
PHOTOGRAPHIC MATERIALS

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30.1 INTRODUCTION

Photographic materials are optical devices. Their fabrication and technical understanding encompass the field of optics in the broadest sense. Light propagation, absorption, scattering, and reflection must be controlled and used efficiently within thin multilayer coatings containing tiny light-detecting silver halide crystals and chemistry. Many subdisciplines within classical optics, solid-state theory, and photochemistry describe these processes.

In Chap. 20 of Ref. 1, Altman sweeps broadly through the basic concepts and properties of photographic materials. His brief, high-level descriptions are still generally valid for today's photographic products, and the reader will profit by reviewing that summary. This chapter focuses more sharply on four fundamental photographic technologies intimately related to the broad field of optics, then gives an overview of photographic materials available today.

Section 30.2 discusses the optical properties of multilayer color photographic films and papers. This section outlines the basic structure of the device and describes the principal function of each layer. Light absorption, reflection, scattering, and diffraction properties are discussed in the context of providing minimum optical distortion to the final image.

Silver halide light detection crystals are solid-state devices described by quantum solid-state photophysics and chemistry in addition to crystallography. These devices absorb light to create an electron-hole pair. Delocalization of the electron in the conduction band of the crystal, trapping, reduction of interstitial silver ions, nucleation and growth of clusters of silver atoms, and reversible regression of these phenomena must be controlled and optimized to produce the most sensitive light detectors that also possess long-term stability.

Section 30.3 describes the basic photophysics of silver halides according to our best understanding today. It outlines the solid-state properties most important to image detection and amplification. Surface chemical treatment and internal doping are discussed in the context of providing silver halide emulsions having the highest sensitivity to light.

A color photographic image is formed by high-extinction and high-saturation dyes structurally designed by chemists to optimize their color, permanence, and other useful characteristics. Their properties in both the ground state and photoexcited states are important to color and stability.

Section 30.4 briefly outlines the photochemistry of photographic image dyes. Excited-state properties are described that are important to the photostability of these dyes for image permanence.

30.2 IMAGING DETECTORS

Color science guides us to optimize all factors in photographic materials conspiring to render an accurate and pleasing image. These include spectral discrimination during the light detection phase and color correction to compensate for imperfect spectral detection and imperfect image dyes.

Section 30.5 sketches the photophysics and color science of photographic spectral sensitizers with an aim toward describing how modern photographic films sense the world in color nearly as the human eye sees it.

Today there exists a large diversity of photographic films. In addition to different manufacturers' brands, films differ by speed, type, color attributes, format, and a multitude of other factors. This can be confusing. And what are the differences between a consumer film bought in a drugstore and a more expensive professional film?

Section 30.6 gives an overview of the different types of films available today. Differences between high- and low-speed films are described with an understanding of the origins of these differences. Consumer films are compared to professional films and some of the special needs of each type of customer are described. Some general guidelines are offered for film choices among color reversal films, black-and-white films, and color negative films.

In addition to Chap. 20 in Ref. 1, several other texts contain useful information about photographic materials. Kapecki and Rodgers² offer a highly lucid and digestible sketch of basic color photographic film technology. Besides Chap. 20 in Ref. 1, this is a good place for the technically astute but nonpractitioner to gain a high level understanding of basic color photography. The technically detailed treatise by James³ is perhaps the best single comprehensive source containing the science and technology of the photographic system outside photographic manufacturers' internal proprietary libraries. Hunt⁴ provides a good comprehensive treatise on all aspects of color science and additionally gives a good technical review of color photographic materials. Chapter 6 in Ref. 1 contains a useful overview of the theory of light-scattering by particles, Chap. 9 contains a good overview of optical properties of solids, and Chap. 26 on colorimetry provides a good introduction to the basic concepts in that field.

