Dyes

These are again divided into water-soluble dyes and solvent/resin-soluble dyes.

9.5.4.1. Water Soluble

Many yellow dyes, especially of the direct dye class, have been evaluated for aqueous ink-jet systems, and the industry standard appears to be CI Direct Yellow 86 (**9-11**).[10] This is a disazo dye formed by linking two amino-monoazo dyes with cyanuric chloride and then blanking off the residual chlorine atom with ethanolamine (Scheme 9.3). It has good properties, including kogation fastness, and is therefore suitable for thermal ink-jet systems as well as the piezoelectric systems.

9.5.4.2. Solvent/Resin Soluble

Colored inks based on these systems are in their infancy so it is unclear which dyes are being used. However, it is safe to assume that they will be of the solvent or disperse dye type.

9.5.5. Magenta Dyes

9.5.5.1. Water Soluble

Obtaining a water-soluble magenta dye having the desired color (brightness and hue) combined with good light fastness is proving extremely difficult
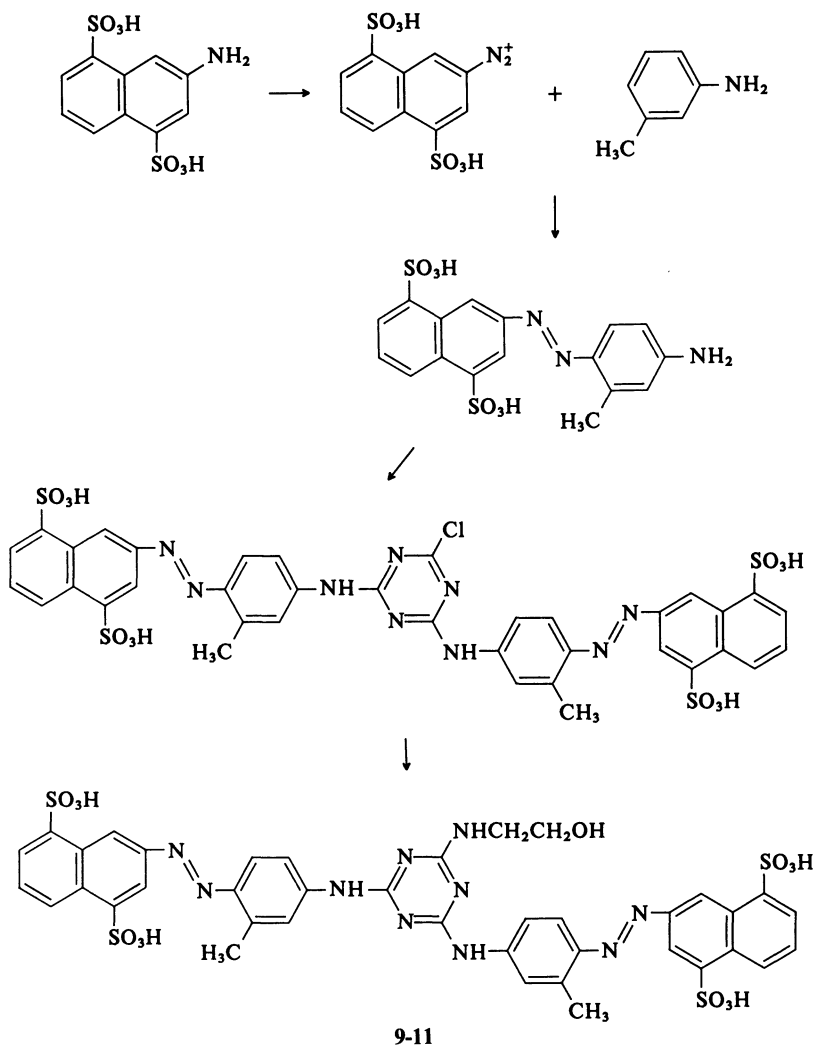
Scheme 9.3. Synthesis of CI Direct Yellow 86.

to achieve. Monoazo dyes derived from H-acid (**9-12**) exhibit the desired magenta color but have poor light fastness. CI Acid Red 35 (**9-13**) is a typical dye (see Scheme 9.4).

Dyes derived from aminonaphthols such as H-acid exist predominantly, if not exclusively, in the hydrazone tautomeric form shown rather than the azo form,[22] and this could be a contributory cause to the poor light fastness exhibited by these dyes.[23] Indeed, one way to obtain magenta dyes having improved light fastness is to couple onto Gamma acid (**9-14**) under acid conditions, so that the coupling takes place *ortho* to the amino group to
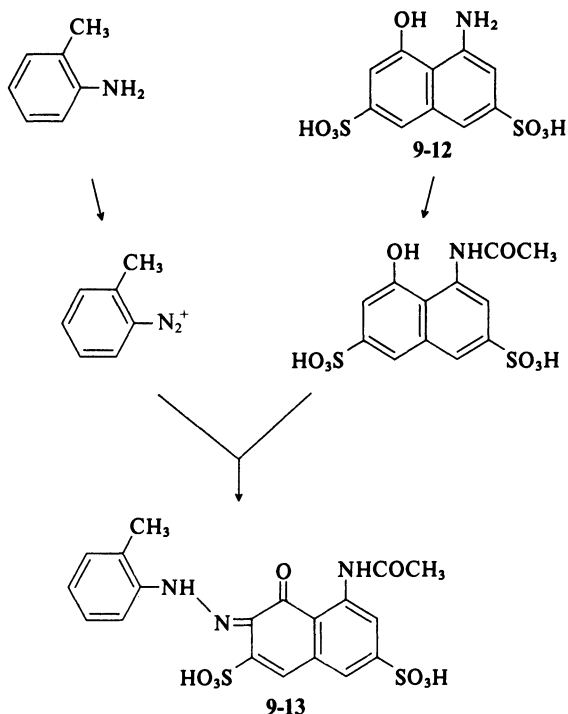
Scheme 9.4. Synthesis of CI Acid Red 35.

produce an aminoazo dye (e.g. **9-15**): such dyes exist in the azo tautomeric form.[24] However, they are duller than the magenta dyes derived from H-acid.
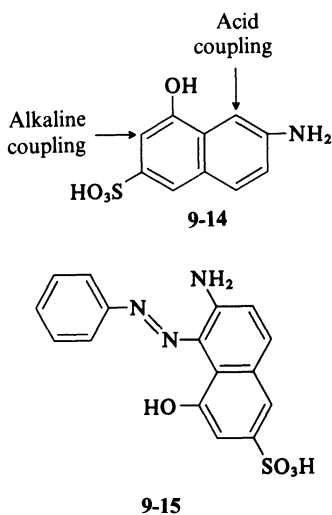
The light fastness can be improved even further by using metal complex azo dyes such as **9-16**. However, this is at the expense of brightness, and, to a lesser extent, solubility.[25,26]

9-16
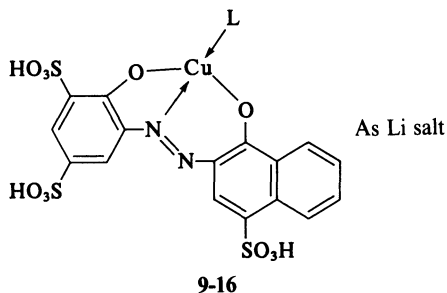
No fully satisfactory magenta dye exists at present. CI Acid Red 249 (**9-17**) is one of the better magenta dyes. Being derived from H-acid, this dye has a very attractive magenta color. It has relatively good light fastness for an H-acid dye, although in absolute terms the light fastness is at best moderate.

9-17
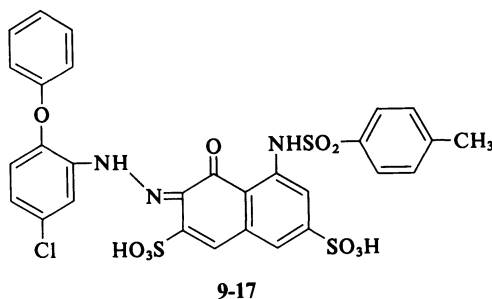
Canon has resorted to synthesizing a novel magenta dye to alleviate the problem. A recent patent[27] suggests it is a monoazo dye of structure **9-18** and, if so, it exhibits surprisingly good light fastness for a magenta dye derived from H-acid.

9-18
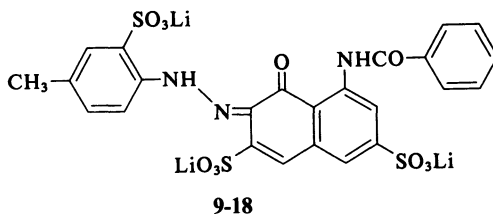
9.5.5.2. Solvent/Resin Soluble

The market for magenta solvent soluble ink-jet dyes is currently very small, and the full-color, hot-melt, ink-jet market has yet to materialize. Consequently, there are no established products for these applications. However, it is likely that the dyes will be of either the solvent type or the disperse type. Likely candidates will be anthraquinones such as CI Disperse Red 60 (**9-19**) and the related anthrapyridone dye, CI Solvent Red 52 (**9-20**).

9-19   9-20
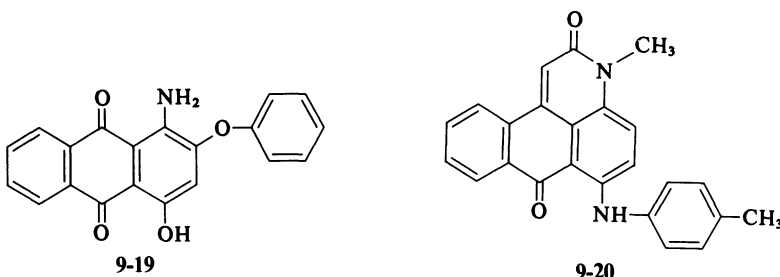
9.5.6. Cyan Dyes

The water-soluble cyan dyes are invariably copper phthalocyanines whereas the solvent/resin soluble are generally anthraquinones.

9.5.6.1. Water Soluble

Copper phthalocyanines represent the pinnacle of cyan dyes and pigments, since they are probably the brightest, strongest, and most stable of all the colorants used today. Therefore, it is hardly surprising that sulfonated derivatives of copper phthalocyanine are the industry standard water-soluble cyan ink-jet dyes, both for piezoelectric systems and thermal systems. The most popular dye is CI Direct Blue 199 (**9-21**). This dye is nominally given the constitution shown but it is, in fact, a mixture of more than one component. CI Direct Blue 199 gives an excellent shade and has good strength, light fastness, and wet fastness. Highly purified brands also have good kogation. The related cyan dye, CI Direct Blue 86 (**9-22**), is also used.[27]

$$CuPc(SO_3H)_2(SO_2NH_2) \qquad CuPc(SO_3H)_2$$
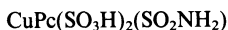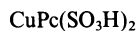
9-21   **9-22**

CuPc = Copper phthalocyanine

9.5.6.2. Solvent/Resin Soluble

The same comment applies as for the yellow and magenta area, namely that there is no significant color market as yet for either solvent or hot-melt

ink-jet. Hence, it is not possible to discuss leading dyes for these applications. However, likely dyes will again emerge in the solvent or disperse dye classes. In contrast to the water-soluble cyan dyes, where copper phthalocyanines reign supreme, it is probable that dye types other than phthalocyanines will also play an important role in providing suitable cyan dyes for solvent and hot-melt ink-jet systems (e.g. azo dyes, indoaniline dyes, and especially anthraquinone dyes). Indeed, anthraquinone dyes such as CI Solvent Blue 36 (**9-23**) are being evaluated in these systems, but this particular dye is probably too red in shade for a true cyan.
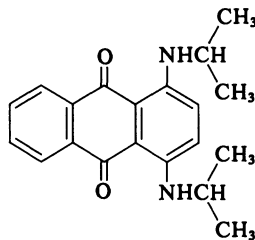
9-23

9.6. APPLICATIONS OF INK-JET PRINTING

Ink-jet printing can be classified into three main application areas as shown in Fig. 9.13. As seen from the figure, the volume decreases in going from industrial through critical industrial to hi-tech but the dye cost (and dye purity) increases.

Industrial ink-jet printing covers the printing of large format areas such as textiles, wall coverings, and advertising displays. Ink-jet printing of carpets and carpet tiles is already done with involvement from companies such as Millikon, with their computerized Millitron Jet Printer. This is a continuous ink-jet system and uses standard commercial quality dyes. Novel or specially purified dyes are not required. Widths of up to 5 m can be printed with a resolution of 10–20 dots per inch. Ink-jet printing of wallcoverings and
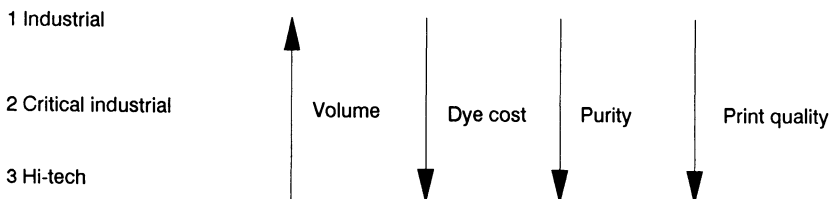
Figure 9.13. Ink-jet printing by application area.

Table 9.6. Worldwide Split of Ink-Jet Inks
by Solvent Type

Solvent	%
Water/Glycol	25
MEK	50
Alcohol (ethanol/n-propanol)	25

posters is still at the prototype production stage, with companies such as Stork X-Cel and Nairn being the pioneers. The larger nozzle size (and hence lower resolution) of industrial ink-jet machines enable pigments as well as dyes to be used in these systems.

The critical industrial area requires dyes of a higher purity than standard commercial dyes but not to the exacting standards needed for hi-tech applications. Uses include the labeling of cardboard (boxes), metal and plastic containers, and industrial components, and the mass marking of mail. Companies involved include Diagraph and Image. Black is the predominant color and both aqueous and solvent inks are employed, although carbon black dispersions are also used. The leading black for aqueous inks is Mobay Black SP Liquid. This is a three-component mixture of a yellow, a red, and a navy blue dye. CI Solvent Black 29 is the leading black for solvent-based inks. The probable split of solvents used worldwide is shown in Table 9.6. The resolution required for the critical industrial area is higher than that for the industrial application but lower than that for the hi-tech application.

The hi-tech area is for office printing where near letter quality text and high quality graphics are required. Indeed, the new machines such as Hewlett-Packard's Desk Jet Printer with a resolution of 300 dots per inch produces letter quality text.[28] Black is again the major color although full-color is becoming more important. The drop-on-demand systems predominate, particularly the thermal ink-jets (Canon's Bubble Jet and Hewlett-Packard's Think Jet). Both use aqueous based inks.

This hi-tech area is the one we have concentrated upon in this chapter and there is little doubt that ink-jet printing has a major role to play in the office of today and especially tomorrow.

9.7. SUMMARY

Ink-jet printing is hardly a new technology but the rapid advances made in the last few years have elevated it into one of the three major reprographics technologies.

Ink-jet printing is conveniently divided into two types: continuous and drop-on-demand. Continuous ink-jet printing employs the selective deflec-

tion of electrically charged droplets to produce an image. In contrast, drop-on-demand ink-jet printing uses uncharged ink droplets which are only produced where they are required to form an image. Drop-on-demand systems may be subdivided further into piezo, which also includes the more recent hot-melt ink-jet, and thermal, or bubble, jet.

Dyes rather than pigments are used in ink-jet printing, particularly in hi-tech applications, where high resolution equates to small nozzle diameters. Highly pure dyes are required for these hi-tech applications. These dyes may be existing dyes, but in a highly purified state, or novel dyes. Water-soluble dyes are required for the aqueous-based ink systems. These are normally of the acid, direct, or food classes and are predominantly azo or phthalocyanine. Solvent-soluble dyes are required for the solvent or resin (hot melt) systems. Black is the major color, although full-color ink-jet printing, which requires yellow, magenta, and cyan dyes, is gaining in importance.

Ink-jet printing is a truly noncontact, versatile, direct imaging method (cf. thermal and electrophotographic techniques) which is ideally suited to either monochrome printing or full-color printing onto (plain) paper. It will be a serious contender for the nonimpact printing market, alongside the thermal and electrophotographic technologies.

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10

Electrography, Ionography, and Magnetography

10.1. INTRODUCTION

Electrography, ionography, and magnetography are three other non-impact printing technologies. They are younger technologies and are currently less prevalent in the marketplace than the electrophotographic, ink-jet and thermal technologies. However, they possess some advantages and could well become more important in the future.

10.2. ELECTROGRAPHY

In electrographic (also called electrostatic) printing a latent electrostatic image is created on a dielectric (insulating) surface, usually special paper or film, and the image made visible by applying the toner.[1,2] The process is very simple and comprises just three steps:

1. Creating the electrostatic image. This is achieved by using a writing head consisting of an array of stylii. Applying a voltage to selected stylii produces ions which are deposited onto the dielectric paper or film.
2. The latent electrostatic image is developed with a liquid toner of opposite charge to the latent image. The small size of the particles in liquid toners enables high resolutions to be obtained (up to 400 dpi).
3. The toner is then fused to the paper or film.

The process is illustrated in Fig. 10.1.

Writing head

1. Write charged image   Dielectric paper
                                                                     (or film)

2. Develop with toner

3. Fuse
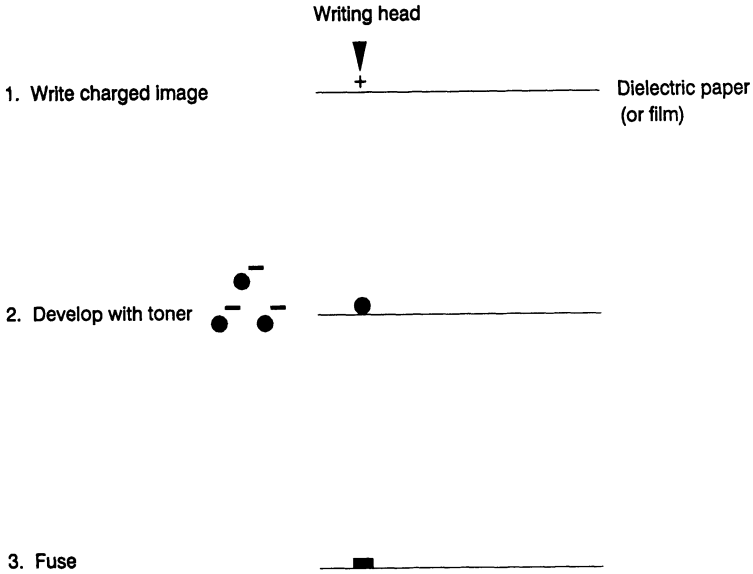
Figure 10.1. Electrostatic printing process.

Electrostatic printing is good for large format images, either mono-
chrome or color. Monochrome printing is the simplest and the fastest, since
it requires just a single pass. Full-color printing is more complex since four
colors are required to produce a full-color image, namely yellow, magenta,
cyan, and black. This colored image may be achieved by using a single toning
station and repeating the process four times. Registration of the paper prior
to each pass is important to ensure a high quality image. This is difficult
since paper isn't dimensionally stable and therefore the transport mechanism
must compensate for shrinkage and stretching of the paper. Nonetheless,
Versatec uses the multipass system in their electrostatic plotters.[2] Figure 10.2
shows a typical electrostatic plotter.

Back Plate Electrode   3 Toner Channels   Drying Channel

                                                              Paper

Writing Head

Toner In   Toner Return

        Toner Applicator
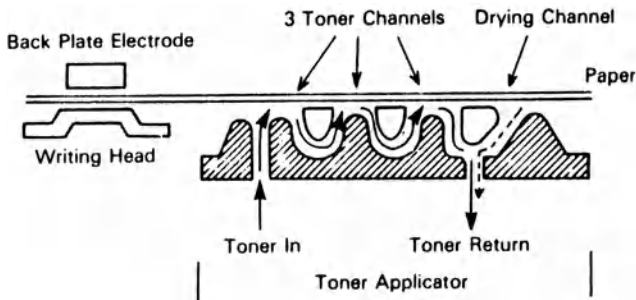
Figure 10.2. Electrographic printer (based on Versatec V80).

An alternative approach used by both Benson and Synergy is to use a single pass but with four toning stations rather than one. This approach has fewer registration problems but is slower, since the paper plus toner must be dry before the next toner is deposited.[2]

Precision Image Corp. uses a helical scanning technique to overcome the registration problem. This technique involves holding the dielectric paper or film onto a drum by vacuum and writing the electrostatic image with a helical scanning head. A single toning cup follows the scanning head and deposits liquid toner. A separate reservoir contains cleaning fluid for flushing the toning cup between color passes.[2]

10.3. IONOGRAPHY

Ionography,[3-5] also known as ion deposition, is a young technology. It was developed by Dennison and has been pioneered by Delphax, now 50% owned by Xerox. It was first used for bar code applications in the mid-1970s but is now used for many other applications including printing tickets, labels, bills, and checks.[6]

Ion deposition printing uses a simple four step process. Step 1 consists of generating an electrostatic image on the surface of a dielectric drum. In step 2 the image is developed on that surface by applying toner to make it visible. Step 3 is the transfix step in which the toner is transferred and fixed to paper. Finally, in step 4, the surfaces are cleaned ready for the next cycle (Fig. 10.3). Figure 10.4 shows the actual set up in a typical ion deposition printer.

The first step, the generation of the image, is accomplished using a print cartridge which deposits a pattern of ions on the dielectric drum surface. The ions are generated via high-voltage radio frequency drive lines which ionize the air in the tiny chambers (Fig. 10.5). Release of the ions is controlled electronically via a system of control electrodes which allows the creation of specific patterns of spots.[5,6]

The dielectric drum is an aluminum cylinder with an extremely hard and smooth anodized outer surface which is specifically treated to hold the deposited ions in position. It can be handled without fear of damage, unlike photoconductor drums. The hardness of the drum is significant because cold pressure rather than heat is used to fix the toner, usually a single component toner, onto the paper. Greater than 99% toner fixation onto the paper is achieved, and hence little cleaning is required and the toner usage is low. For comparison, the toner transfer efficiency in electrophotography is 70%–80%. Good capabilities exist with ion deposition both for gray scale and color.

Ion deposition printers are very rugged, very fast (120 ppm), and

1. Write

2. Develop

3. Transfix

4. Clean
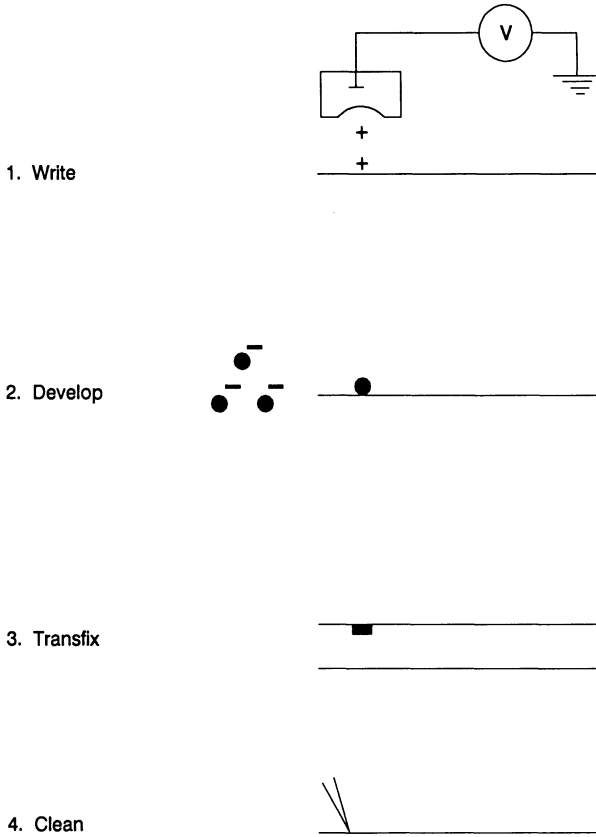
Figure 10.3. Ion deposition printing process.
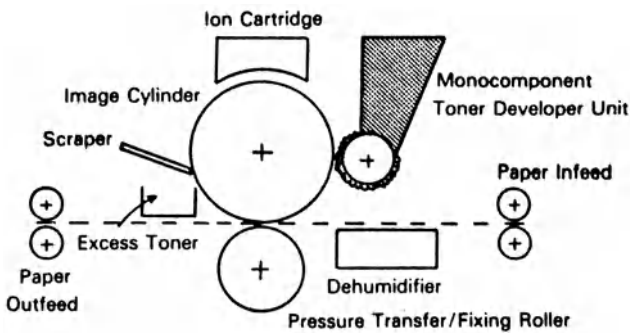
Figure 10.4. Ion deposition type (Delphax) nonimpact printer.
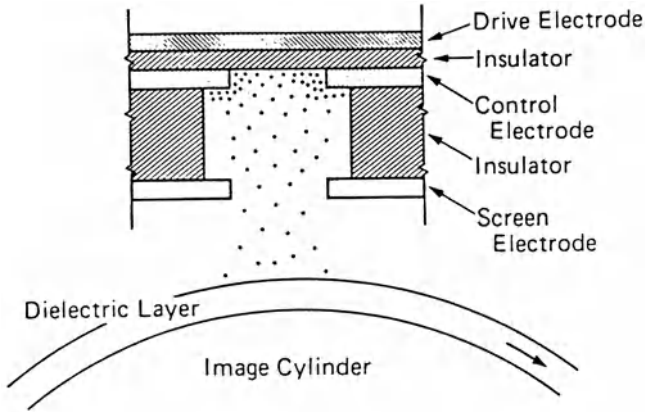
Figure 10.5. Ionographic printhead, as used in Delphax printers.

reliable. Delphax and Denison guarantee the print cartridge for 125,000 pages and the drum for 1.25 million copies. This figure is in striking contrast with the 10,000 copies per lifetime of an organic photoconductor drum.

The main area for improvement is toner fixation to the paper. Cold pressure, though it uses less energy, is not as efficient as heat fusing the toner onto paper. Additionally, it imparts a sheen to the toner and paper which is undesirable in some applications.

The quality of ion deposition is not yet equal to that of laser printing. However, the simpler process and durability of ion deposition printers make them serious contenders for a share of the printing market of the future.

10.4. MAGNETOGRAPHY

Like electrophotography, electrography, and ion deposition, magnetography is also a toner-based technology. However, in contrast to these technologies, magnetography utilizes magnetic rather than electrostatic forces to produce an image.

In magnetography a magnetizable alloy (e.g. cobalt alloy) or metal oxide (e.g. gamma-Fe_2O_3) dispersed in an organic binder is used as the imaging surface. This is selectively magnetized by a magnetic writing head, similar to that in a tape recorder, to produce the latent magnetic image on the drum. As in the electrophotographic and electrostatic processes, the image is rendered visible by development with a toner, in this case a magnetic toner. The toner is transferred from the magnetic drum to paper using a corona transfer. Finally, the toner is fixed using heat and/or pressure. Figure 10.6 shows a typical magnetographic printer.
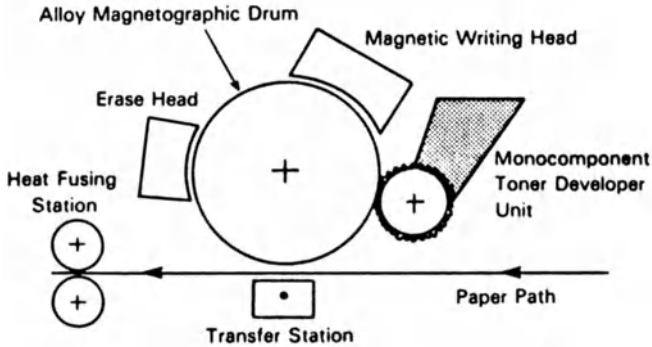
Figure 10.6. Magnetographic nonimpact printer.

The advantages of magnetography include multiple prints from a single image and potentially very high printing speeds, for example, 500–800 ppm. Disadvantages include limited resolution (due to the design of the magnetic writing head) and the tendency of the drums to corrode, especially in humid environments, although Bull claims a drum lifetime of 10 million copies.[7]

10.5. SUMMARY

Like electrophotographic copying and printing, electrography, ion deposition, and magnetography are toner-based technologies. However, unlike electrophotography, electrography and ion deposition utilize only electricity, not electricity and light, to produce an image. As the name implies, magnetography utilizes magnetism to produce an image. All three technologies are simpler than electrophotography and offer some advantages, although there are also some disadvantages.

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IV

Future Perspectives

Infrared absorbing chemicals is another area of growing importance in both the electronics and reprographics fields and a chapter is therefore devoted to this topic. The toxicological aspect of chemicals, especially dyes and pigments and the intermediates used to make them, is also of paramount importance and this topic is considered with regard to organic colorants. Finally, there is a brief chapter in which the pros and cons of the various technologies are reviewed and future trends predicted.

11

Infrared Absorbers

11.1. INTRODUCTION

Infrared absorbers absorb infrared radiation. Therefore, it is prudent to consider first the nature of infrared radiation, its properties, and where it lies in the electromagnetic spectrum.

The infrared region of the electromagnetic spectrum lies between the visible region and the microwave region. Infrared radiation is normally considered as comprising the wavelengths from 700 to 10,000 nm which can be subdivided into the near, medium, and far infrared regions[1] (Fig. 11.1). Since energy is inversely proportional to the wavelength of electromagnetic radiation (Eq. 11.1), infrared radiation has lower energy than either ultraviolet or visible radiation. It has a maximum energy of 40 kcal mole^{-1} at 700 nm falling to 0.3 kcal mole^{-1} at 10,000 nm. This level of energy is insufficient to break organic single, double, or even triple bonds (Fig. 11.1) but certain ionic reactions may be possible such as the deprotonation of the ammonium ion[2] (Eq. 11.2).

$$E = h\nu \qquad (11.1)$$
$$= \frac{hc}{\lambda}$$

where E = Energy
h = Planck's constant
ν = frequency
λ = wavelength

$$NH_4^+ \rightarrow NH_3 + H^+ \qquad (11.2)$$

The energies of ca 10–1 kcal mole^{-1} associated with the medium infrared region are of the right order to cause the vibrational changes in organic

Electronic transitions ——— | ——— Vibrational ———

LASERS

He-Cd	Argon ion	He-Ne	Semiconductor	Nd/YAG	OH	NH	CH	CN	CO	CO₂
325	488 514	632.8	Ga Al As	1060	2857	2950	3333	4444	5882	10000
			780 830							

No radiation
<290 nm
reaches the
Earth's surface

LEDs

Silicon (~900-950) detectors

Near ir   Medium ir   Far ir

Sunlight spectrum

visible

uv   Blue   Green   Red

λ (nm)   290 300 400   700   1000 2000 3000 4000 5000 6000
(For micron, divide by 1000)

Energy
(Kcal mole⁻¹)   98.6   71.5   40.9   27   10   4.9
                                                    (1060)   (2857nm)   (5882nm)

Temperature   ~900-1000°C   ~640°C
(Black body)

BE's

C-C 83.2	N=N 98
C=C 146.4	C=O 178
C-H 98.6	C-Cl 81
C-N 73	C-Br 66
C-O 86	O-H 110.8
C-S 87.6	N-H 92.8

Figure 11.1. Some useful spectroscopic data.
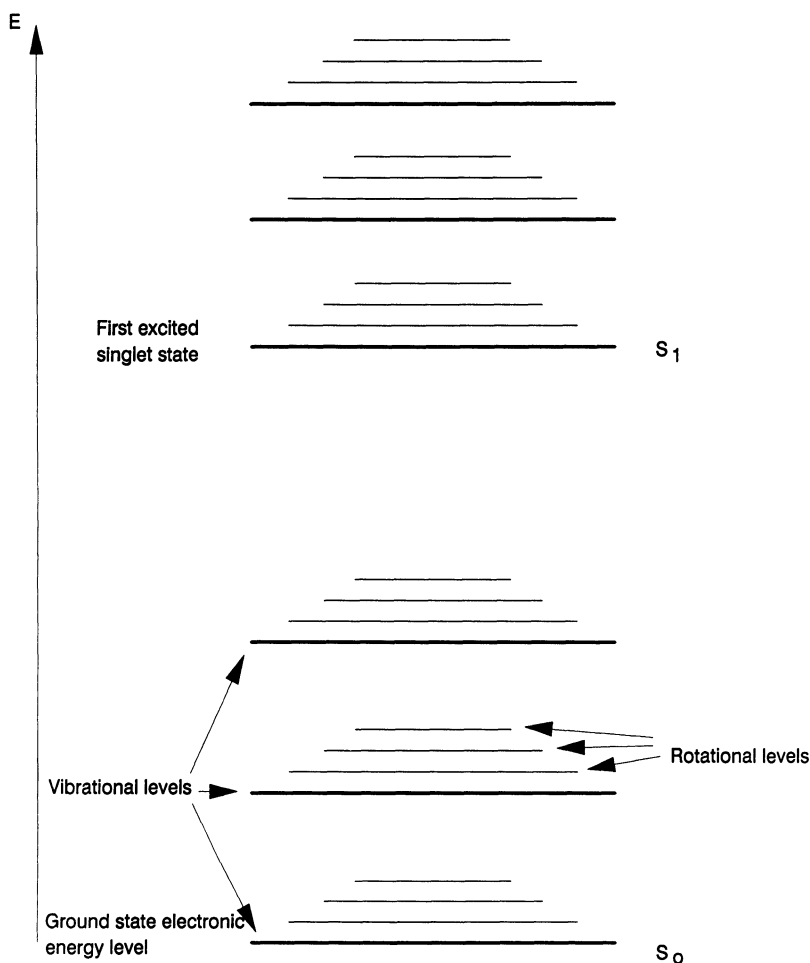
Figure 11.2. Electronic, vibrational, and rotational energy levels of organic molecules.

molecules. These vibrational changes produce the familiar infrared spectra of organic molecules used for characterization purposes. The absorptions of some common groups in infrared spectroscopy are shown in Fig. 11.1. The rotational changes of molecules require even less energy than the vibrational changes and correspond to the microwave region of the electromagnetic spectrum (Fig. 11.2).

For the purpose of this chapter it is the near infrared region that is important. This covers the wavelengths from 700 to 2000 nm, with the 750–1300 nm region being particularly important. It is in this region that the infrared radiation still possesses sufficient energy to cause pi-pi* electronic transitions in organic molecules, i.e. $S_0 - S_1$ in Fig. 11.2, and thereby absorb

Table 11.1. Applications of Infrared Absorbers

Classification	Effect	Application

Heat-ray blocking	Broad absorption of near infrared radiation to block out the heat	Solar screening
		   Car windscreens
		   Architectural glass
		   Agricultural film
		Safety glasses

Energy conversion	Absorption of near infrared radiation (both electromagnetic and laser) to generate heat	Thermal imaging: direct, transfer (specific absorption matched to laser used–typically a Nd-YAG) Flash fusion of (colored) toners (broad absorption for xenon flash) Solar heating (broad) Optical data storage (specific absorption matched to semiconductor laser)
Optical	Selective absorption of near infrared radiation, which can be laser radiation	Optical data storage Automatic identification (bar codes) Organic photoconductors

strongly the infrared radiation. Molecules that undergo these pi-pi* transitions are termed infrared absorbers. At wavelengths greater than 2000 nm, the higher energy vibrational transitions start to occur, such as those of the OH and NH groups (Fig. 11.1). One of the major reasons for the importance of the near infrared region is that it is the region in which the new generation of lasers, namely the semiconductor lasers such as the gallium-aluminum-arsenide (GaAlAs) lasers, emit. Also, it is the region where silicon detectors have peak sensitivity (Fig. 11.1).

11.2. EFFECTS OF INFRARED ABSORBERS

Infrared radiation produces heat when absorbed. Infrared absorbers are being designed (a) to block out this heat (heat ray blockers) and (b) to utilize this heat (energy conversion). Also, the fact that infrared radiation is still electromagnetic radiation is utilized (optical effects) (Table 11.1). Only the electronic and reprographic applications of infrared absorbers are considered in any detail in this chapter.

11.3. CLASSIFICATION OF INFRARED ABSORBERS

The major structural types of organic molecules that absorb near infrared radiation are shown in Table 11.2. Some of these are old, established

Table 11.2. Classification by Structure of Near
Infrared Absorbers

Nitroso
Cyanine
Nigrosine
Triphenylmethane
Imminium and diimminium
Squarilium and croconium
Nickel dithiolenes and related compounds
Quinone
Phthalocyanine
Azo
Indoaniline
Donor–acceptor molecules
Others
Sulfur dyes
Vat dyes

dyes whose absorption bands just happen to extend into the near infrared. Examples are nitroso dyes, cyanine dyes, and nigrosine dyes. The other infrared absorbers have generally been designed to absorb near infrared radiation, even though the basic structural types have, in some cases, been known for many years. Modern theoretical techniques such as molecular orbital calculations have been used to help design infrared absorbers.[3,4]

11.3.1. Nitroso
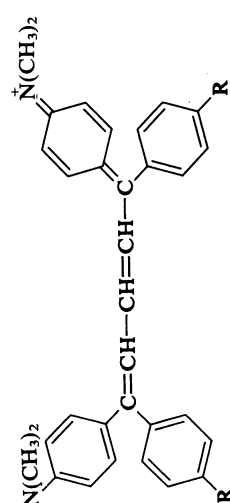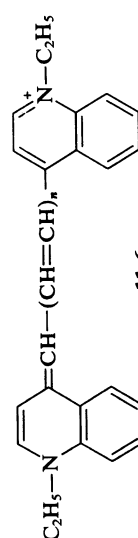
Nitroso dyes have been known for many years. The commercially important ones are the iron complexes of nitrosonaphthols such as Cl Acid Green 1 (**11-1**).[5] Although their tinctorial strength is relatively low (ε_{max} 10,000), they are inexpensive. Their main absorption occurs at ca 750 nm and tails off into the near infrared (Fig. 11.3).

11-1
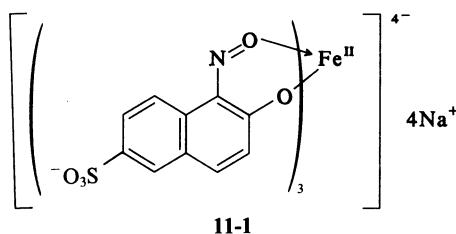
11.3.2. Cyanines

Cyanine dyes have been known for a long time and there has been extensive research into infrared cyanine dyes as sensitizers in photography.[3]

Table 11.3. Cyanine Infrared Absorbers

Structural formula		λ_{max} (Solvent)	ε_{max}
$(CH_3)_2N-(CH=CH)_3-CH=\overset{+}{N}(CH_3)_2$ **11-2**	ClO_4^-	735 nm (Dichloromethane)	353,000
11-3 $(CH_3)_2N-[\text{phenyl}]-(CH=CH)_n-CH=[\text{ring}]=\overset{+}{N}(CH_3)_2$	$n=2$ $n=3$	790 883 (Acetic acid)	
11-4 (diaryl structure with $N(CH_3)_2$ and R groups)	(PMMA) R = H (TPMP) R = $N(CH_3)_2$	833 810	208,000 183,000
11-5 (bis-quinoline, C_2H_5, $-CH-(CH=CH)_n-$)	$n=2$ $n=3$	708 818	
11-6 (bis-quinoline, C_2H_5, $-CH-(CH=CH)_n-$)	$n=1$ $n=2$	704 810	

11-7

ClO_4^-
I^-

773
758

210,000

11-8

ClO_4^-

755
(Ethanol)

240,000

11-9

$R = R' = CH_3$
$R = (CH_2)_4SO_3Na$
$R' = (CH_2)_4SO_3^-$

782 (Ethanol)
795 (DMSO)

188,000
196,000

11-10

ClO_4^-

787
(Dichloromethane)

340,000

Table 11.3. (Continued)

Structural formula		λ_{max}(Solvent)	ε_{max}
11-11	ClO_4^- (IR-140)	823 (DMSO)	156,000
Azulenium compounds			
11-12	I^-	728 (Dichloromethane)	169,000

Pyrilium and thiapyrilium compounds
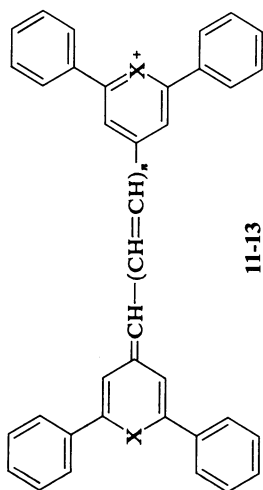
$n=1$	$X=S$	755
$n=2$	$X=S$	879
$n=2$	$X=O$	798
$n=2$	$X=N{-}C_2H_5$	748
		(Nitromethane)

11-13

11-14
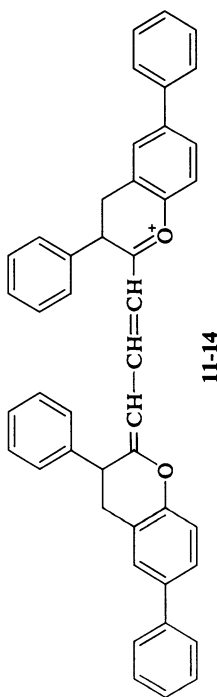
749
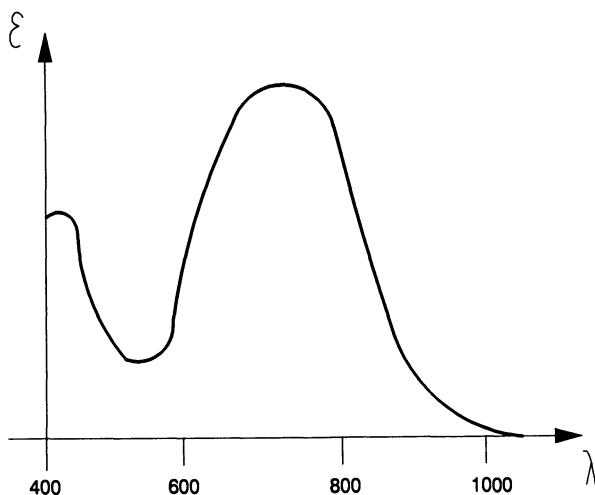
Figure 11.3. Absorption curve of CI Acid Green 1 in water.