30.2 THE OPTICS OF PHOTOGRAPHIC FILMS AND PAPERS

Introduction

Color photographic materials incorporate design factors that optimize their performance across all features deemed important to customers who use the product. These materials are complex in composition and structure. Color films typically contain over 12 distinct optically and chemically interacting layers. Some of the newest professional color reversal films contain up to 20 distinct layers.* Each layer contributes a unique and important function to the film's final performance. Careful design and arrangement of the film's various layers ultimately determine how well the film satisfies the user's needs.

One very important customer performance feature is film *acutance*, a measure of the film's ability to clearly record small detail and render sharp edges. Because images recorded on color film are frequently enlarged, image structure attributes such as acutance are very important. Magnifications such as those used to place the image on a printed page challenge the film's ability to clearly record fine detail.

The ability of a photographic material to record fine detail and sharp edges is controlled by two factors. The first includes light scatter, diffraction, and reflections during the exposure step. These are collectively called *optical* effects. This factor dominates the film's ability to record fine detail and sharp edges and is therefore critical to the film's design.

*Fujichrome Velvia 50 RVP professional film.

Chemical adjacency effects collectively known as *Eberhard effects* (see Chap. 21 in Ref. 3) are the second factor. In today's color and black-and-white film products these are present during film development and are caused by accumulating development by-products such as iodide ions or inhibitors released by development inhibitor-releasing (DIR) chemicals that restrain further silver development in exposed regions of the image, leading to a chemical unsharp mask effect (pp. 274 and 365 of Ref. 4). These chemical signals also give rise to the film's interlayer interimage effects (HE; see p. 278 of Ref. 4) used for color correction. Film sharpness and HE are strongly related.

This section describes multilayer factors that contribute to light scatter, reflection, diffraction, and absorption in photographic materials. Factors that influence the nonoptical part of film acutance, such as Eberhard effects, were briefly reviewed by Altman.¹ More information about these processes can be found in references cited therein.

Structure of Color Films

Color film structures contain image-recording layers, interlayers, and protective overcoat layers. These layers suspend emulsions and chemistry in a hardened gelatin binder coated over a polyacrylate or polyester support. Figure 1 shows the principal layers in a color multilayer film structure.

The overcoat and ultraviolet (UV) protective layers contain lubricants; plastic beads 1 to 5 μm in size called *matte* to impart surface roughness that prevents sticking when the film is stored in roll form; UV-light-absorbing materials; and other ingredients that improve the film's handling characteristics and protect the underlying light-sensitive layers from damage during use and from exposure to invisible UV light. Ultraviolet light is harmful for two reasons: it will expose silver halide emulsions, thereby rendering an image from light invisible to humans, and it promotes photodecomposition of image dyes, leading to dye fade over time (p. 977 of Ref. 2). Visible light exposure must first pass through these overcoats, but they typically do little harm to acutance as they contain nothing that seriously scatters visible light.

The blue-light-sensitive yellow dye imaging layers appear next. Silver halides, with the exception of AgCl—used primarily in color papers—have an intrinsic blue sensitivity even when spectrally sensitized to green or red light. Putting the blue-light-sensitive layers on top avoids incorrect

Overcoat
UV protective layer
Fast yellow layer
Slow yellow layer
Yellow filter layer
Barrier layer
Fast magenta layer
Mid magenta layer
Slow magenta layer
Optional magenta filter layer
Barrier layer
Fast cyan layer
Mid cyan Layer
Slow cyan layer
AHU layer
Plastic support
Optional pelloid AHU layer

FIGURE 1 Simplified diagram showing the key layers in a color photographic film (not drawn to scale).

exposure leading to color contamination because a blue-light-absorbent yellow filter layer, located beneath the blue-sensitive imaging layers, absorbs all blue light that has passed completely through the blue-sensitive layers.