Of all the dye classes the cyanine dyes are the easiest to push into the infrared, simply by extending the conjugation (adding more double bonds to the conjugated chain). Normally at least five double bonds are needed between the nitrogen atoms at the termini of the conjugated chain to shift the absorption into the near infrared, as shown in Fig. 11.4. The extinction coefficients of cyanine dyes are high and initially increase with increasing chain length (up to 250,000). However, as the chain becomes longer (e.g. $n = 4$ and especially $n = 5$), the extinction coefficient drops dramatically and this is accompanied by a flattening of the absorption curve. As seen from
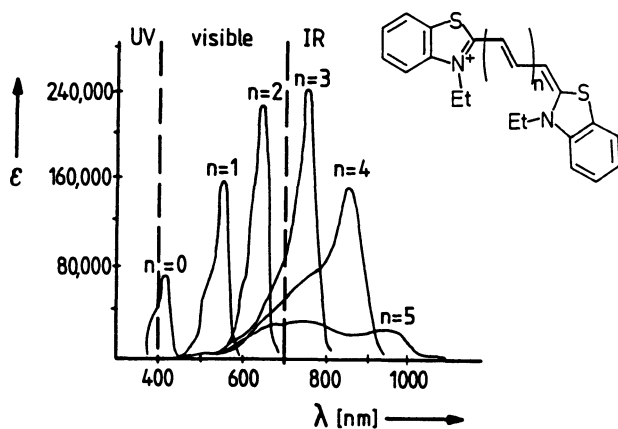
Figure 11.4. Absorption spectra for symmetrical cyanine dyes.

Fig. 11.4, this causes some absorption in the visible region of the spectrum making it unlikely that a colorless cyanine infrared absorber will be found. Cyanine dyes, having optimum near infrared absorption, generally contain between five and seven double bonds in the conjugated chain, for example, $n = 3$ (five double bonds) and $n = 4$ (six double bonds) in Fig. 11.4. Examples of cyanine infrared absorbers are shown in Table 11.3.[3]

As seen from Table 11.3, cyanine infrared absorbers generally absorb in the region of 700–900 nm. However, this can extend to 1100 nm if a more rigid end group such as thiapyrilium is used.

As in the case with conventional cyanine dyes, stability is a major problem. Cyanine infrared absorbers have poor stability, especially to light, although this is improved if oxygen is excluded.[3]

11.3.3. Nigrosines

Nigrosines are an old class of cationic dyes used for providing cheap black solvent and acid dyes. Chemically they are mixtures of highly arylated phenazines of structure **11-15**.
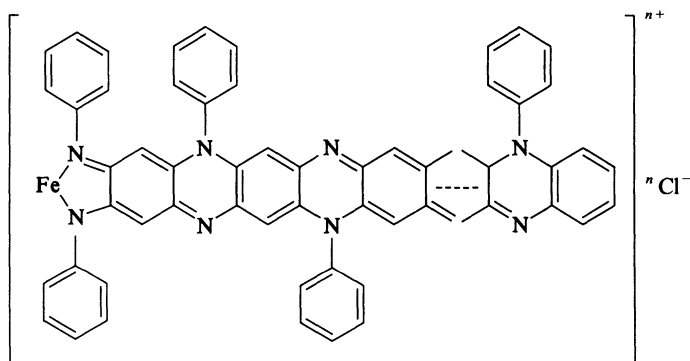
11-15

The fact that nigrosines are a mixture of chemicals of indeterminate constitution, some of which are suspect mutagens, detracts from their usefulness.

11.3.4. Triphenylmethanes

Triphenylmethane dyes are also an old class of cationic dyes. They normally provide red, blue, and green dyes such as Fuchsine, Crystal Violet (really a blue), and Malachite Green. Two techniques have been applied to extend the absorption into the near infrared. The first of these is to make the molecule more planar: this is achieved by using fluorene derivatives so that two of the phenyl rings are held coplanar by a bridging bond. Typical

structures are **11-16** and **11-17**.[3] The latter is an infrared color former used in carbonless paper (see *Chapter 8, Section 3*).
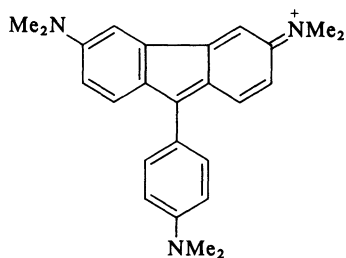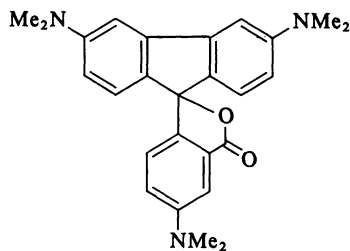
11-16   **11-17** λ_{max} 625 and 850 nm (in a thermal paper)

The second technique is to extend the conjugation. This has been achieved by inserting extra double bonds into the triphenylmethane structure, as in **11-18** and **11-19**[3] and by inserting extra phenyl rings, as in structure **11-20** (see *Chapter 8, Section 3*).
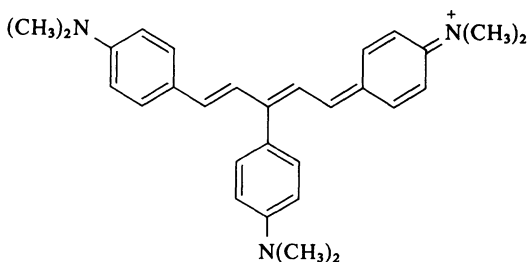
11-18 (Acetic acid) λ_{max} 770 nm
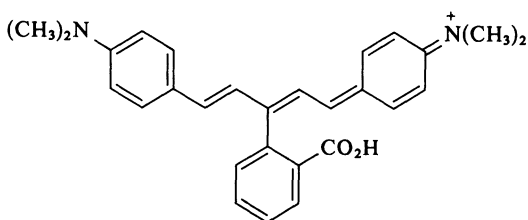
11-19 λ_{max} 850 nm

In general, triphenylmethanes absorb up to 950 nm but, like the cyanines, they are colored due to the presence of other bands in the visible region of the spectrum. The triphenylmethane infrared absorbers are significantly

more stable (ca. 100 times) than the cyanines but, even so, have no better stability than conventional triphenylmethane dyes.

11-20 Colorless

Green/black with near infrared absorption (λ_{max} 680 and 875 nm)
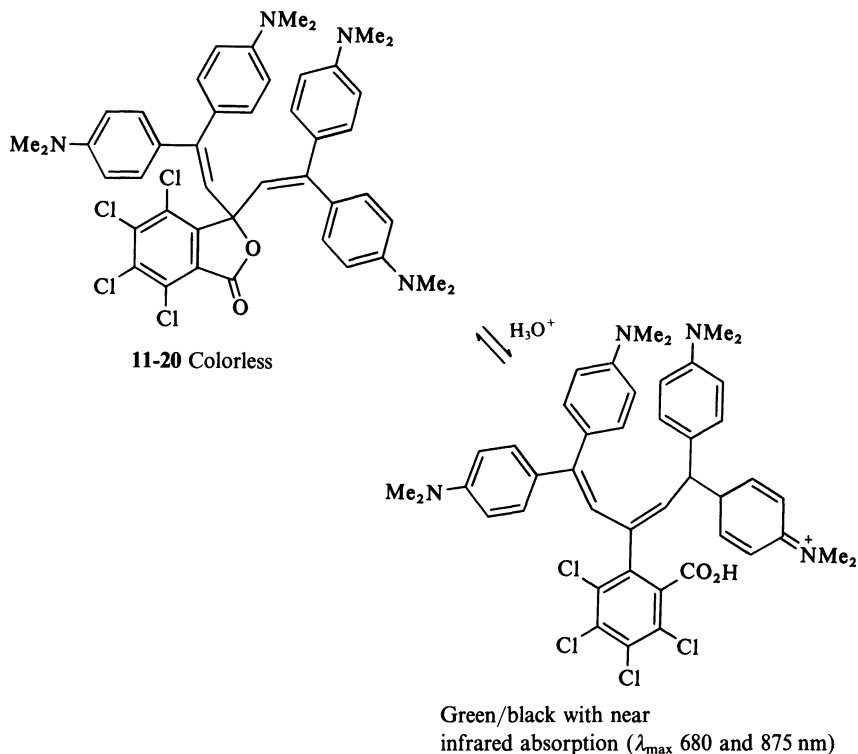
11.3.5. Immimium and Diimminium

The arylimminium and diimminium cations are based upon Bindschleder's Green (**11-21**), which absorbs at 725 nm in water. Addition

11-21 λ_{max} 725 nm
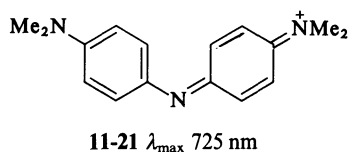
of a further dialkylaminophenyl ring produces the radical cation (**11-22**) which absorbs at 920 nm. The diarylimminium cation (**11-23**) absorbs at 1090 nm.[3]

The compounds usually have antimony hexafluoride (SbF_6^-) anions, which may be related to the synthetic method, stability, or solubility factors.

Me$_2$N — [ring] — [ring] — NMe$_2$

$\overset{+\cdot}{N}$

SbF$_6^-$

[ring]

NMe$_2$

11-22 Imminium λ_{max} 920 nm

(C$_4$H$_9$)$_2$N — [ring] — [ring] — N(C$_4$H$_9$)$_2$

$\overset{+}{N}$ — [ring] — $\overset{+}{N}\cdot$

2 ClO$_4^-$

[ring]   [ring]

(C$_4$H$_9$)$_2$N   N(C$_4$H$_9$)$_2$

11-23 Diimminium CH$_2$Cl$_2$ λ_{max} 1090 nm, ε_{max} 102,000
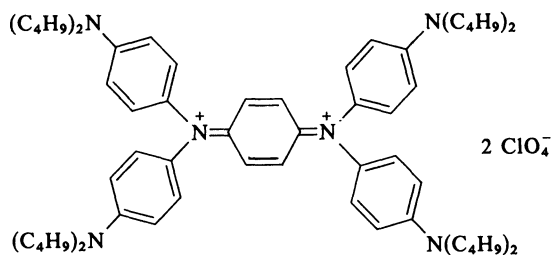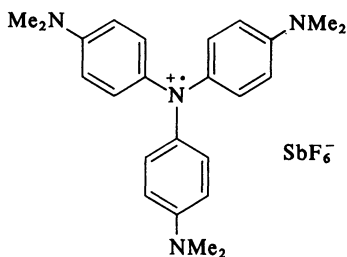
Table 11.4. Squarilium and Croconium Infrared Absorbers
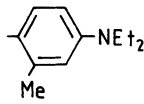
Structure	Type	λ_{max} (nm)
11-24	Squarilium	700
11-25	Squarilium	800
11-26	Croconium	845

These compounds are expensive to make and their solubility is poor. Compounds of type **11-23** are marketed by American Cyanamid and are used in safety spectacles (Table 11.1).

11.3.6. Squariliums and Croconiums

Squarilium and croconium dyes have very narrow absorption bands (ca. 25 nm) and high extinction coefficients (up to 350,000). They usually absorb around 700 nm, (e.g. **11-24**). Heterocyclic end groups such as (thia)pyrilium (e.g. **11-25**) and quinolinium (e.g. **11-26**) push the absorption

$$E-\langle\rangle=E^+$$

E =
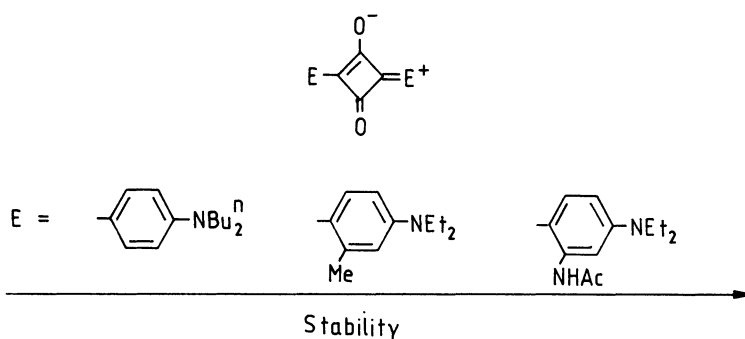
Stability

Stability data for E =

HF ($\sim 190\,^{\circ}$C for $\frac{1}{2}$h)	Squarilium	-5%
	Control	-15%
LF	Squarilium	-10%
	Control	-10%

11-27
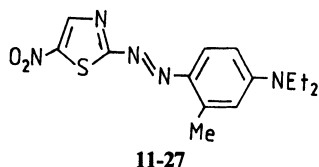
Figure 11.5. Relative stability of squarilium infrared absorbers. HF, heat fastness; LF, light fastness.

into the near infrared (up to 900 nm) but at the expense of stability (Table 11.4). These compounds have broader absorption curves with lower extinction coefficients (ca. 100,000). They are insoluble in water.

As an alternative to using heterocyclic end groups, Bello[6] has employed electron-rich aniline derivatives. The dyes obtained absorb to 800 nm and have improved stability to both light and heat over those from heterocyclic end groups. Representative structures and stability data for squariliums and a conventional blue azo control dye (11-27) are shown in Fig. 11.5.

Squariliums have better heat and light stability and are less colored than either cyanines or triphenylmethanes. Indeed, squariliums offer one of the best prospects for a colorless near infrared absorber.

11.3.7. Nickel Dithiolenes and Related Compounds

Metal complexes, particularly nickel complexes, of dithiols, oxathiols, and diamines have been studied extensively.[3,4,7] This class of compounds absorb well into the near infrared, spanning the range from 750 to 1200 nm. The absorption maximum and extinction coefficient depend upon both the
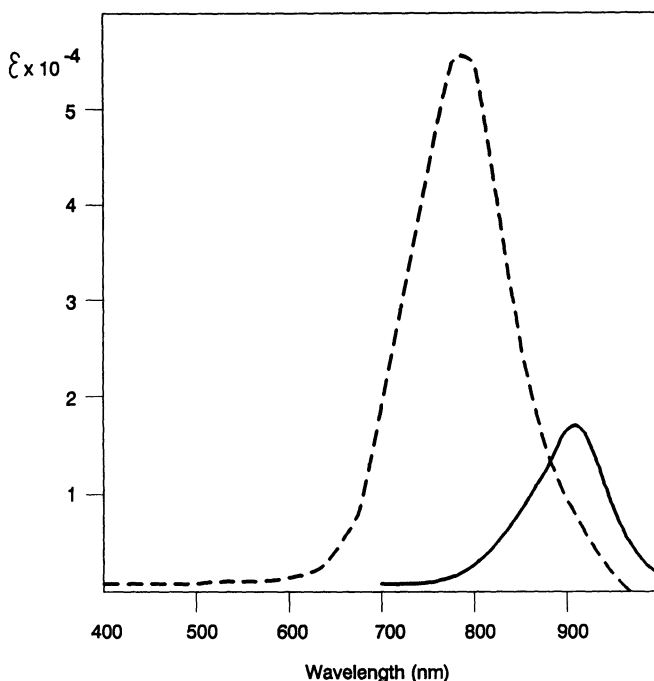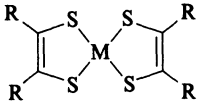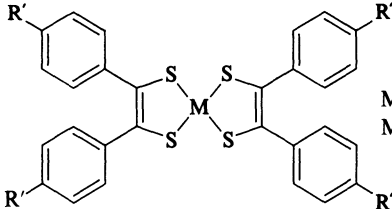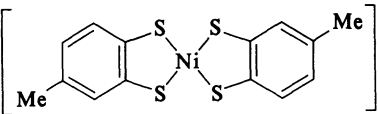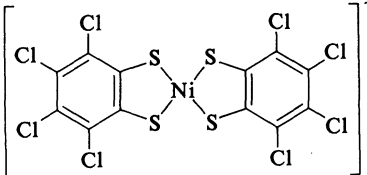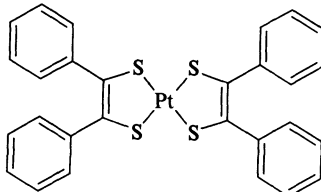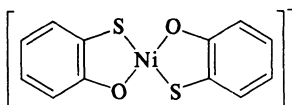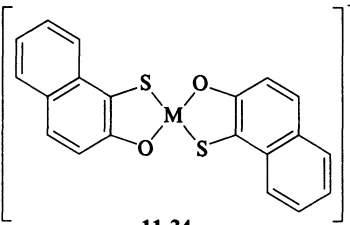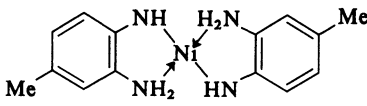
Figure 11.6. Comparison of the absorption spectra of 2:1 nickel complex dyes **11-30** (*solid lines*) and **11-35** (*broken lines*).

Table 11.5. Metal Complex Infrared Absorbers

Structure and type		λ_{max} (nm)	ε_{max}
Dithiol Complex Salts			
11-28	M = Ni R = C₃H₇	780 (Dichloromethane)	19,000
11-29	M = Ni R' = H M = Ni R' = OCH₃	866 925 (Chloroform)	31,000 35,000
11-30	$\overset{+}{N}(C_4H_9)_4$	890 (DMF)	14,000
11-31	$\overset{+}{N}(C_4H_9)_4$	885	15,700
11-32		802 (Chloroform)	43,000
Complex Mercaptophenol and Mercaptonapthol Salts			
11-33	M⁺	984	14,600

(continued)

Table 11.5. (Continued)

Structure and type		λ_{max} (nm)	ε_{max}
11-34	$\overset{+}{N}(C_4H_9)_4$ M = Ni M = Co M = Pt	1110 1150 1200	12,000 14,000 15,000
Complex Diamines 11-35		790 (DMF)	53,200

ligand and the metal. Table 11.5 shows some representative structures and spectroscopic data.[3,4]

As seen from Fig. 11.6, the nickel complex of the aromatic diamine **(11-35)** has the highest extinction coefficient (53,200) but absorbs at shorter wavelengths (790 nm) than the dithia complex **(11-30)**. The solubility of the diamine complex in organic solvents is also low.
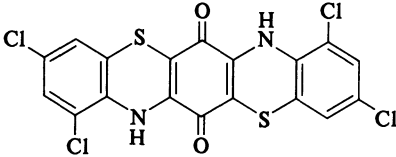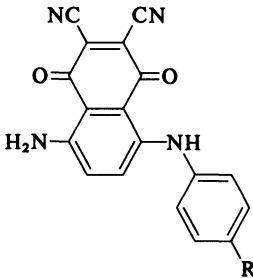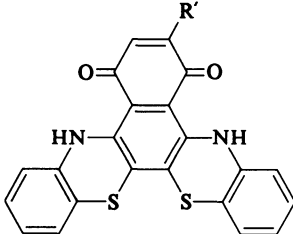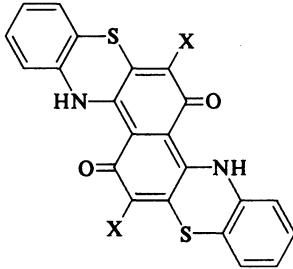
In general, electron-donor groups in the ligand produce a bathochromic shift. Compare, for example, the compounds **(11-29)** when R = H (866 nm) and R = OMe (925 nm).

A common feature of this class of infrared absorber is that the metal exists in an unusually high oxidation state, for example, 3 and 4 for nickel (normally 2) and 4 for cobalt (normally 3). The compounds possess a good visible window and offer one of the best prospects for colorless infrared absorbers. They also have better stability than cyanine, triphenylmethane, arylimminium, and squarilium infrared absorbers.