A collection of layers adjacent to one another that contain silver halide sensitized to a common spectral band is called a *color record*. Color records in films are always split into two or three separate layers. This arrangement puts the highest-sensitivity emulsion in the upper (fast) layer, where it gets maximum light exposure for photographic speed, and places low-sensitivity emulsions into the lower layer (or layers), where they provide exposure latitude and contrast control.

One or more interlayers separate the yellow record from the green-light-sensitive magenta record. These upper interlayers filter blue light to avoid blue light exposure color contaminating the red- and green-sensitive emulsion layers below. This behavior is called *punch through* in the trade. These interlayers also contain oxidized developer scavengers to eliminate image dye contamination between color records caused by oxidized color developer formed in one color record diffusing into a different color record to form dye.

The traditional yellow filter material is Carey Lea silver (CLS), a finely dispersed colloidal form of metallic silver, which removes most of the blue light at wavelengths less than 500 nm. The light absorption characteristics of this finely dispersed metallic silver are accounted for by Mie theory.⁵ Unfortunately this material also filters out some green and red light, thus requiring additional sensitivity from the emulsions below. Bleaching and fixing steps in the film's normal processing remove the yellow CLS from the developed image.

Some films incorporate a yellow filter dye in place of CLS. Early examples contained yellow dyes attached to a polymer mordant in the interlayer. A *mordant* is a polymer that contains charged sites, usually cationic, that binds an ionized anionic dye by electrostatic forces. These dyes are removed during subsequent processing steps. Although these materials are free from red and green light absorption, it is a challenge to make them high in blue light extinction to avoid excessive chemical loads in the interlayer with consequent thickening.

Most recently, solid-particle yellow filter dyes⁶ are seeing more use in modern films. These solid dyes are sized to minimize light scatter in the visible region of the spectrum and their absorption of blue light is very strong. They can be made with very sharp spectral cuts and are exceptionally well suited as photographic filter dyes. In some films solid-particle magenta filter dyes⁷ are also used in the interlayers below the magenta imaging layers. Solid-particle filter dyes are solubilized and removed or chemically bleached colorless during the film's normal development process.

Because the human visual system responds most sensitively to magenta dye density, the green-light-sensitive image recording layers are positioned just below the upper interlayers, as close as practical to the source light exposure side of the film. This minimizes green light spread caused when green light passes through the turbid yellow record emulsions. It gives the maximum practical film acutance to the magenta dye record.

A lower set of interlayers separates the magenta record from the red-light-sensitive cyan dye record. These lower interlayers give the same type of protection against light and chemical contamination as do the upper interlayers. The magenta filter dye is absent in some films because red-light-sensitive emulsions are not as sensitive to green light exposure as to blue light exposure.

Located beneath the cyan record, just above the plastic film support, are antihalation undercoat (AHU) layers. The black absorber contained in this bottom layer absorbs all light that has passed completely through all imaging layers, thereby preventing its reflection off the gel-plastic and plastic-air interfaces back into the imaging layers. These harmful reflections cause a serious type of light spread called *halation*, which is most noticeable as a halo around bright objects in the photographic image.

The opacity required in the AHU is usually obtained by using predeveloped black filamentary silver, called *gray gel*, which is bleached and removed during the normal photographic processing steps. Alternatively, in many motion picture films a layer of finely divided carbon suspended in gelatin (*rem jet*) is coated on the reverse side of the film. When placed in this position the layer is called an *AHU pelloid*. It is physically removed by scrubbing just before the film is developed. The newest motion picture films incorporate a black solid-particle AHU filter dye that is solubilized and removed during normal development of the film and does not require a separate scrubbing step.

The overall thickness of a film plays an important role in minimizing harmful effects from light scatter. Because color films are structured with the yellow record closest to the light exposure source, it is especially important to minimize thickness of all film layers in the yellow record and below it, because light scattered in the yellow record progressively spreads as it passes to lower layers. The cyan record shows the strongest dependence on film thickness because red light passes through both yellow and magenta record emulsions en route to the cyan record. Because both emulsions often contribute to red light scatter, the cyan record suffers a stronger loss in acutance with film thickness.