11.3.8. Quinones
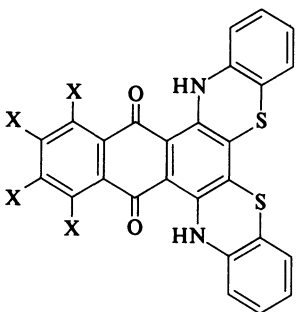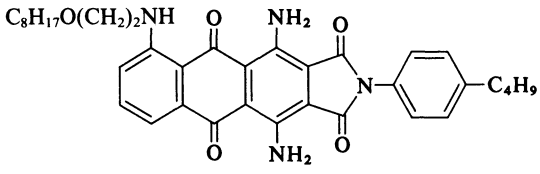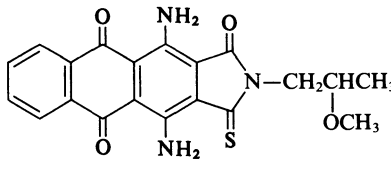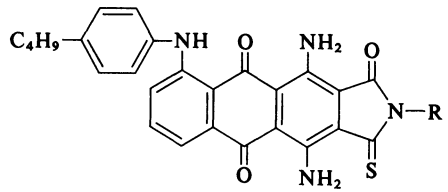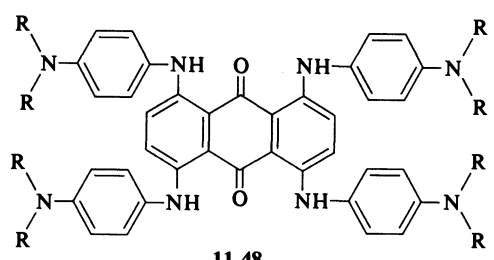
Quinone infrared absorbers is another class which is being researched extensively.[3] The quinone infrared absorbers may be subdivided into four

Table 11.6. Quinone Infrared Absorbers

Structure	λ_{max} (nm)	ε_{max}

Benzoquinones

11-40

| | 748 | 67,000 |

Naphthoquinones

11-41

| R = H | 768 | 15,200 |
| R = OC_2H_5 | 774 | 16,700 |

11-42

R′ = H	725	15,200
R′ = OCH_3	732	10,300
R′ = $NHCH_2$—	735	12,500

11-43

| X = H | 750 | 32,000 |
| X = Br | 785 | — |

(continued)

Table 11.6. (Continued)

Structure	λ_{max} (nm)	ε_{max}

Anthraquinones

X = H	712	15,000
X = F	770	15,000

11-44

| | 705 (Liquid crystal) | 24,000 |

11-45

| | 750 (Xylene) | 22,000 |

11-46

| | 810 (Liquid crystal) | — |

11-47

| | — | — |

11-48

types: (1) simple naphthoquinones, (2) extended quinones, (3) CI Disperse Blue 60 types, and (4) benzoquinones.

11.3.8.1. Simple Naphthoquinones

The simple naphthoquinones have the general formula **11-36**. Their absorption extends to about 800 nm (Table 11.6). Unfortunately, these simple naphthoquinones usually have poor stability. Griffiths[8] pioneered the work in this area, particularly the dicyanonaphthoquinone infrared absorbers typified by **11-41**. Subsequently, simple naphthoquinones have been patented extensively by NEC for use in optical data storage[3,9] (see *Section 11.4.3.2*).
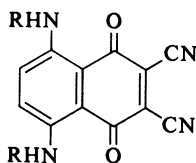
11-36

11.3.8.2. Extended Quinones

The extended quinones include both naphthoquinones and anthraquinones in which the delocalized pi-system has been expanded. Most of this class have the general formula **11-37** (Table 11.6). They have also been evaluated extensively by Japanese companies, particularly NEC,[10] for use in optical data storage.
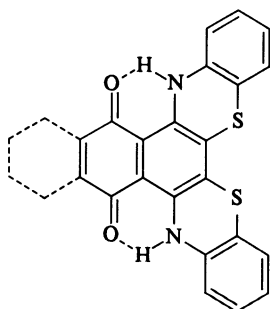
11-37

Both simple quinones and extended quinones have multiple absorption bands, some of which occur in the visible range and are therefore quite colored.

11.3.8.3. CI Disperse Blue 60 Analogues

CI Disperse Blue 60 (**11-38**) is the only true anthraquinone cyan dye (see *Chapter 8, Section 6*). Chemical modification has produced analogues of general structure **11-39** which absorb in the near infrared, typically in the 700–850 nm region (Table 11.6). Since CI Disperse Blue 60 types are used in liquid crystal displays (*Chapter 1*), it is hardly surprising that the derived infrared absorbers also find use in liquid crystal displays (see *Section 11.4.4*).
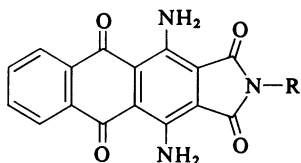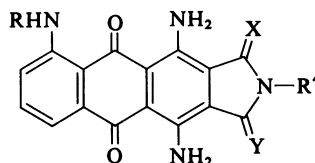
11-38   **11-39** X, Y selected from O or S, usually at least one S

11.3.8.4. Benzoquinones

Benzoquinone infrared absorbers have been studied less than the naphthoquinone and anthraquinone types. Significantly, they appear to have much higher extinction coefficients (structure **11-40** in Table 11.6).

11.3.9. Phthalocyanines

Phthalocyanines are one of the most stable and tinctorially strongest chromogens known. Being blues and greens they already absorb close to the near infrared.[11] It is hardly surprising, therefore, that the phthalocyanine chromogen has received considerable attention for providing near infrared absorbers.

Basically, there have been four approaches to push the absorption of phthalocyanines from the red into the near infrared: the use of (1) polymorphic pigments, (2) metallation, (3) donor substituents, and (4) extended conjugation.

11.3.9.1. Polymorphic Pigments

A number of polymorphs of both metallized and metal-free phthalocyanines are known and used commercially. The most prevalent polymorphs are the alpha and beta forms. Both these have their absorption maxima in the visible region, around 660–690 nm (Fig. 11.7). However, X-form metal-free phthalocyanine has twin absorption maxima; one peak is at 660 nm and is typical of conventional phthalocyanines, but the major peak is in the near infrared at 830 nm[12] (Fig. 11.7). X-form metal-free phthalocyanine is
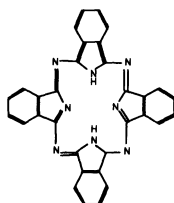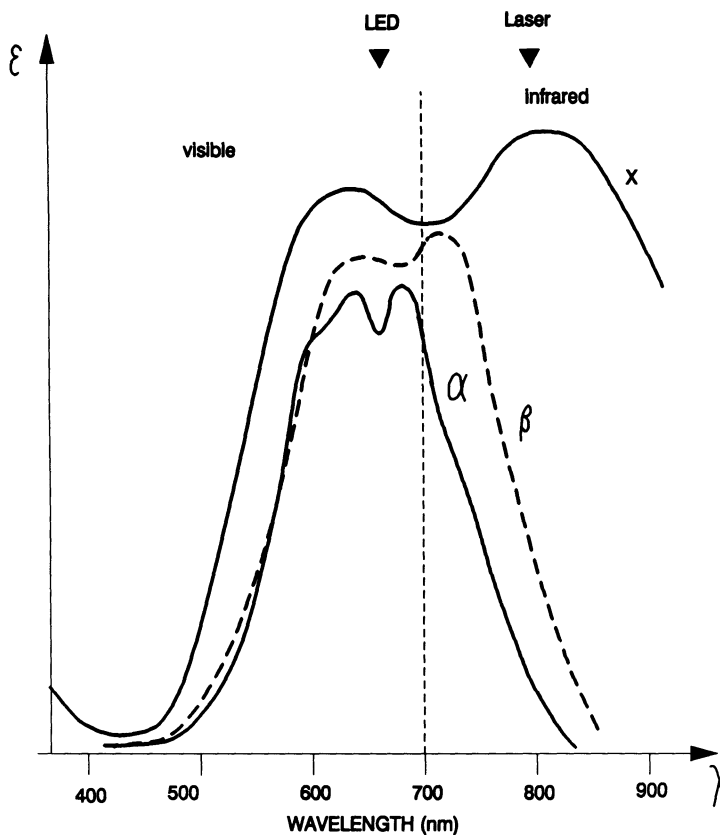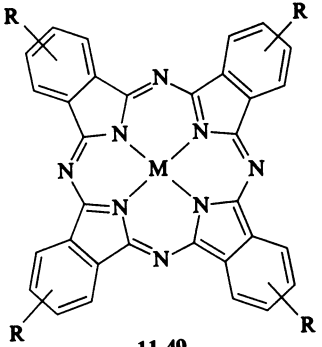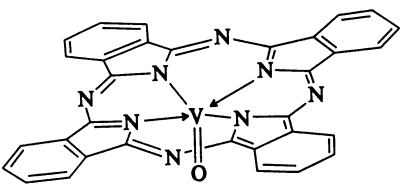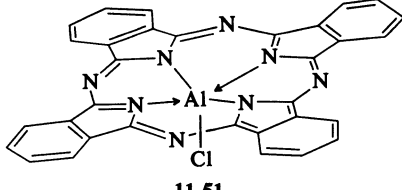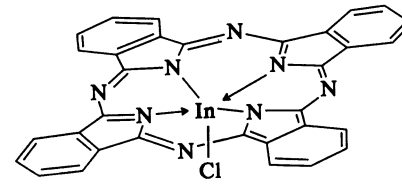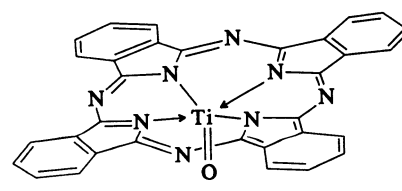
Figure 11.7. Absorption spectra of α, β, γ and X-form metal-free phthalocyanine.

particularly useful as a charge generation material in organic photoconductors (see *Chapter 7, Section 4.3*).

11.3.9.2. Metallation

The central metal atom can have a profound influence on the spectral properties of phthalocyanines and this effect has been used to produce infrared absorbers. Copper is the metal normally used in phthalocyanine dyes

Table 11.7. Phthalocyanine Infrared Absorbers

Structure	λ_{max}	ε_{max}

11-49 $R = $ (phenyl) $M = Pb$ 725   250,000

	Original λ_{abs}[a]	After treatment	
VOPc (**11-50**)	630	630	—
	740	740	
	830	830	
ClAlPc (**11-51**)	660	640	—
	750	720	
		820	
ClInPc (**11-52**)	660	650	—
	740	740	
		810	
TiOPc (**11-53**)	—	—	

[a] Before and after solvent-induced dimorphic change.[12a]

and pigments. Copper phthalocyanines absorb in the red region of the visible spectrum and produce blues and greens. Metals that push the phthalocyanine absorption into the near infrared include lead, vanadium, aluminum, indium, and titanium (Table 11.7). Like X-form metal-free phthalocyanine, these compounds are used as charge generating materials in organic photo-conductors (see *Chapter 7, Section 4.3*), except for lead phthalocyanine, which is used as a green pigment in color filters (see *Chapter 2, Section 4.2*).

11.3.9.3. Donor Substituents

The introduction of electron-donating substituents into the phthalocy-anine molecule produces a bathochromic shift and pushes the absorption into the near infrared. BASF[13] has patented amino substituted phthalo-cyanines as infrared absorbers and ICI[14] has patented phthalocyanines substituted by Group VB or VIB atoms, typically nitrogen, sulfur, and selenium. Structure **11-54** is typical.

$$CuPi \left(S - \!\!\left\langle \!\!\!\bigcirc \!\!\! \right\rangle \!\!\! - CH_3 \right)_{15/16}$$
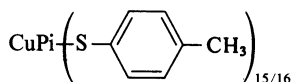
11-54 λ_{max} 770 nm, ε_{max} 180,000 (CHCl$_3$)

11.3.9.4. Extended Conjugation

Extended conjugation also pushes the phthalocyanine absorption into the near infrared. One way to increase the conjugation is to extend the hydrocarbon skeleton. Thus, naphthalocyanine (**11-55**) is an infrared
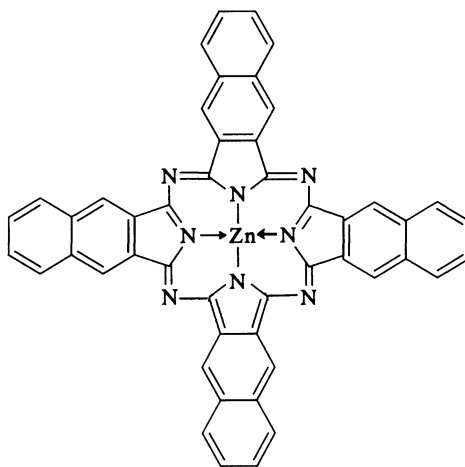
11-55 λ_{max} 760 nm, ε_{max} 140,000

absorber.[3] Another technique is to diazotize and couple aminophthalocyanines to introduce azo groups into the phthalocyanine skeleton[15] (e.g. **11-56**).
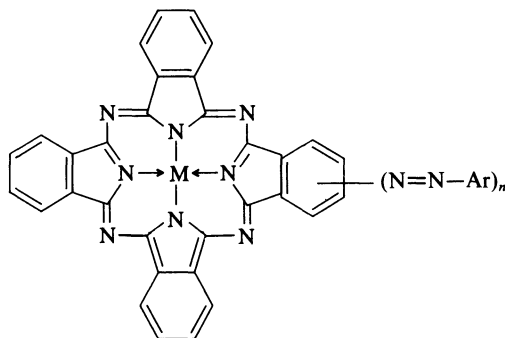
11-56 $n = 2-4$

Phthalocyanine dyes and pigments are exceptionally bright (narrow absorption curves), exceptionally strong (ε_{max} up to 200,000) and are exceptionally stable. Consequently, it may be expected that the phthalocyanine-based infrared absorbers also possess these attributes.

11.3.10. Azo

Azo dyes span the whole of the visible spectrum from yellow through red, blue to green, and even black. 2:1 Chromium (III) azo dye complexes containing nitro groups are normally black. These may be pushed into the near infrared by either incorporating a *peri* amino group into the naphthol coupler, as in (**11-57**),[16] or by extending the conjugation with additional azo groups, as in (**11-58**).[17] Both types are claimed to have good stability to light

11-57 λ_{max} 730 nm, ε_{max} 60,000 (DMF)
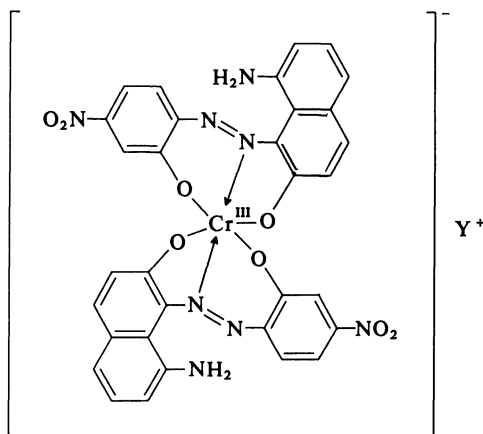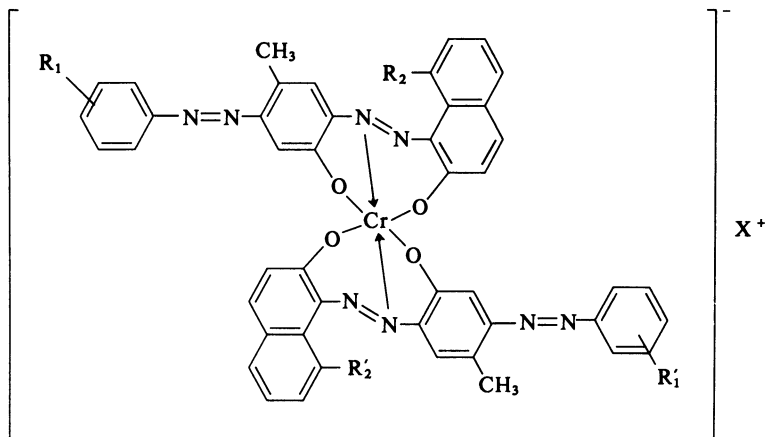
11-58 λ_{max} 700–900 nm, $\varepsilon_{max} \geqslant 30{,}000$

and heat. These structures are similar to the negative charge control agents discussed in *Chapter 7, Section 5.2.1.*

Certain symmetrical polyazo dyes have broad absorption bands which extend into the near infrared. The trisazo dye **(11-59)** is typical: its absorption spectra is shown in Fig. 11.8,[18] and, because its absorption spans the visible spectrum, it is black in color. Dyes of this type are used as the charge generating material in organic photoconductors (see *Chapter 7, Section 4.3*).
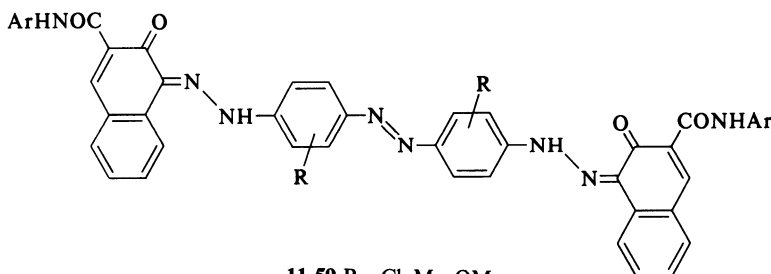
11-59 R = Cl, Me, OMe

Azo dyes containing sulfur heterocycles and powerful electron-withdrawing groups also absorb in the infrared; for example, the thiazole azo dye[19] **(11-60)** and the thiophene azo dye **(11-61)**. Dyes of type **11-61** are claimed to have high tinctorial strength ($\mathscr{E}_{max} > 70{,}000$).[20]
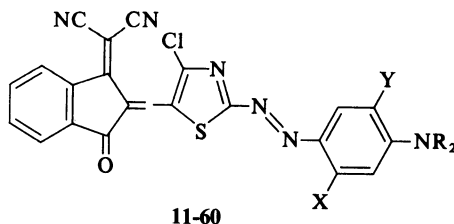
11-60
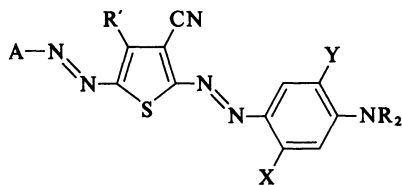
11-61

A = Electron-withdrawing radical, e.g.
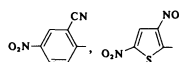
11.3.11. Indoanilines

Indoanilines are the dyes used to produce cyan colors in conventional silver halide photography. They have an absorption maximum around 660 nm. By incorporating two powerful electron-withdrawing groups such as cyano into the quinone ring, it is possible to push the absorption maximum almost to 800 nm (**11-62**).[4]
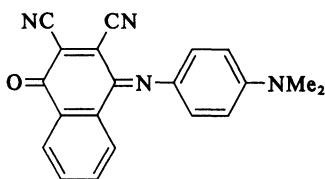
11-62 λ_{max} 795 nm (CHCl$_3$)
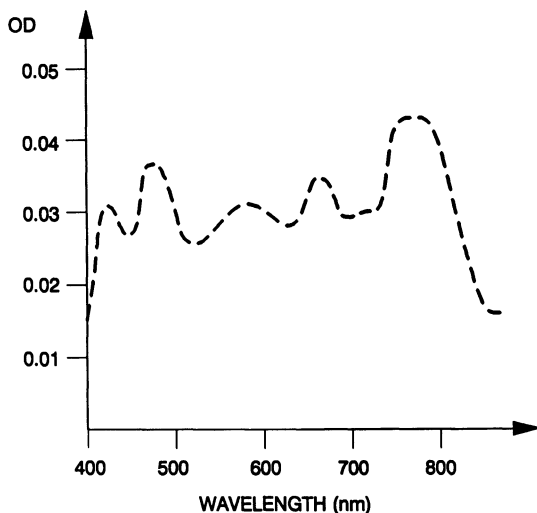
Figure 11.8. Absorption spectrum of the trisazo pigment (**11-59**). OD, optical density.

11.3.12. Donor–Acceptor Molecules

Both the azo dyes and the indoaniline dyes fall into the donor–acceptor category but are well known classes in their own right. To produce infrared absorbers from donor–acceptor dyes very powerful donors and very powerful acceptors are required. Dyes such as **11-63** are typical of this class.[21]
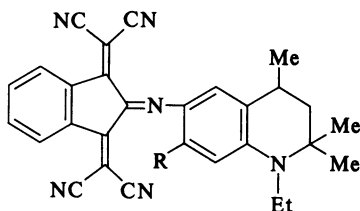
11-63 $\lambda_{max} \sim 800$ nm, $\varepsilon_{max} \sim 40,000$

11.3.13. Other Classes

These include vat dyes such as indanthrone (**11-64**), sulfur dyes, and aniline blacks. The latter types of colorants have variable and indeterminate constitutions.
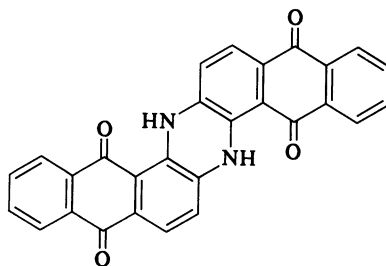
11-64 λ_{max} 721 nm, ε_{max} 13,000

11.4. APPLICATIONS OF INFRARED ABSORBERS

The following discussion of the applications of infrared absorbers follows the format indicated in Table 1, with the major emphasis on electronic and reprographic applications, particularly those that have not been previously discussed.