Structure of Color Papers

The optical properties of photographic paper merit special consideration because these materials are coated in very simple structures on a highly reflective white Baryta-coated paper support. *Baryta* is an efficient diffuse reflector consisting of barium sulfate powder suspended in gelatin that produces isotropically distributed reflected light with little absorption.

Photographic papers generally contain about seven layers. On top are the overcoat and UV protective layers, which serve the same functions as previously described for film.

The imaging layers in color papers contain silver chloride emulsions for fast-acting development, which is important to the industry for rapid throughput and productivity. Generally only one layer is coated per color record, in contrast to films, which typically contain two or three layers per color record. The order of the color records in photographic papers differs from that in films due mainly to properties of the white Baryta reflective layer.

Because color paper is photographically slow, exposure times on the order of seconds are common. Most light from these exposures reflects turbidly off the Baryta layer. The imaging layers getting the sharpest and least turbid image are those closest to the reflective Baryta where light spread is least, not those closest to the top of the multilayer as is the case with film.

In addition, the Baryta layer as coated is not smooth. Its roughness translates into the adjacent layer, causing nonuniformities in that layer. Because the human visual system is most forgiving of physical imperfections in yellow dye, the yellow color record must be placed adjacent to the Baryta to take the brunt of these imperfections.

The magenta color record is placed in the middle of the color paper multilayer, as close to the Baryta layer as possible, since sharpness in the final image is most clearly rendered by magenta dye. This leaves the cyan record nearest to the top of the structure, just below the protective overcoats.

The magenta color record in the middle of the multilayer structure is spaced apart from the other two color records by interlayers containing oxidized developer scavengers to prevent cross-record color contamination, just as in films. However, no filter dyes are needed in color paper because silver chloride emulsions have no native sensitivity to light in the visible spectrum.

Light Scatter by Silver Halide Crystals

Because they consist of tiny particles, silver halide emulsions scatter light. Scattering by cubic and cubo-octahedral emulsions at visible wavelengths is most intense when the emulsion dimension ranges from 0.3 to 0.8 μm , roughly comparable to the wavelengths of visible light. This type of scattering is well characterized by Mie⁸ theory and has been applied to silver halides.⁹ We are often compelled to use emulsions having these dimensions in order to achieve photographic speed.

For photographic emulsions of normal grain size and concentration in gelatin layers of normal thickness, multiple scattering predominates. This problem falls within the realm of radiative transfer theory. Pitts¹⁰ has given a rigorous development of radiative transfer theory to the problem of light scattering and absorption in photographic emulsions. A second approach that has received serious attention is the Monte Carlo technique.¹¹ DePalma and Gasper¹² were able to obtain good agreement between their modulation transfer functions (MTFs) determined by a Monte Carlo calculation and experimentally measured MTFs for a silver halide emulsion layer coated at various thicknesses.

Scattering by yellow record emulsions is especially harmful because red and green light must first pass through this record en route to the magenta and cyan records below. All other things being equal, the amount of light scattered by an emulsion layer increases in proportion to the total amount of silver halide coated in the layer.

Color films are constructed with low-scattering yellow record emulsions whenever possible. The amount of silver halide coated in the yellow record is held to a minimum consistent with the need to achieve the film's target sensitometric scale in yellow dye.

High-dye-yield yellow couplers¹³ having high coupling efficiency are very useful in achieving silver halide mass reductions in the yellow record of color reversal films. These provide high yellow dye densities per unit silver halide mass, thereby reducing the amount of silver halide needed to achieve target sensitometry. Some upper-scale (high-density) increase in granularity often results from using these couplers in a film's fast yellow layer, but the benefits of reduced red and green light scatter overcome this penalty, especially because the human visual system is insensitive to yellow dye granularity.