11.4.1. Heat-Ray Blocking

Efficient heat-ray blocking requires broad absorption of near infrared radiation in the range 750–2000 nm. Therefore, broad band infrared

absorbers acting over this spectral range are required. The prime outlets are glass and plastic used, for example, in car windscreens, windows of buildings, and agricultural film, with the goal being to keep the interiors of cars and buildings cool in hot summer weather. Obviously, high durability is required, especially to light, since the expected lifetimes of the products are long and the exposure conditions severe. At present, no suitable infrared absorbers exist. However, infrared absorbers with the greatest chance of success in the future will be those derived from the most stable chromogens such as phthalocyanines.

11.4.2. Energy Conversion

In energy conversion, infrared absorbers convert infrared radiation into heat to effect some thermally driven process. The infrared radiation may be highly specific laser radiation, such as 780 and 830 nm from semiconductor lasers and 1060 nm from a Nd-YAG laser, or broad band electromagnetic radiation, such as that from a xenon flash. Infrared absorbers for energy conversion may be divided into two basic types, narrow band and broad band. Narrow band infrared absorbers tuned to the laser wavelength are used for laser applications whereas broad band infrared absorbers are used to convert electromagnetic radiation, such as a xenon flash, into heat. The potential major use of laser radiation in energy conversion is thermal imaging and that for electromagnetic radiation is the flash fusion of toners and solar heating.

11.4.2.1. Thermal Imaging

Infrared absorbers may be used in both direct thermal imaging and in the thermal transfer processes in conjunction with infrared emitting lasers. There are several advantages for laser thermal imaging, the most important being greatly increased speed and higher resolution. Indeed, if successful, lasers could revolutionize the thermal imaging processes in the same way they have revolutionized electrophotography (see *Chapter 7, Section 2.2*).

In general, direct thermal imaging requires less energy than thermal transfer since the only process involved is one of melting at a relatively low temperature, such as 70°C (see *Chapter 8, Section 2*). Therefore, lower power lasers such as the semiconductor lasers, which emit at 780 and 830 nm, can be used. The full-color direct thermal imaging method described by Polaroid (see *Chapter 8, Section 4*) requires three different lasers and three compatible infrared absorbers. The thermal transfer processes, such as thermal wax transfer and especially dye diffusion thermal transfer (D2T2), require more energy since here the dyes have to be transferred from a dyesheet to a receiver sheet. High temperatures (ca. 400°C) are required for D2T2 (see *Chapter 8, Section 6*). Consequently, high power lasers such as the Nd-YAG laser

are required. Since the Nd-YAG laser emits at 1060 nm, different infrared absorbers are required from those used with the semiconductor lasers.

The use of lasers and compatible infrared absorbers to effect thermal imaging is in its infancy, and therefore trends have not emerged regarding the use of the various types of infrared absorbers. For high efficiency the infrared absorbers must have high absorption at the laser outputs (currently 780 and 830 nm, and especially 1060 nm) and have good thermal stability. The infrared absorbers which come closest to meeting these criteria are the squariliums, nickel dithiolenes, quinones, and phthalocyanines.

11.4.2.2. Flash Fusion of Toners

Most copiers and printers use hot rollers to fuse the toner to the paper in the final fixation stage. This technique is a contact process and suffers from problems such as offsetting and shiny prints. Flash fusion is an attractive alternative. Here, a xenon flash provides the energy. This is absorbed by the carbon black and converted into heat to cause fusion. The attractions of flash fusion are increased speed and a noncontact process, which gives improved print appearance. However, flash fusion also has its problems.[22,23]

With black toners the carbon black acts both as a colorant and as an infrared absorber. However, in the case of colored toners neither the yellow, magenta, or cyan colorants absorb infrared radiation. Consequently, an infrared absorber is required for the flash fusion of colored toners. The infrared absorber must be essentially colorless so that it doesn't affect the yellow, magenta, and cyan colors of the toners; it must be thermally stable and compatible with the toner resins. Furthermore, the absorption characteristics should match the emission spectrum of the xenon flash. As seen from Fig. 11.9, broad absorption from 700 to 1100 nm is required.

Agfa-Gevaert and Fujitsu are the two main manufacturers to employ flash fusion of toners commercially.[23] Fujitsu has published a number of patents in which infrared absorbers are used to aid the flash fusion of toners, especially colored toners. The types of infrared absorbers claimed are diimminiums,[24] and nickel dye complexes of dithiolenes,[25] oxathiolenes,[26] and diamines.[27] Xerox also has a patent[28] using cyanines as infrared absorbers for the flash fusion of toners.

11.4.2.3. Solar Heating

Here, the infrared absorbers are used to speed up the rate of heating (and evaporation) of water both for industrial and domestic purposes. The requirements are stability to water and low cost. Currently, iron complexes of, for example, nitroso dyes are used.
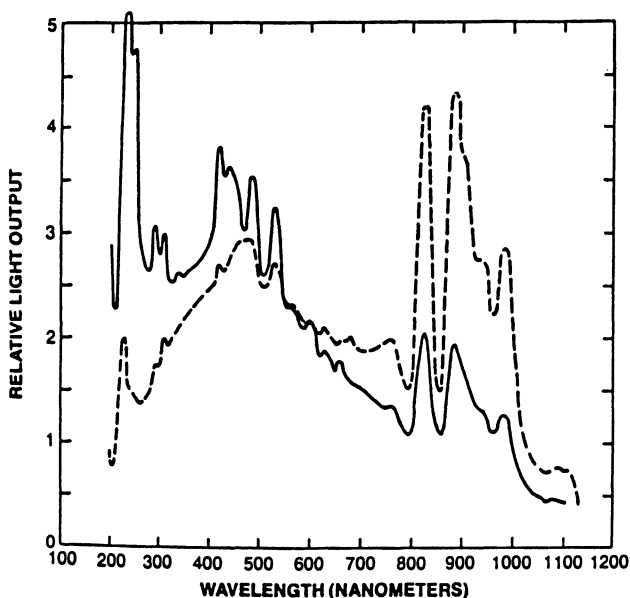
Figure 11.9. Xenon flashtube spectral output data. *Solid lines*, normal emission; *broken lines*, optimized for infrared emission.

11.4.3. Optical Effects (Utilizing Laser Radiation)

Infrared absorbers using optical effects consist of those that use laser radiation and those that use electromagnetic radiation. Optical effects of infrared absorbers that use laser radiation include organic photoconductors, optical data storage, and automatic identification.

11.4.3.1. Organic Photoconductors

The new generation of laser printers employ semiconductor lasers such as the GaAlAs laser. These emit in the near infrared at 780 and 830 nm. Therefore, organic photoconductors having maximum sensitivity in this region are required. The charge generation material used in organic photoconductors for laser printers must not only possess high absorption at 780 and 830 nm but also satisfy the many other demanding criteria required. Of the various chemical classes of infrared absorbers available, the phthalocyanines, squariliums, and azos are the most widely used infrared sensitive organic photoconductors. (See *Chapter 7, Section 4.3* for discussion of infrared sensitive organic photoconductors.)

11.4.3.2. Optical Data Storage[3]

As the name implies, optical data storage is a means of storing and retrieving data using optical techniques. At present, most data are stored
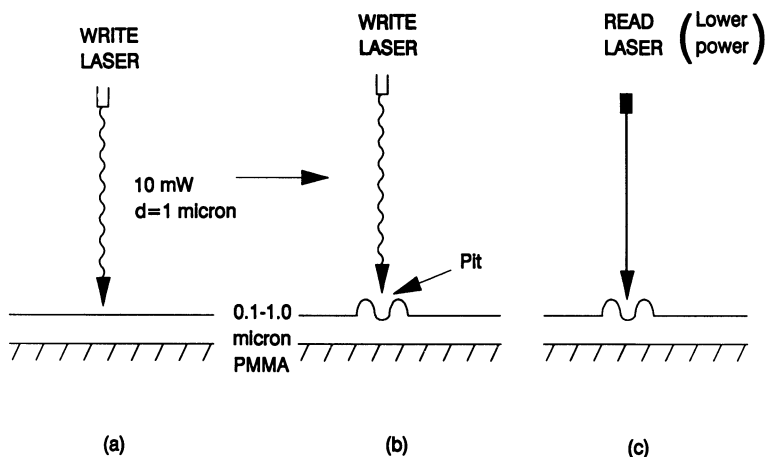
Figure 11.10. Principle of optical data storage.

magnetically on either discs (e.g. floppy discs) or tapes (e.g. video tapes). The driving force toward optical data storage is the step change increase (hundreds of times more) in the amount of data that can be stored per unit area. Typically, a single reel of optical tape can store up to 1 terabyte (1 million megabytes) which translates to 1 billion typewritten pages.[29] Ideally, optical data storage should parallel magnetic data storage in that the data should be able to be written and read many times, i.e. the disc or tape would be reusable. However, this is difficult to achieve technically and so the initial work is centered upon a write once read many (WORM) optical disc approach.

The principle behind optical data storage is shown in Fig. 11.10. A semiconductor laser writes the data on the optical disc. These lasers emit in the near infrared at 780 and 830 nm. They have 10 mW power and emit a beam of approximately 1 μ in diameter. The optical disc consists of a thin (1.0–0.1 μ) uniform film of a near infrared absorber on a polymethylmethacrylate substrate and is prepared using standard techniques such as spin coating and vacuum evaporation. Where the laser radiation hits the disc, a shallow pit is formed by the infrared absorber absorbing the radiation and converting it into sufficient heat to cause melting. (The temperature can reach 300–400°C). These pits constitute the recorded data. To read the data a lower power laser is used such that the energy of the beam is insufficient to cause melting. Instead, a detector records the amount of laser radiation reflected from the disc. Where the disc material is unexposed, there are no pits and there is high reflectivity. In contrast, the reflectivity is low from the data pits.

Infrared absorbers intended for use in optical discs need to satisfy a number of demanding criteria:

1. They should absorb strongly the laser radiation and have melting points that are neither too high nor too low (typically between 100 and 200°C). This ensures good pit formation.
2. Their reflectivity should be high.
3. It should be easy to prepare the infrared absorbers in the form of thin, uniform films. This necessitates good solubility in organic solvents and good thermal stability to withstand both evaporation of the solvent and the high temperatures reached with the write laser.
4. The infrared absorbers should have good durability. They should be resistant to light, heat, atmospheric oxidation, and humidity changes.
5. The thermal conductivity should be low so that the pits have a sharp outline.
6. The reflectivity of the unexposed part should not change when the read laser is used repeatedly.

Several classes of infrared absorbers have received attention for use in optical data storage. Cyanines have the advantage of high absorption coefficients but are low on durability, especially to oxidation. Typical cyanine infrared absorbers are shown in Table 11.3. Squariliums have also been used in optical discs (Table 11.4). These have better durability than cyanines but generally have lower absorption coefficients. The nickel dithiolene (**11-31**) (Table 11.5) is also being evaluated in optical discs. Phthalocyanines have the twin advantages of high absorption coefficients and good durability and so it is hardly surprising that they are receiving considerable attention for use in optical discs. However, the quinone class has probably received most attention for use in optical discs, typical structures being **11-41–11-44** (Table 11.6).

11.4.3.3. Automatic Identification[30]

Automatic identification is the machine readability of data using an optical source and a detector. The most common optical sources are the He-Ne laser (633 nm) and the red light emitting diodes (LEDs) (ca. 660 nm), both of which emit in the red region of the visible spectrum, and the semiconductor lasers and infrared LEDs, which emit at 780–830 nm and 900 nm, respectively (Fig. 11.11). The most common detectors are photodiode arrays based upon silicon. These have peak sensitivity in the near infrared at 900 nm, although the sensitivity curve is broad (Fig. 11.12). Consequently, infrared absorbers that absorb strongly at 800 nm and 900 nm are needed for efficient machine readability.

Black is the major color of commerce and the predominant black colorant is the pigment carbon black. Carbon black exhibits essentially uniform absorption both throughout the visible region and the near infrared region
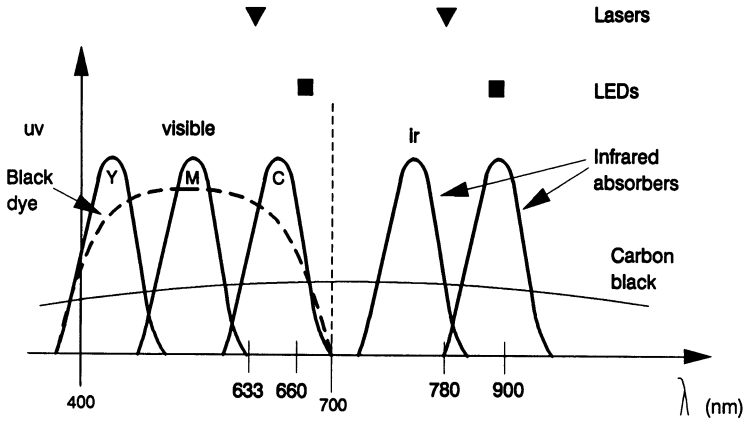
Figure 11.11. Some laser and LED emissions and spectral responses of colorants and infrared absorbers.

of the spectrum (Fig. 11.11). Thus, it provides both a good black and good machine readability in the near infrared. Carbon black has another advantage: it is inexpensive. However, it also has some deficiencies. These originate from its pigmentary nature. Thus, the abrasive properties of carbon black cause wear and reduce the lifetime of the styli used in dot matrix printing and the thermal heads used in thermal wax transfer printing. Carbon black is obviously unusable in carbonless copying, whether it be pressure-sensitive (see *Chapter 8, Section 3*) or direct thermal (see *Chapter 8, Section 2*). Here, infrared color formers of the triphenylmethane type are used, such as **11-17**,
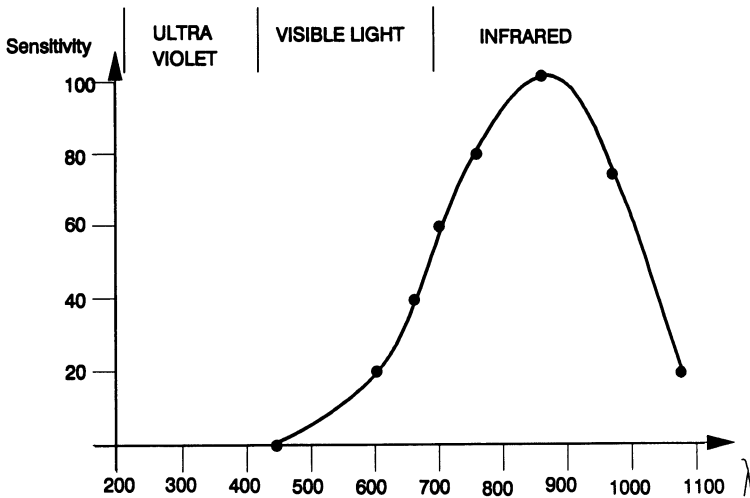
Figure 11.12. Spectral response of the photodiode array is centered in the infrared region.

or related compounds, such as **11-20**. Perhaps most significantly of all, carbon black is unusable in the aqueous and solvent-based ink-jet systems that are rapidly gaining importance for the bar coding of articles such as cardboard boxes, automotive parts, mail, and medical and army records.

Conventional black inks based on dyes use either a homogeneous black dye or a mixture of dyes, such as yellow, magenta, and cyan. Neither ink has significant absorption in the near infrared. Therefore, they cannot be read by conventional infrared lasers or LED scanners. To make these inks machine-readable, an infrared absorber must be added. Such an ink, whether it is yellow, magenta, cyan, or black, then becomes machine-readable in the near infrared (Fig. 11.11).

A critical parameter in determining the efficiency of machine readability is the print contrast ratio.[30] The print contrast ratio measures the difference in reflectance between the print and the background (Eq. 11.3). Inks having excellent machine readability have a print contrast ratio greater than 75%.

$$PCR = \frac{RB - RO}{RB} \times 100 \qquad (11.3)$$

where RB = reflectance of background
               (typically >85% for a good white paper)
         RO = reflectance of the object (print)
               (typically <18% for a good ink)

It is too early to note any trends as to which class of infrared absorbers is most suitable for automatic identification purposes. However, a prime consideration must be that of cost effectiveness, since the users have been conditioned to low-cost inks based upon carbon black. Thus, the infrared absorbers most likely to succeed are those produced from relatively inexpensive chromogens and which have high absorption coefficients, for example, phthalocyanines and various vat dye derivatives.

Infrared absorbers, particularly those having low visible color, i.e. essentially colorless, could play a role in various security applications. Such compounds, if incorporated into currency, checks, bonds, credit cards, etc., would provide a much more secure feature than the ultraviolet compounds used currently.

11.4.4. Optical Effects (Utilizing Electromagnetic Radiation)

The areas that utilize the optical effects of infrared absorbers are photography, fluorescence, liquid crystals, and filters.

The use of infrared dyes as sensitizers in conventional silver halide photography is well known and this is not discussed further here. Cyanines

are the infrared absorbers used. Near infrared fluorescence is utilized in laser dyes (*Chapter 3*). Again, cyanines are the dyes used. Extended anthraquinones such as **11-47** are used as infrared absorbing liquid crystal compounds (see *Chapter 1, Section 3*). Anthraquinones of type **11-48** have also been developed by Kodak for use in filters. Because of their high stability, anthraquinone infrared absorbers are also used in optical remote control of electrical apparatus such as videos and televisions.[3]

11.5. COLORLESS INFRARED ABSORBERS

For many applications, including security and flash fusion of colored toners, the ideal infrared absorber would be colorless. However, for a number of reasons, which are discussed below, this is very difficult to achieve.

Figure 13a shows that the energy associated with the boundaries of the visible region of the electromagnetic spectrum is 70 and 40 kcal mole^{-1}. Figure 13b shows the electronic energy levels of a typical ultraviolet absorber, dye, and infrared absorber. In all molecules the major contribution to the longest wavelength electronic transition is the HOMO-LUMO transition. For ultraviolet absorbers, this is greater than 70 kcal mole^{-1}. For a dye the HOMO-LUMO transition must be between 70 and 40 kcal mole^{-1}. This is normally achieved by the introduction of a powerful electron-donating substituent containing a $2p_z$ lone pair of electrons. These interact with the delocalized pi-system to produce a charge transfer band which absorbs in the visible region of the spectrum. Generally, this increased conjugation also reduces the energy differences between the other molecular orbitals. Infrared absorbers are obtained when the HOMO-LUMO transition is less than 40 kcal mole^{-1}. However, the energy levels between the other molecular orbitals are reduced correspondingly so that the next absorption band, from the HOMO-NLUMO, is less than 70 kcal mole^{-1} and therefore occurs in the visible region of the spectrum giving rise to color. In order to obtain a colorless infrared absorber, the unusual molecular energy levels shown in Fig. 13c are required whereby the HOMO-LUMO transition is less than 40 kcal mole^{-1} but the HOMO-NLUMO transition is greater than 70 kcal mole^{-1}. This is theoretically very difficult, so the truly colorless infrared absorbers are going to be few and far between.

11.6. SUMMARY

The need for materials that absorb in the near infrared region has increased dramatically in the past few years. The two major factors that have provided the impetus for infrared absorbers have been the discovery,
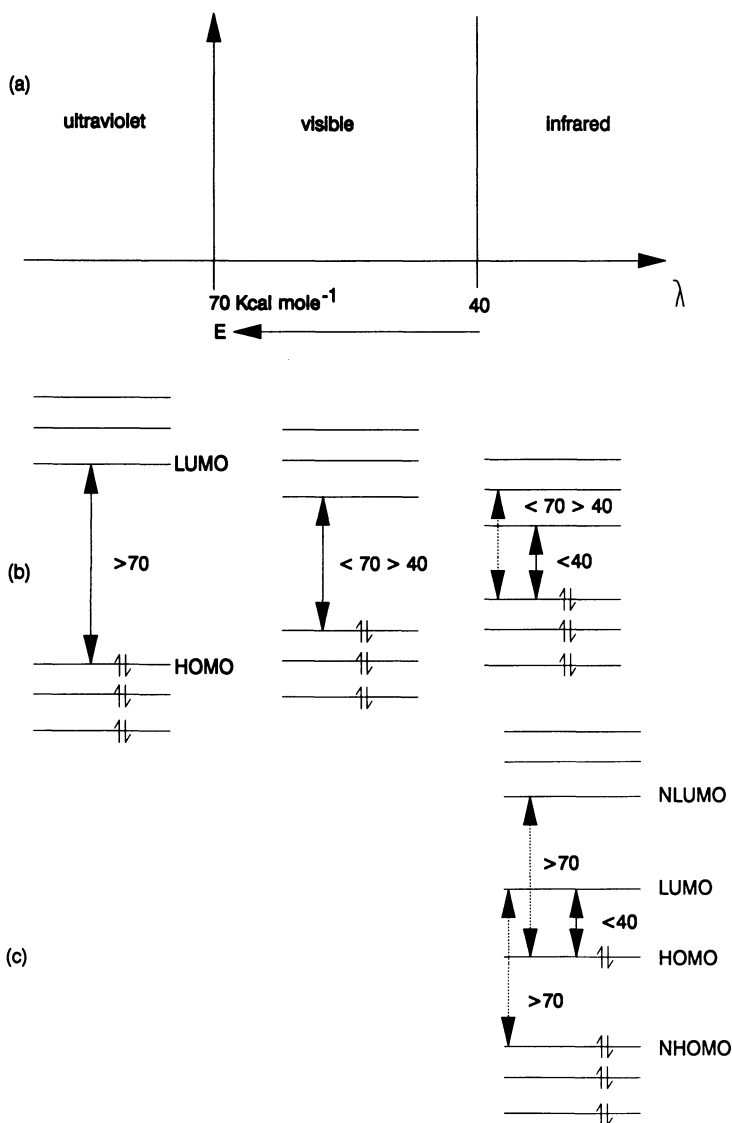
Figure 11.13. Energy levels (a) for colored (b) and colorless (c) infrared absorbers.

development, and commercial exploitation of the solid state semiconductor lasers and the silicon detectors, both of which operate in the near infrared. Laser printers, which require infrared sensitive organic photoconductors, have revolutionized page printers and infrared lasers are set to make a significant impact in the thermal technologies. Ink-jet printing of bar codes is growing rapidly in importance and, here again, infrared absorbers are required.

Nonelectronic or nonreprographic applications for infrared absorbers include security, car windscreens, architectural glass, and agricultural film.

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12

Toxicology

12.1. INTRODUCTION

Health, safety, and environmental issues have become increasingly important in recent years, especially in manufacturing industries such as the chemical industry. Therefore, it is prudent to devote a short chapter to outlining the position of organic colorants in this context. The chapter has several aims: to (a) alert people to the safety aspect of organic colorants, (b) outline the major regulatory bodies and registration procedures required of new chemicals, (c) focus on the important area of mutagenicity/carcinogenicity, highlighting key structure–activity relationships, and (d) discuss briefly risk assessment.

12.2. HAZARDS OF COLORANTS

Organic colorants have been used by mankind for thousands of years. Until the late 19th century these colorants were obtained from nature (see *Part I*). It was not until after Perkin's discovery of the first synthetic dye, Mauveine, in 1856 that organic colorants and their precursors, the dye intermediates, began to be manufactured on a large scale. This meant that workers in dyestuffs plants became exposed on a large scale to both the colorants themselves and the chemical intermediates used to manufacture them. Over many years it gradually became apparent that workers who produced dyes based upon 2-naphthylamine (12-1) and benzidine (12-2) developed a high incidence of bladder cancer, and it was later established that both these chemicals are potent bladder carcinogens. Subsequently, chemicals structurally related to benzidine, such as *ortho*-tolidine (12-3) and *ortho*-dianisidine (12-4) were also found to be carcinogenic. Once this information was known, all responsible color manufacturers took action to cease manufacture of these proven human carcinogens and any dyes using them.
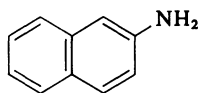
12-1
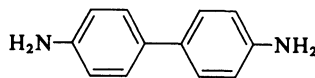
12-2
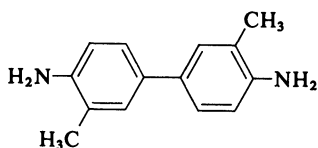
12-3
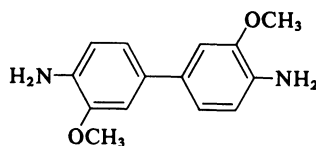
12-4

12.3. REGULATIONS AND REGISTRATION

The positive links between benzidine derivatives and 2-naphthylamine with bladder cancer prompted the introduction of stringent government regulations to minimize such occurrences in the future. Currently, the three major regulatory bodies worldwide are European Core Inventory (ECOIN) and European Inventory of Existing Commercial Substances (EINECS) in Europe, Toxic Substances Control Act (TOSCA) in the United Sates, and Ministry of Technology and Industry (MITI) in Japan. Each of these bodies has its own set of data and testing protocols for registration of a new chemical substance.

For registration in the European Economic Community (EEC)[1] the information required is shown in Table 12.1. Items 1 and 2 refer to the chemical structure of the substance (or its method of preparation if the structure is unknown) and information on its appearance.

Physicochemical properties required include the following:

Melting point
Boiling point
Density
Vapor pressure
Surface tension
Water and fat solubility
Partition coefficient
Flammability and explosion characteristics

The toxicological studies include acute toxicity tests and mutagenicity tests, as shown below:

Acute toxicity: Oral, inhalation, and dermal; skin and eye irritation; and skin sensitization.

Table 12.1. Information Required for Registration
of a New Chemical Substance for the EEC

1. Identity of the substance
2. Information on the substance
3. Physicochemical properties of the substance
4. Toxicological studies
5. Ecotoxicological studies
6. Possibility of rendering the substance harmless

Subacute toxicity: oral, inhalation, and dermal.

Mutagenicity: *In-vitro*: reverse mutation assay (Ames text) on *Salmonella typhimurium* and/or *Escherichia coli*; mammalian cytogenic test. *In-vivo*: Mouse micronucleus test.

Finally, the ecotoxicological studies, designed to assess the impact of the substance on the environment, embrace acute toxicity tests to fish and Daphnia, and a battery of tests for the biodegradable properties of the substance and its biological oxygen demand characteristics.

Registration of a new chemical substance in the United States and Japan requires a similar comprehensive set of data, although there are some differences. Obtaining all the data for a full registration can be time consuming and costly. In 1989 it cost approximately $150,000 and took about a year to register a new substance in Europe.

In order to expedite the launch of a new chemical and allow further time to complete the toxicological package for full registration, a "limited announcement" is normally used. This requires only parts of the full toxicological package, usually acute toxicity and Ames test. Consequently, it is less expensive ($20,000) and quicker (90 days) than full registration. However, only 1 tonne or less of the chemical per year is allowed to be sold in the EEC.

The outcome of these toxicological tests determines the fate of the chemical. If the chemical is a potential human carcinogen then it is abandoned. If it is nontoxic in all the tests then it is free to be sold as a commercial product. If the chemical gives inconclusive results at the first stage of screening, for example, an Ames positive response, then one of two courses of action is taken: either further *in-vivo* testing is authorized or the chemical is abandoned. Which course of action is taken depends upon the likely economic viability of the chemical. For a technically excellent product with a high profit margin aiming at a large market, further expensive animal testing would be justified. However, a chemical with a borderline technical profile and/or aimed at a smaller, more uncertain market would probably be abandoned.

The remainder of this chapter is devoted primarily to correlations between the mutagenic/carcinogenic effects of colorants and their related intermediates and their chemical constitution.

12.4. STRUCTURE–CARCINOGENICITY GUIDELINES FOR ORGANIC COLORANTS AND RELATED INTERMEDIATES

In this section the relationship between chemical structure and mutagenicity/carcinogenicity is examined. The discussion is confined to organic colorants, particularly those considered in this volume, and their associated intermediates. It is in no way intended to be a comprehensive or detailed account of the subject. Instead, it is meant to provide an insight into structure–activity relationships and rationalize the diverse types of carcinogens on a chemical basis.

Genotoxic chemicals such as mutagens and carcinogens damage DNA, the genetic blueprint material, usually by chemical reaction. It follows therefore that a genotoxic chemical must satisfy two basic conditions:

1. It must reach the DNA (which resides in the nucleus of a cell) in order for the chemical to interact with the DNA.
2. It must possess the ability to interact with the DNA, usually by chemical reaction.

12.4.1. Effect of Physical Properties on Carcinogenicity

To express a genotoxic effect a chemical must first come into contact with the DNA present in a cell. To do this, it must be able to transport across the protective cell membranes; physical factors such as molecular size and solubility are of paramount importance in determining whether this transport occurs.

In general, smaller molecules are transported across cell membranes more easily than larger molecules. Above a certain molecular size (ca. 800) molecules become too large to transport across membranes, which affords one means of producing nongenotoxic chemicals. Indeed, this approach was adopted by Dynapol to produce nontoxic, polymeric food dyes.[2] In the hi-tech area, substituted phthalocyanine infrared absorbers with molecular weights greater than 2000 (see *Chapter 11*) may also be too large to reach the DNA and should therefore be nongenotoxic.

The two extreme cases of total insolubility on the one hand and high water solubility on the other hand generally result in nongenotoxic chemicals.[3] By definition, pigments are insoluble in both organic solvents

and water. This insolubility, combined with the relatively large size of pigment particles, which are aggregates of molecules, ensures that most pigments are not transported across cell membranes. Consequently, the majority of pigments are noncarcinogenic.[4] Molecules with high water solubility are also nongenotoxic.[3] In this case, the hydrophobic (fatty) nature of the cell membrane is impervious to the hydrophilic water-soluble molecules. Furthermore, water-soluble molecules are generally excreted rapidly by a living organism. The best chemical grouping for imparting water solubility is the sulfonic acid group ($-SO_3H$). Carboxylic acid groups and hydroxy groups are also useful water solubilizing groups, especially when ionized. These three types of groups are employed extensively in aqueous ink-jet dyes (see *Chapter 9*). A quaternary nitrogen atom ($-N^+R_4$) also imparts water solubility.

12.4.2. Classes of Carcinogens by Chemical Structure

For most carcinogenic chemicals the active species, known as the ultimate carcinogen, is an electrophile, E. In many cases the electrophile is either a nitrenium ion R_2N^+ or a carbonium ion R_3C^+. This attacks a nucleophilic site in DNA, which may be a carbon, nitrogen, or oxygen atom, to form a covalent chemical bond (Eq. 12.1).

$$E + [DNA] \rightarrow E\mathord{-}DNA] \tag{12.1}$$

In addition to chemical reaction, intercalation is another common way that organic molecules interact with DNA. Here, a flat portion of a molecule inserts itself into the DNA helix.

12.4.2.1. Carcinogens from Nitrogen Electrophiles

Since an electron-deficient nitrogen atom is a key feature of this class, then obviously all carcinogens belonging to this group must contain at least one nitrogen atom. The types of chemicals vary considerably but amines, amine precursors, and amine derivatives are the largest and most important types. Specific classes are aromatic nitro compounds (**12-5**), aromatic amines (**12-6**), nitrosamines (**12-7**), hydroxylamines (**12-8**), hydrazines (**12-9**), and dyes, such as aminoanthraquinone (**12-10**) and particularly aminoazo dyes (**12-11**). As seen from Scheme 12.1, all these compounds produce a common ultimate carcinogen, a nitrenium ion (**12-12**).

a. Aromatic Nitro and Amino Compounds. Aromatic amines and aromatic nitro compounds are particularly important as far as organic colorants are concerned since they are the precursors to many dyes and pigments,

R'
\
  N—NO   RNHOH
/
R   **12-8**
  12-7

        R'   R'
        \   \
          N—NH₂ ⟶   N—$\overset{+}{N}$H
        /   /
        R   R
            12-9

Ar—NO₂ → Ar—NH₂ → Ar—$\overset{+}{N}$H
12-5   **12-6**

                                                    R—$\overset{+}{N}$R
                                                    12-12

Ar—N   Ar—N
     ‖   →   ‖
      N—Ar—NR₂   N—Ar—$\overset{+}{N}$R
   12-11

AQ—NR₂ → AQ—$\overset{+}{N}$R
12-10
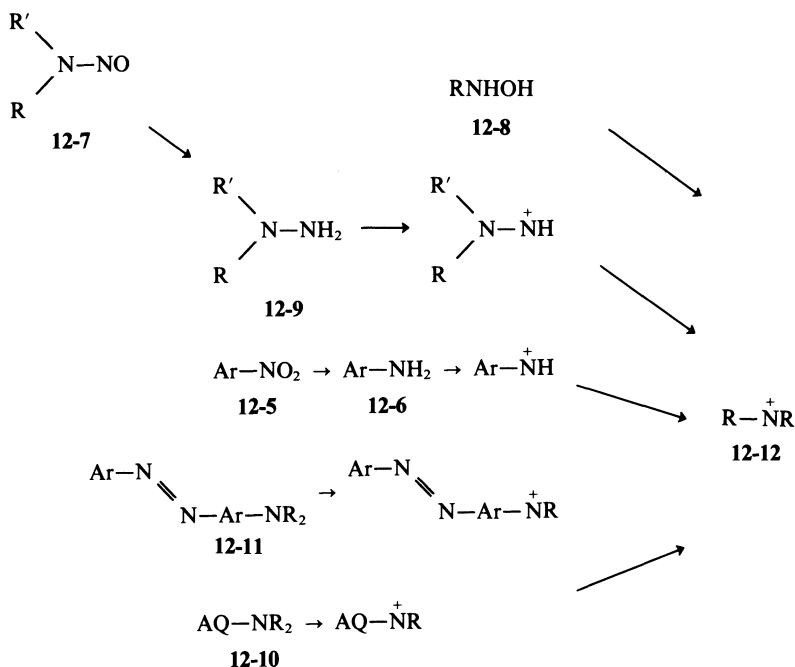
Scheme 12.1

Ar = Aryl

AQ = Anthraquinone

especially azo dyes. The most potent carcinogens within this class contain two or more aromatic rings and either primary amino (—NH₂) or methylamino (—NHMe, —NMe₂) substituents. In the case of nitro aromatics it is believed that a reduced species, such as amino or hydroxylamino, is the carcinogen. Typical carcinogens are shown below. The structural relationships within the benzidine (**12-2**) and 2-naphthylamine (**12-1**) series are clearly evident.

   b. Nitrosamines. Nitrosamines are important because nearly all azo dyes are prepared by diazotization of a primary aromatic amine followed by coupling to an electron-rich hydroxy or amino compound. As seen from Scheme 12.2, the first step in the diazotization process is the formation of the *N*-nitroso species (**12-13**); this quickly rearranges to a diazohydroxide (**12-14**). Protonation of (**12-14**) followed by the elimination of water yields the resonance stabilized diazonium compound (**12-15**). Nitrosamines such as **12-16**, derived from secondary amines, cannot undergo the rearrangement to the diazohydroxides.
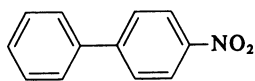
4-nitrobiphenyl
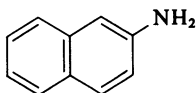
2-Naphthylamine
12-1
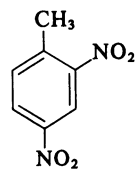
2,4-Dinitrotoluene
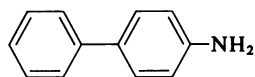
4-Aminobiphenyl
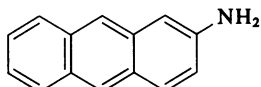
2-Aminoanthracene
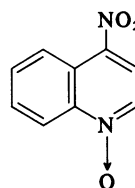
4-Nitroquinoline-*N*-oxide
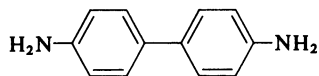
Benzidine
12-2
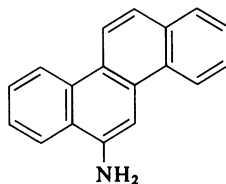
6-Aminochrysene
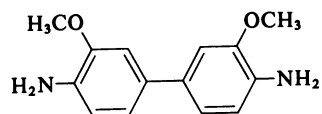
12-4
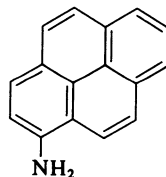
3-Aminopyrene
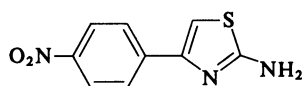
12-3
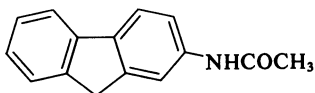
2-Acetylaminofluorene

2-Aminofluorene

$$Ar-NH_2 \xrightarrow{HNO_2} Ar-\overset{\overset{\displaystyle H}{|}}{N}-N{=}O$$

12-13

$$Ar-N{=}N-OH$$

12-14

$$\Big\downarrow\; H_3O^+$$

$$Ar-N{=}\overset{+}{N} \longleftarrow Ar-N{=}N-\overset{+}{O}H_2$$

$$\updownarrow$$

$$Ar-\overset{+}{N}{\equiv}N$$

12-15

Scheme 12.2

$$Ar-\overset{\overset{\displaystyle R}{|}}{N}-N{=}O \quad \xrightarrow{\;\;\times\;\;} \quad Ar-N{=}N-OR$$
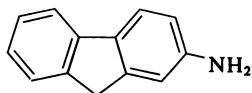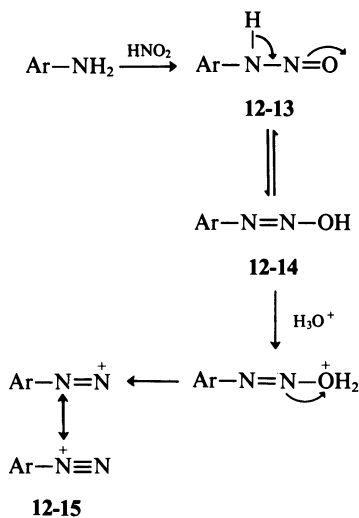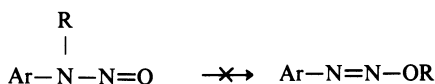
12-16   R = Alkyl or aryl

Almost all nitrosamines are carcinogenic, (e.g. **12-17**). The few known exceptions are when R and R′ are nonalkyl, (e.g. **12-18**), or fully substituted alkyl.

$$\begin{matrix} H_3C \\ \qquad\diagdown \\ \qquad\qquad N-NO \\ \qquad\diagup \\ H_3C \end{matrix}$$
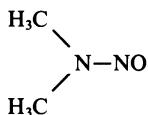
NN-dimethylnitrosamine
12-17

12-18

$$NH_2-NH_2$$
12-19

$$CH_3NH-NHCH_3$$
12-20
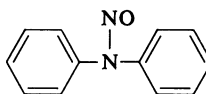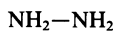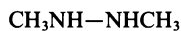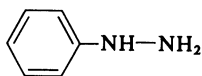
—NH—NH₂
12-21

   c. Hydrazines and Hydroxylamines. Hydrazine (**12-19**) and many of its derivatives, such as dimethylhydrazine (**12-20**) and phenylhydrazine (**12-21**), are carcinogenic. Phenylhydrazines are used to produce heterocyclic coupling components such as pyrazolones (**12-22**) (Scheme 12.3).
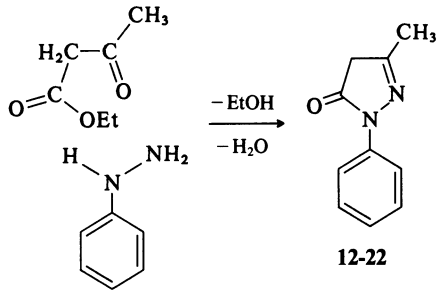
Scheme 12.3
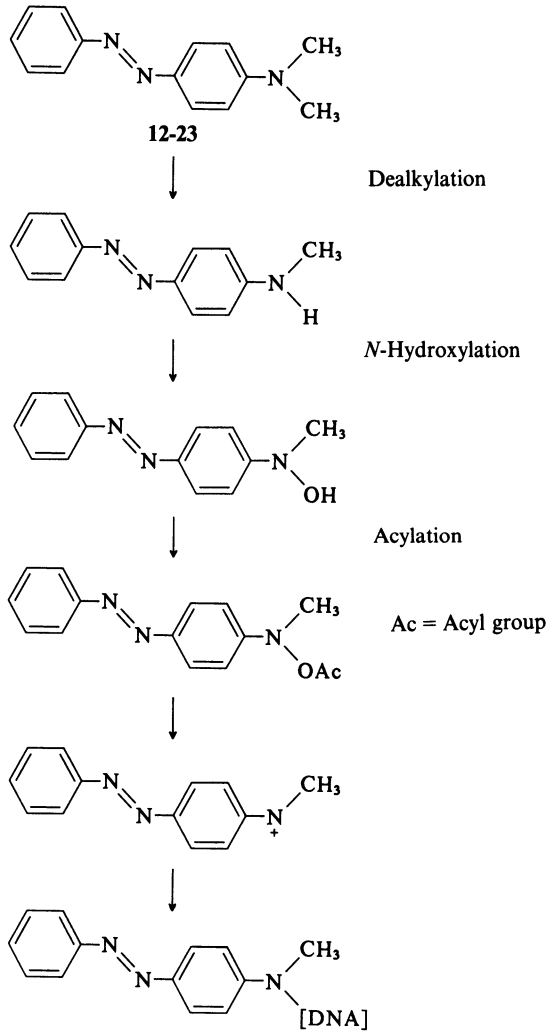
Scheme 12.4

d. Azo Dyes. Azo dyes have been studied most because of their commercial importance and their relationship to the aromatic nitro and amino compounds discussed previously. (They are synthesized from aromatic amino compounds and can also degrade to such compounds.) The carcinogenicity of azo dyes may arise from the dye itself, as in Butter Yellow, or where reductive cleavage of the azo group generates an active amine *in situ*. One example of each type is discussed.