Tabular emulsion grains offer a way to achieve typical photographic speeds using large-dimension emulsions, typically 1.0 to 3.0 μm in diameter, although smaller- and larger-diameter crystals are sometimes used. These do not scatter light as strongly at high angles from normal incidence with respect to the plane of the film as do cubic or octahedral emulsions having comparable photographic speeds. However, diffraction at the edges and reflections off the crystal faces can become a detrimental factor with these emulsions.

Silver halide tabular crystals orient themselves to lie flat in the plane of the gelatin layer. This happens because shear stress during coating of the liquid layer stretches the layer along a direction parallel to the support and also because the water-swollen thick layer compresses flat against the support after it dries by a ratio of roughly 20:1.

Reflections can become especially harmful with tabular emulsion morphologies since light reflecting from the upper and lower faces of the crystal interferes, leading to resonances in reflected light. The most strongly reflected wavelengths depend on the thickness of the tabular crystal. The thickness at which there is a maximum reflectance occurs at fractional multiples of the wavelength¹⁴ given by:

$$t = \frac{\left(m + \frac{1}{2}\right)\lambda}{2n}$$

where t is the thickness of the tabular crystal, λ is the wavelength of light, n is the refractive index of the crystal, and m is an integer.

In an extreme case, tabular emulsions act like partial mirrors reflecting light from grain to grain over a substantial distance from its point of origin. This is called *light piping* by analogy with light traveling through an optical fiber (see Fig. 2). It is especially serious in the cyan record, where red light often enters at angles with respect to perpendicular incidence caused by scattering in upper layers.

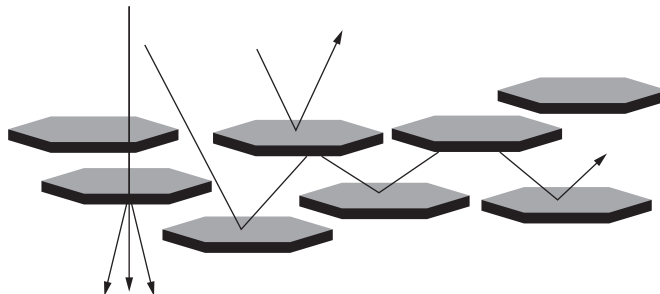


FIGURE 2 Light undergoes reflection, diffraction, and multiple reflections that may lead to light piping in film layers containing tabular silver halide crystals.

Another cause of light piping is the presence of small-grain emulsion contaminants within a tabular grain population. A highly turbid contaminant emulsion, even if present in small amounts, can scatter light at sufficient angles to induce severe light piping through the tabular grain matrix. Modern emulsion science takes great pains to produce tabular emulsions free from highly scattering contaminants.

Gaspar¹⁵ treated the problem of scattering from thin tabular silver halide crystals in a uniform gelatin layer. For very thin and large-diameter tabular silver bromide crystals (thickness $<0.06\text{ }\mu\text{m}$, diameter $>1.0\text{ }\mu\text{m}$) light at normal incidence is scattered almost equally in the forward and backward hemispheres. As the grain thickness increases there appears increasing bias for forward scatter in a narrow cone. The efficiencies for scatter and absorption were found to be independent of grain diameter for crystal diameters larger than $\sim 1.0\text{ }\mu\text{m}$. For such crystals, the backscatter and absorption efficiencies are approximately equal to the specular reflectance and absorption of a semiinfinite slab of the same material and thickness.

But the forward scattering efficiency does not approximate the specular transmittance of the semiinfinite slab as a result of interference between the directly scattered forward field and the mutually coherent unscattered field, a process analogous to diffraction that does not occur for the semiinfinite slab with no edge. The specific turbidity depends on grain thickness, but not diameter for diameter $>1.0\text{ }\mu\text{m}$.

A light-absorbing dye is sometimes added to a film to reduce the mean free path of scattered and reflected light leading to an acutance improvement. This improvement happens at the expense of photographic speed, since light absorbed by the dye is not available to expose the silver halide emulsions. However, the trade-off is sometimes favorable if serious light piping is encountered.