Butter Yellow (**12-23**) and related dyes have been studied extensively[5] and the generally agreed mode of action is as depicted in Scheme 12.4. *N*-Hydroxylation appears to be the rate-determining step since it correlates well with the observed carcinogenic activity.[6]

Dyes related to Butter Yellow, such as **12-24**–**12-27**, are also carcinogenic. Again, primary amino and methylamino groups produce carcinogens. One way to reduce the toxicity of these dyes is to incorporate cycloalkyl groups, such as piperidino, as in the dye **12-28**.[7]

12-24

12-25

12-26

12-27

12-28
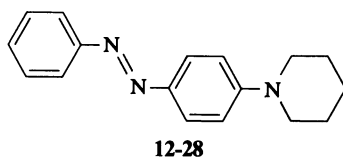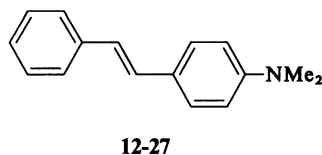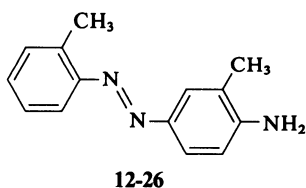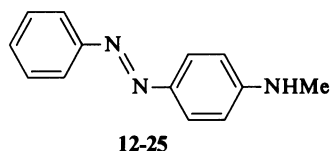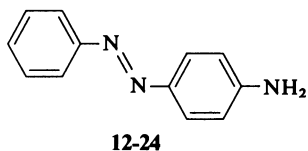
Azo dyes, which are carcinogenic because reductive cleavage of the azo group generates a carcinogenic amine, tend to be polyazo dyes derived from naphthols or aminonaphthols. The trisazo dye, CI Direct Black 38 (**12-29**) derived from the aminonaphthol H-acid (**12-30**), is a typical dye. Reductive cleavage of all three azo groups produces four amines, one being the known carcinogen benzidine (**12-2**) and another being the mutagen 1,2,4-triaminobenzene (**12-31**).

Water-soluble polyazo dyes of this type are important for aqueous ink-jet applications (see *Chapter 9*) and care has to be taken to ensure that such dyes are nonmutagenic. One way of acomplishing this is to ensure that each

12-30

12-29

12-31   **12-2**
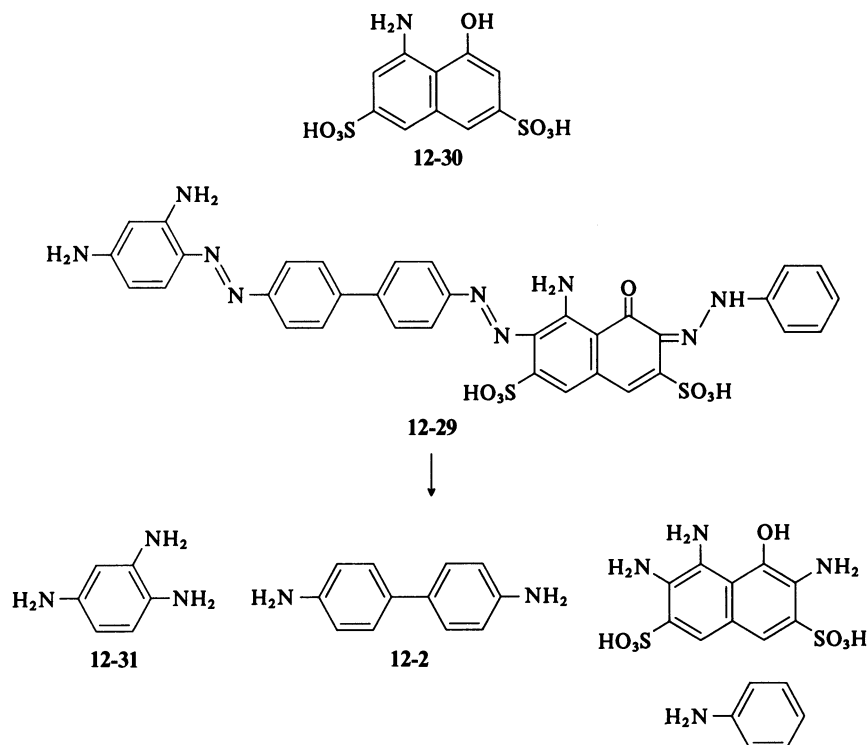
potential reductive fragment of the dye is water-soluble, since water-soluble species are generally nonmutagenic (see *Section 12.4.1*). Even the most potent carcinogens are rendered harmless by making them water soluble, a fact which is clearly demonstrated by the following example. The nonsulfonated and therefore non-water-soluble analogue (**12-32**) of the aqueous ink-jet dye, CI Direct Yellow 86, would, upon reductive cleavage of the azo

12-32

12-1
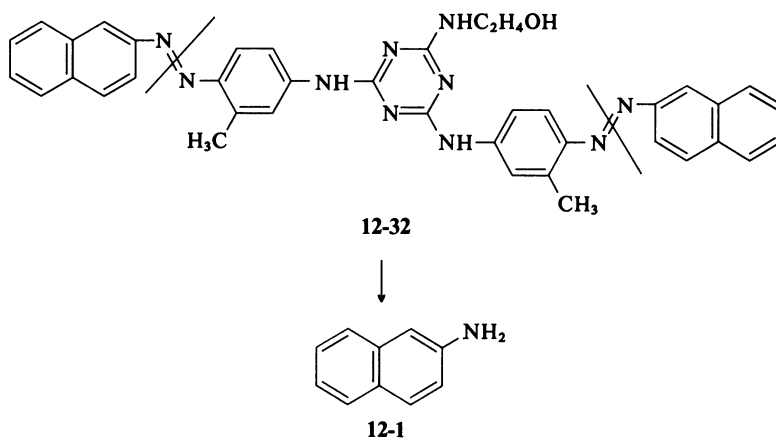
group, produce the potent carcinogen 2-naphthylamine (**12-1**). Consequently, **12-32** would be potentially carcinogenic. In contrast, CI Direct Yellow 86 (**12-33**) is nonmutagenic since the reduction product, namely 2-naphthylamine disulfonic acid (**12-34**), is water soluble and harmless.

12-33

12-34
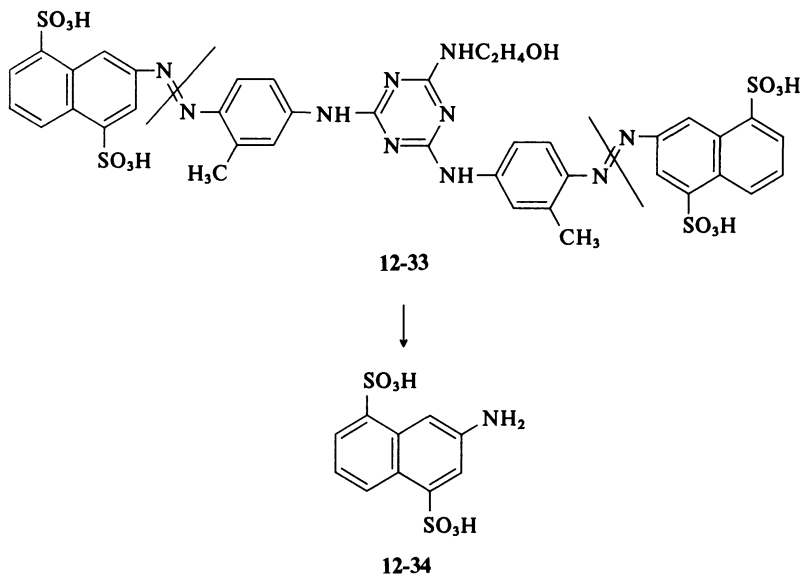
e. Anthraquinone Dyes. Anthraquinones are another important class of dyes. They have been studied less extensively than azo dyes but structure–activity relationships appear to follow similar trends to the azo dyes.[8] Thus, anthraquinone dyes of the solvent or disperse class containing one or more primary amino or methylamino substituents, such as CI Disperse Violet 1 (**12-35**), tend to be mutagenic.

12-35
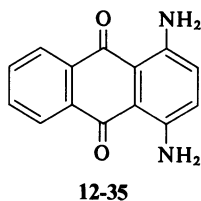
Certain anthraquinone dyes express mutagenicity by intercalation. Initial work indicates that they act via insertion of the anthraquinone unit of the dye between adjacent base pairs of the DNA helix (Fig. 12.1).

f. Cationic Dyes. Certain cationic dyes containing a delocalized positive charge are also mutagenic. The red fluorescent dye, Pyronine B (**12-36**), is an example.[9]
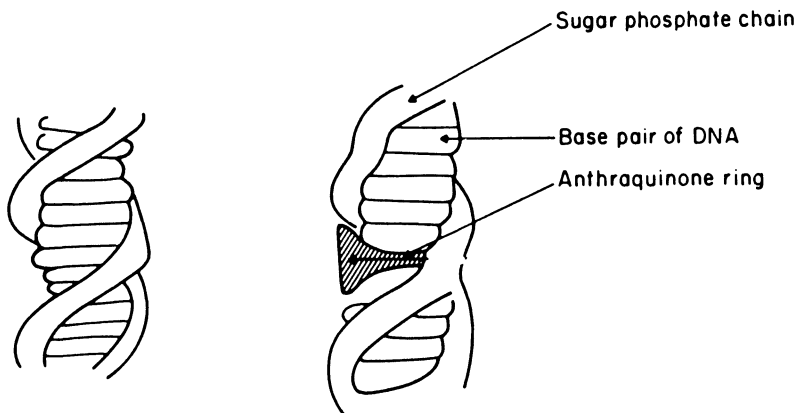
Figure 12.1. Intercalation of anthraquinone dyes in DNA.

12-36
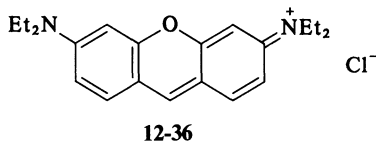
12.4.2.2. Carcinogens from Carbon Electrophiles

These carcinogens may be subdivided into three types: direct acting alkylating agents, polycyclic aromatic hydrocarbons, and Michael acceptors.

a. Direct Acting Alkylating Agents. These are chemically reactive alkylating agents which produce an electrophilic carbon atom as the reactive site (Scheme 12.5). These compounds contain either alkyl groups bearing a leaving group, such as chlorine, bromine, and methosulfate, or a strained small ring system, normally three-, four-, or occasionally five-membered rings, which ring open to generate the electrophilic center. They are normally

R_3C-X

$\left(\begin{smallmatrix} Y \\ (CH_2)_n \end{smallmatrix}\right)$

$\longrightarrow$ $\longrightarrow$ $(R)-C^+$

X = Leaving group

$Y = O, NH, -\overset{\overset{\displaystyle O}{\|}}{C}O-, -SO_2O-$

n = 2 or 3
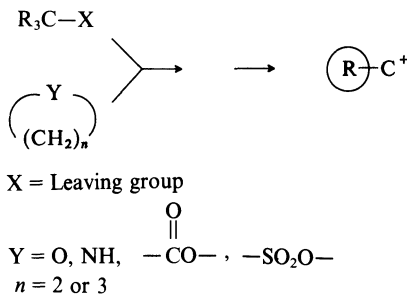
Scheme 12.5

employed as reagents in the synthesis of the intermediate and/or dyes although chloroalkyl groups have also been present in some dyes. Some common examples of each type are shown below.

    b. Polycyclic Aromatic Hydrocarbons. The aromatic hydrocarbons benzene (**12-37**), naphthalene (**12-38**), and anthracene (**12-39**) are the feedstock for the majority of dyes. These lower homologues are usually nonmutagenic (benzene is atypical since it is a weak liver carcinogen). In contrast, many compounds containing four or more fused aromatic rings, plus a few with three aromatic rings, are carcinogenic. Some typical examples are shown below.
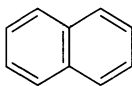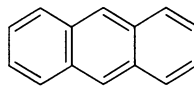
12-37   **12-38**   **12-39**
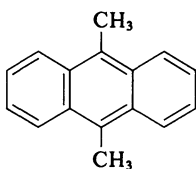
9,10-Dimethylanthracene   1,2-Benzanthracene   3,4-Benzphenanthrene
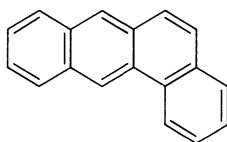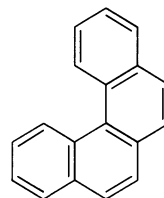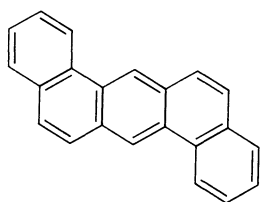
1,2,5,6-Dibenzanthracene   1,2,5,6-Dibenzfluorene   3,4-Benzpyrene
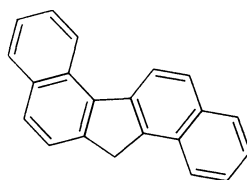
CH_2CH_2Cl
H_3CN
CH_2CH_2Cl

N-mustard

CH_2CH_2Cl
S
CH_2CH_2Cl

S-mustard

CH_2CH_2Cl
N
CH_2CH_2Cl
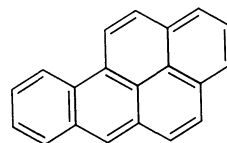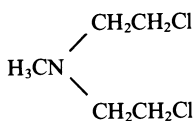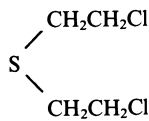
Chlornaphthazine
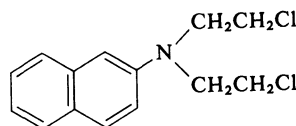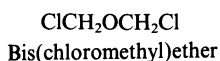
$ClCH_2OCH_2Cl$ $BrCH_2CH_2Br$
Bis(chloromethyl)ether   1,2-Dibromoethane
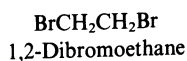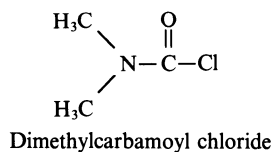
H_3C O
    N$-$C$-$Cl
H_3C
Dimethylcarbamoyl chloride

ClCH$_2$OCH$_3$
Chloromethylmethyl ether

$$H_3CO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OCH_3$$

Dimethylsulfate

CH$_2$N$_2$
Diazomethane

$$\overset{NH}{\overset{/\backslash}{H_2C-CH_2}}$$

Aziridine

$$\overset{O}{\overset{/\backslash}{ClCH_2HC-CH_2}}$$

Epichlorohydrin

$$\overset{O}{\overset{/\backslash}{CH_3HC-CH_2}}$$
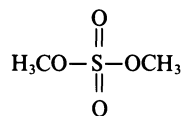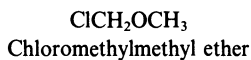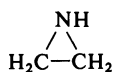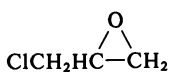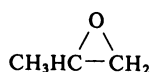
Propene oxide
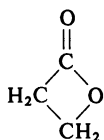
β-Propiolactone
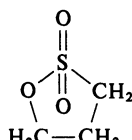
Propane sultone

Polycyclic aromatic hydrocarbons are believed to express their activity via epoxide formation (Scheme 12.6). In some cases it is possible to calculate the active site of the molecule using molecular orbital calculations.[10]
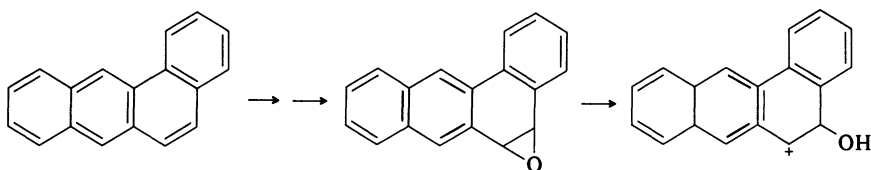
Scheme 12.6

c. Michael Acceptors. These compounds have an electron-withdrawing group attached directly to ethylene. Vinyl chloride (**12-40**), acrylamide (**12-41**), and acrylonitrile (**12-42**) are typical examples. The electrophilic carbon atom is produced by the polarization induced by the electron-withdrawing group, as shown for acrylonitrile. As was the case for the direct-acting alkylating agents, these Michael acceptors are used primarily as reagents in the synthesis of dyes. For example, acrylonitrile is used to introduce cyanoethyl groups in amine moieties (Scheme 12.7). A notable exception is the vinyl sulfone group (**12-43**) employed in certain reactive dyes for cotton, for example, CI Reactive Black 5 (**12-44**).

CH$_2$=CHCl

12-40

CH$_2$=CH—CONH$_2$

12-41

CH$_2$=CH—C≡N

↕

$^+$CH$_2$—CH=C=N$^-$

12-42

$$[Dye]-SO_2CH=CH_2$$
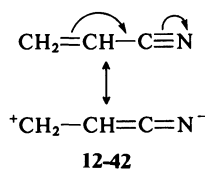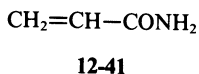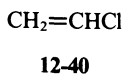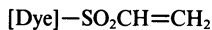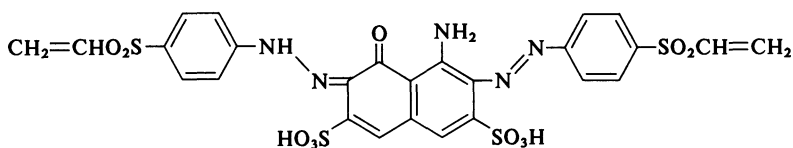
12-43

12-44
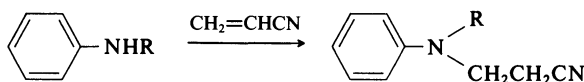
Scheme 12.7

12.4.3. Metals

Certain metals are also carcinogenic. These include chromium, nickel, cadmium, arsenic, and beryllium. In many cases it is a particular oxidation state of the metal which is the active species. For example, in the case of chromium it is chromium (VI), present in chromate pigments, which is believed to be the active agent. In chromium complex azo dyes, such as those used as charge control agents, chromium exists as chromium (III).

12.4.4. Carcinogenic Impurities

There is no simple answer as to what level (percentage or parts per million) of a carcinogenic impurity should be regarded as safe. The carcinogen 4-aminobiphenyl as an impurity in another chemical is currently regulated to less than 1%, which seems very high. In contrast, peanuts allowed for human consumption are regulated to parts per billion levels of the potent animal carcinogen aflatoxin B_1 (**12-45**). Clearly, each case must be judged on its merit and according to its likely significance.
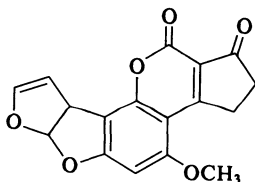
12-45

12.5. RISK ASSESSMENT

The hazard presented by a chemical depends not only upon its inherent toxicity profile but also on the degree of exposure to that chemical. For example, a highly toxic chemical presents no hazard whatsoever if it is completely contained, since the exposure to the chemical is zero. In contrast, a chemical of low toxicity would pose a hazard if the exposure to it was very high. Therefore, assessing the risk presented by a particular chemical in particular environments is an extremely important area in deciding the hazard presented by a chemical.

The main facts to be considered in risk assessment are the inherent toxicity profile of the chemical and the degree of exposure to that chemical. The inherent toxicity can be determined from the various toxicological tests described in *Section 12.3*. The degree of exposure depends upon several factors, the major one being the length of time people (or other animals) are exposed to the chemical (usually in the air). This factor is obviously grossly different for workers in chemical manufacturing plants at one extreme and the general public at the other extreme. Important parameters that affect the exposure level are the quantity of the substance and its volatility. Solids are less volatile than liquids which, in turn, are less volatile than gases. If toxicity is plotted against exposure, the least risk is from minimal exposure to a chemical of low toxicity. In contrast, the highest risk is from prolonged exposure to a toxic chemical (Fig. 12.2).
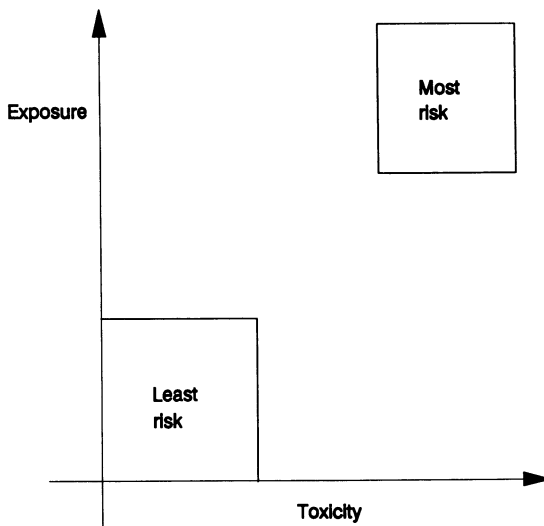
Figure 12.2. Risk assessment.

12.6. SUMMARY

The public is becoming increasingly aware of the potential toxic hazards of chemicals, and chemical manufacturers and regulatory authorities are making strenuous efforts to ensure that both existing products and new chemicals are completely safe.

One of the most important and emotive issues is the potential carcino-genicity of chemicals. The Ames test is a useful initial screening test for carcinogenicity. However, *in vivo* tests give more meaningful and reliable assessments of the potential carcinogenicity of a chemical but they are more expensive and time consuming than the Ames test. Useful structure–activity guidelines have been developed based on an understanding of the mode of action of carcinogens.

In addition to the inherent toxicology profile of a chemical, the degree of exposure to that chemical is an equally important factor. Risk assessment is an increasingly important area in producing a safe environment.

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13

Future Trends

13.1. INTRODUCTION

Crystal ball gazing is without doubt one of the most difficult and tricky things to attempt and many eminent people have fallen flat on their face in attempting to predict the future. Nonetheless, this chapter attempts to predict some of the future trends in the hi-tech uses of organic colorants. Essentially, this means predicting the future of organic colorants in the electronics and reprographics industries. As in the main body of the book we will concentrate on the reprographics area, since this is where the major growth for organic colorants will occur. Obviously, this growth is directly related to the growth in hard copy output, particularly color hard copy output.

The use of organic colorants in reprographics will grow spectacularly. However, the volumes will never exceed, or even approach, those required for conventional applications such as imparting color to a substrate. This lack of volume will be offset to some extent by the colorants, most of which are specialty products, commanding higher prices.

13.2. COLORANTS FOR ELECTRONICS

Colorants for electronics outlets will be a small volume, generally high added value business, for the foreseeable future. There are two reasons for this. First, the growth rate in electronics has slowed down. Second, and more importantly, the usage of colorants in electronics is small. The colorant is used primarily as part of an electronic device rather than for imparting color to a substrate (compare reprographics applications) and, as the saying goes, "a little goes a long way." This means that in established applications such as liquid crystal dyes and laser dyes the quantity of dye consumed is measured in tens of kilos rather than tens of tonnes. More futuristic uses,

such as solar cells and especially communications applications such as nonlinear optics and flat screen televisions, will consume significant amounts of colorants: however, these technologies have yet to establish themselves in the marketplace.

13.3. COLORANTS FOR REPROGRAPHICS

The future of colorants for reprographics depends upon the future of the reprographics industry, which is inextricably linked with hard copy output. Both these aspects need to be considered when discussing the future of organic colorants in reprographics. In the context of hard copy output we begin with a prediction made some years ago, namely that of the "paperless office."

13.3.1. The Paperless Office

The rapid advances in electronic data processing and transmission coupled with the widespread use of computers and work stations in the office led many people to predict that the paperless office was approaching rapidly. What utter folly this has proved to be. The paperless office is further away than ever! The growth in electronic data processing has had the totally opposite effect to that predicted: it has increased, not decreased, the amount of hard copy generated. Why should this be so? The answer is not hard to find. Since the earliest of times man has recorded his culture and knowledge and it has always been as "hard copy." Indeed, the earliest recordings of animals on cave walls and writings on "tablets of stone" were literally (rock) hard copies. Since that time, wood, cloth, and especially paper have been used as the substrate for hard copy. Thus, there is a very strong tradition of mankind using hard copy to record information and traditions are hard to break. This leads on to the fact that people are "comfortable" when handling information in hard copy form: there are a number of reasons for this:

It is easier to handle physically than electronic information on a screen.
It is easier to read and is less tiring on the eyes than electronic information on a screen.
It is easier for the individual to carry around.
It is permanent (archival).
Many people are uncomfortable about using computers.

The author can vouch for these feelings firsthand. The typescript for this book was prepared (at home) on a microcomputer word processor. The information was first written longhand on paper (easier and more comfort-

Table 13.1. North American Supplies Revenues by Output Device
(in Millions of Retail Dollars)[a]

Output device	1986	1991	Compound annual growth rate (%)
Color printers	201	1,209	43
Intelligent copiers/printers	1,779	5,221	24
Facsimile	53	151	23
Copiers	4,557	5,416	4
Impact printers	6,967	8,064	3
Duplicators	1,139	780	−7
Total	$14,696	$20,841	7

[a] Source: CAP International, Inc.

able than typing it directly on to the screen) and then typed on the word processor and stored on disk. It was then printed on to paper for corrections and editing. Indeed, until a piece of work was actually transferred from the disk to a hard copy on paper the author felt distinctly uneasy, however irrational this may have been. This was in case something "went wrong" with the disk and the information was lost. Obviously, this way of working generates a lot of hard copy (most of which is discarded) and uses a lot of paper. In line with this, the total paper consumption in reprographics (North America only) is predicted to increase from $4619 million in 1986 to $6793 million in 1991.[1] In fact, the revenue from paper exceeds that of any other reprographics consumable (Table 13.2).

Having established that hard copy is increasing rapidly, not in spite of but largely because of electronic data processing, let us see which technologies will dominate the hard copy market.

13.3.2. Competing Technologies

The technologies for producing hard copy are the traditional impact printing methods and the more recent hi-tech or nonimpact printing methods. For office output dot matrix, typewriters and daisywheel printers are the important impact printing technologies although, in a wider context (newspaper and magazine printing), offset lithography and gravure printing are also important. The important nonimpact printing technologies are electrophotography, thermal, and ink-jet, although magnetography and especially ion deposition may become more important in the future.

The key factors that determine which technology is used are cost, speed, and performance, a vitally important trio of interrelated variables. The ideal case is to have the highest speed combined with the highest performance and the lowest cost but, as so often happens, this is not the case in practice: compromises have to be made.

13.3.3. General Predictions

Some general predictions are given first before discussing predictions specific to the major reprographics technologies.

1. *Nonimpact printing technologies will increase.* The first prediction is that the nonimpact printing technologies will increase at the expense of the impact printing technologies. There are a number of reasons for this, the more important ones being speed, quality, versatility (text plus graphics), color capability, and noise. Compare, for example, a laser printer with either a dot matrix or a daisywheel printer. A laser printer is quiet, fast (from 6 to 240 A4 pages per minute depending upon cost, i.e. cost/speed/performance relationship), produces text and graphics, and gives high quality prints. It can also produce colored output (e.g. Canon's Color Laser Copier). In contrast, both dot matrix and daisywheel printers are noisy, slow, and operate in monochrome (black). Daisywheel printers give letter quality prints but cannot produce graphics whereas dot matrix printers can produce text or graphics but of poor quality. It is because of these advantages that non-
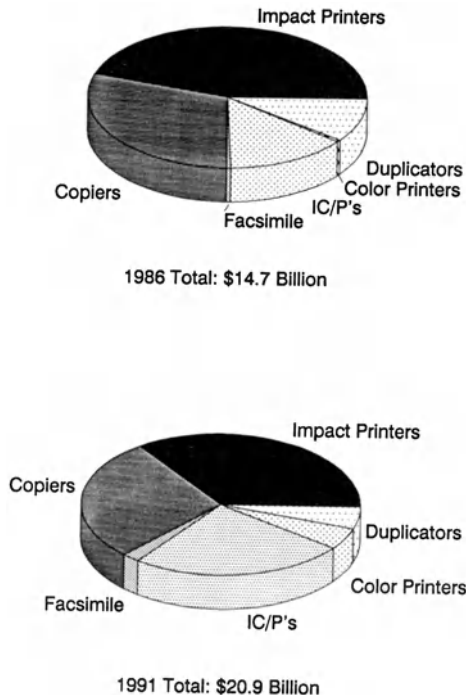
Figure 13.1. North American supplies revenues by output device (in billions of retail dollars).

impact printers are predicted to take a large slice of the hard copy market (Fig. 13.1 and Table 13.1).[1] Thus, the compound annual growth rate (CAGR) of the nonimpact printing technologies, except copiers, is predicted to be 23%–43% in contrast to only 3% for impact printers.

2. *Color will increase*. When people have a choice they prefer color to monochrome, even if color costs more. This has been demonstrated very clearly by the trends in both televisions and photography. The use of color in reprographics will never be as dominant as it is in television and photography because of the amount of text involved. However, color will increase steadily for a number of reasons:

> More color monitors requiring color hard copy output.
> Color conveys more information.
> Color produces a more attractive display which is easier on the eye.
> There will be more primary publications in color. This will also increase the demand for color copiers.

Indeed, the two fastest growth areas are for colored ink-jet inks (67% CAGR) and color thermal transfer ribbons (47% CAGR).[1] There will also be a trend away from pigments toward dyes to improve properties such as brightness and transparency.

3. *There will be a move toward plain paper*. The growth in paper consumption fueled by electronic data processing has been discussed already. However, the big expansion will be in *plain* paper. This is because of cost, handling, and general ease of use. In other words, people expect paper to be paper. Furthermore, they expect photographs to be photographs (dye diffusion thermal transfer, D2T2) and transparencies to be transparent.

4. *All the technologies will find a niche*. All the major technologies, both impact and nonimpact, will find a niche in the marketplace.

5. *Primary nonimpact printing processes will dominate eventually*. A primary technology is one which operates in a truly single step without any intermediate steps or materials. The prime example is ink-jet printing where the only process is ink being fired at the substrate. It also has the advantages of being a truly noncontact process and can use plain paper. Other technologies, such as impact printing and thermal transfer, employ a ribbon as an intermediate material whereas electrophotography is a multistage process which also employs an intermediate material, the photoconductor drum or belt. Direct thermal printing is a primary process but it is a contact process and needs special paper.

6. *Undiscovered technologies will make an impact in the future*. Technologies as yet undiscovered will no doubt make a significant contribution in the future.

13.3.4. Specific Predictions

13.3.4.1. Electrophotography

Several aspects need to be considered such as monochrome, color, copying, and printing.

Monochrome photocopying will remain a dominant technology for many years since it remains the quickest way of producing copies of high quality and low cost on plain paper. The user can choose from low cost, compact, personal copiers producing several pages per minute (ppm) to expensive, larger office copiers producing 200 ppm. No other nonimpact printing technology can match photocopying for producing *copies* of an original.

Laser/light emitting diode (LED) printers have revolutionized monochrome printing. It is the cost/speed/performance characteristics which makes them outstanding. As is the case with copiers, users can choose from low cost (<$2000) compact, moderate speed (6–15 ppm) laser printers to expensive, larger, high speed (200 ppm) laser printers, all of which give high quality prints (text and/or graphics) on plain paper. A future trend will be so-called intelligent copiers, which will function both as copiers and printers.

Thermal ink-jet printers and ion deposition are likely future competitors to laser printers.

The future is not as rosy for electrophotographic color processes. The complex technology, slower speed (at least three times slower than for monochrome) and the high cost of the color copiers (currently $20,000) makes the cost/speed elements of the cost/speed/performance relationship unattractive. However, the performance of the latest color copiers, such as

Table 13.2. North American Hard Copy Supply Product Groups' Revenues (in Millions of Retail Dollars)[a]

Supply product groups	1986	1991	Compound annual growth rate (%)
Ink-jet inks	18	226	67
Thermal ribbons	93	458	37
Transparencies	127	461	29
Specialty papers[b]	144	323	18
Toners/developers	972	1,532	10
Photoreceptors	1,576	2,387	9
Paper	4,619	6,793	8
Print elements	188	265	7
Impact ribbons	2,401	2,859	4
Business forms	4,558	5,537	4
Total	$14,696	$20,841	7

[a] Source: CAP International, Inc.
[b] Only includes thermal direct and dielectric revenues.

Canon's Laser Color Copier and Eastman Kodak's Color Edge, is good. A single pass color copying system such as photoactive pigment electrophoresis would improve the cost/speed elements and make color copying more competitive, but this is unlikely to be realized in the near future. There may be a trend to liquid toners for color copying (higher resolution) and to the use of dyes rather than pigments (transparency).

How does all this affect organic colorants? Quite well! The photoconductor usage will increase steadily from $1576 million in 1986 to $2387 million in 1991 (Table 13.2) and the majority of these will be organic photoconductors.[1] Even at these levels the charge generation material usage will only be several tonnes per annum and the charge transport material usage 50–100 tonnes per annum.

Toner production is predicted to increase from $972 million in 1986 to $1532 million in 1991 with the biggest increase in monocomponent toners ($335.6 million to $587.1 million).[1]

Carbon Black will remain the biggest colorant but yellow, magenta, and cyan colorants, especially dyes, will increase in line with color copying/printing.

Charge control agents (CCAs) will continue to be used but the trend will be towards a universal noncolored negative CCA and a universal noncolored positive CCA, preferably devoid of heavy metals. Such universal CCAs could be used in either black or colored toners.

13.3.4.2. Thermal

The thermal area encompasses three technologies: direct thermal, thermal wax transfer, and D2T2. None are truly primary processes. Direct thermal printing uses thermal paper containing color formers and an acidic coreactant whereas thermal wax transfer and D2T2 both employ a transfer ribbon.

Direct thermal printing is suited to monochrome (blue and especially black). It will continue to be used primarily in facsimile machines and will undergo a steady growth (Fig. 13.2). However, the unsuitability of direct thermal printing for producing full-color images combined with the stability problems of thermal paper both before (premature discoloration) and after printing (poor print durability, especially to light), will limit its long-term future. Mead's full-color CYCOLOR process is a related technology which employs pressure rather than heat to generate the image. Nonetheless, it utilizes color formers and therefore suffers the same disadvantages as thermal paper, particularly suspect light stability of the final image. This feature could restrict its usefulness.

Both thermal transfer processes will play major roles in the future of color hard copy. Thermal wax transfer will compete for the middle quality
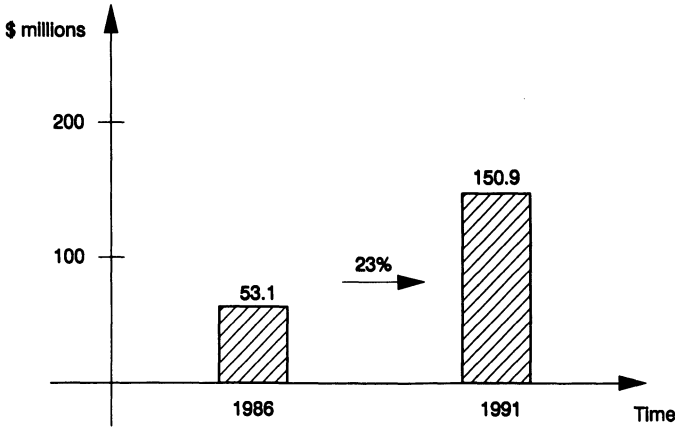
Figure 13.2. Projected growth of direct thermal printing.

area with the major competition coming from ink-jet. Major improvements will be made both in the quality of print on plain paper, speed, and transparency. Improved transparency, especially for overhead projector slides, will be achieved by using more transparent waxes and colorants. Color thermal transfer ribbons are predicted to have the second highest growth rate of all the reprographics consumables[1] (Fig. 13.3).

The newest thermal technology, D2T2, will capture most of the high quality color hard copy area because it is the only technology capable of producing continuous tones without loss of resolution and high print optical
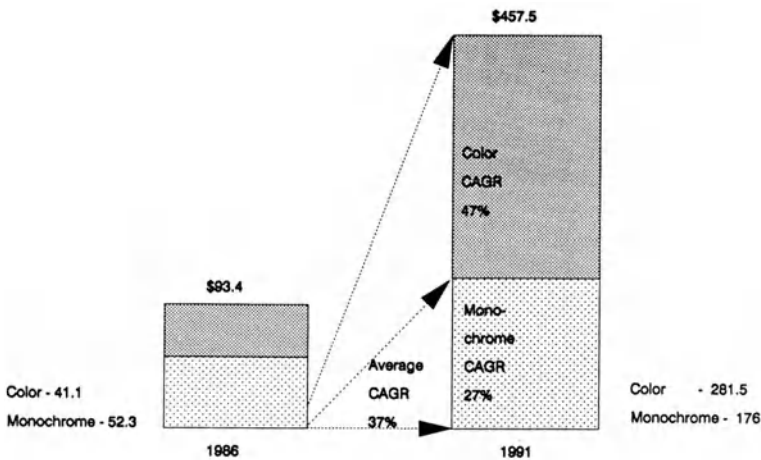
Figure 13.3. North American thermal ribbon revenues (in millions of retail dollars).

densities. Ultimately, D2T2 will capture a significant share of the conventional silver halide color photographic market once electronic photography becomes established.

Lasers could make as big an impact in the thermal technologies as they have in electrophotography. Using lasers instead of thermal heads to provide the heat energy offers several important advantages, namely increased speed, increased resolution, lower energy usage, and noncontact process. Relatively bulky lasers such as the YAG laser (1060 nm) have to be used at the moment to provide sufficient energy. The major breakthrough will occur when semiconductor lasers of the gallium–aluminum–arsenide type (780 and 830 nm) having sufficient power are developed. These low cost, compact, reliable devices would then be easily incorporated into a range of thermal printers. Infrared absorbers compatible with the laser output will be needed to convert the laser radiation into heat energy.

13.3.4.3. Ink-Jet

Ink-jet has the greatest potential of all the current technologies. It is a truly primary process (cf. electrophotography and thermal). Furthermore, it is also a noncontact process and can therefore print on any surface including plain paper. Ink-jet will be a major contender for the hard copy market both in the office and in industrial applications. It is well suited for producing both monochrome and color on almost any surface. Thermal drop-on-demand systems such as Hewlett Packard's Think Jet and Canon's Bubble Jet will be the dominant ink-jet office technology. They will compete with laser printers for monochrome output and thermal and electrophotographic for color output. Reliability has been a problem with ink-jet printers but improved hardware, including Hewlett Packard's disposable heads, and improved inks are overcoming this problem.

There will be a trend away from coated papers to plain paper. This will be led by black and followed later by color.

In the cost/speed/performance relationship ink-jet printers do not match laser printers in terms of speed and performance, although the gap is narrowing, but compensate for this by being of lower cost. In the color sector, ink-jet, particularly hot-melt ink-jet, will compete with thermal wax transfer and color copiers in the middle quality market. Ink-jet will not match the high quality produced by D2T2 for full-color prints.

In line with its potential, ink-jet printing has the largest predicted growth rate (67%) of all the reprographics technologies. The North American market for ink-jet inks is forecast to grow from $17.6 million in 1986 to $226.2 million in 1991, with the demand for colored inks being almost as great as that for monochrome inks[1] (Fig. 13.4).

Monochrome $9.5 m

Color $8.1 m

1986 Total: $17.6 m

Monochrome $116.6 m

Color $109.6 m

1991 Total: $226.2 m
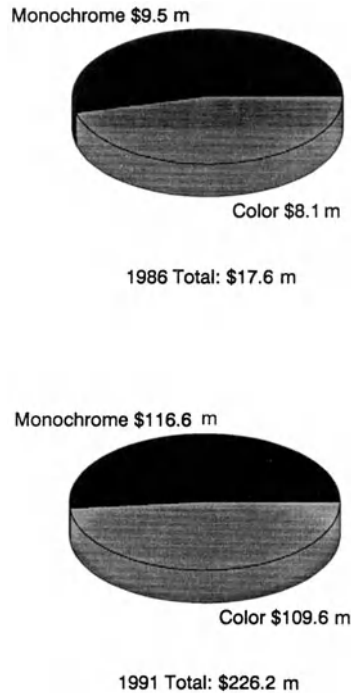
Figure 13.4. North American ink-jet revenues (in millions of retail dollars).

13.3.4.4. Other Technologies

Of the technologies known today ion deposition is likely to become a major competitor to both laser printing and ink-jet printing for monochrome output. It is a simpler technology than laser printing (closer to but not quite a primary printing process) and is capable of very high speeds. For example, experimental ion deposition printers can already produce 11 A4 pages per second. The quality is comparable to laser printers. However, once the electrophotographic, ink-jet, and thermal technologies become established in the marketplace, it will become increasingly difficult for other technologies to displace them.

13.4. TOXICOLOGY

The safety in use of products, particularly chemically based products, will become increasingly important and this means that new chemicals,

including organic colorants, will have to be safe. In essence, this means that all commercial candidates will have to pass a battery of toxicological tests and be registered in the major countries of the world (see *Chapter 12*). The associated high costs of such testing means that only those new chemicals which have special properties and are likely to be successful commercially will reach the marketplace.

13.5. SUMMARY

The future of organic colorants in hi-tech applications is inextricably linked to the future of the electronics and especially the reprographics industries. Nonimpact printing processes, such as electrophotographic, thermal transfer, and particularly ink-jet printing, will enjoy an increasing share of the hard copy market at the expense of the traditional impact printing technologies such as dot matrix and daisywheel. The usage of organic colorants in hi-tech applications will increase dramatically but the volumes will never approach those of traditional uses, such as imparting color to a substrate.

REFERENCE

1. C. E. Case, C. T. Ashley, and T. Largey, *Overview of the 1988 Electronic Imaging Supplies Marketplace*. The 1988 Datek Imaging Supplies Annual, pp. 6–22.

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