Light-absorbing interlayers between color records are sometimes used in color films to help eliminate the harmful effects of reflected light. For example, some films have a magenta filter dye interlayer between the magenta and cyan records. In addition to its usefulness in reducing light punchthrough (green light passing through the magenta record to expose the red-sensitized layers), this filter layer helps eliminate harmful reflections of green light off cyan record tabular emulsions, which bounce back into the magenta record. These reflections, although potentially useful for improving photographic green speed, can be harmful to magenta record acutance.

30.3 THE PHOTOPHYSICS OF SILVER HALIDE LIGHT DETECTORS

Chapter 20 in Ref. 1 gave a very brief sketch of the general characteristics of silver halide crystals used for light detection and amplification in photographic materials. These crystals, commonly termed *emulsions*, are randomly dispersed in gelatin binder layers in photographic films and papers. For photographic applications the most commonly used halide types are AgCl, AgBr, and mixed halide solid solutions of $\text{AgCl}_{x_y}\text{I}_{1-y}$ and $\text{AgBr}_{x_y}\text{I}_{1-y}$. In addition, pure phases of AgCl and AgI are sometimes grown epitaxially on AgBr crystals to impart special sensitivity and development properties.

Upon exposure to light, silver halide crystals form a latent image (LI) composed of clusters of three to hundreds of photoreduced silver atoms either within the interior or most usefully on the surface of the crystal where access by aqueous developing agents is easiest.* Higher light exposures result in larger numbers of silver atoms per latent image cluster on average in addition to exposing a larger number of crystals on average.

The detection of light by a silver halide crystal, subsequent conversion to an electron hole pair, and ultimate reduction of silver ions to metallic silver atoms is in essence a solid-state photophysical process. The application of solid-state theory to the photographic process began with Mott and

*Some specialized developing agents can etch into the silver halide crystal to develop the internal latent image (LI), but the most commonly used color negative and color paper developers have little capability to do this. They are primarily surface-developing agents. The color reversal black-and-white developer can develop slightly subsurface LI in color reversal emulsions.

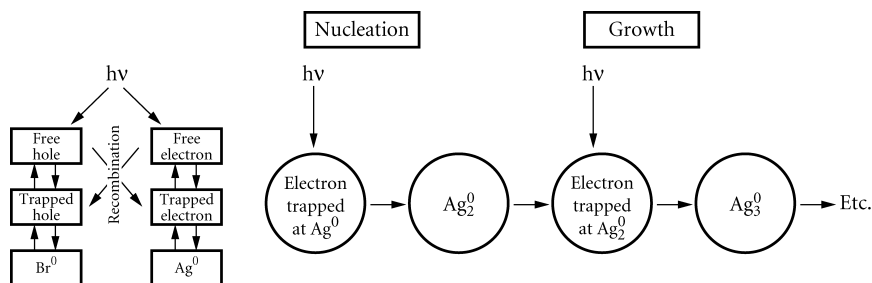


FIGURE 3 Diagram showing the basic features of the nucleation and growth mechanism for formation of a developable latent image site by light exposure of a silver halide crystal.

Gurney¹⁶ and was extended by Seitz.¹⁷ Additional reviews were published^{18–20} as our understanding of these processes grew.

According to the nucleation and growth mechanism,¹⁸ the photographic LI forms through a series of reversible electronic and ionic events (see Fig. 3). An electron is generated in the conduction band either by direct band gap photoexcitation of the crystal in its intrinsic spectral absorption region or by injection from a photoexcited spectral sensitizing dye on the crystal's surface. As this mobile electron travels through the crystal it becomes shallowly and transiently trapped at lattice imperfections carrying a positive charge. The ionized donor may be an interstitial silver ion or a surface defect. The kinked edge of a surface terrace, having a formal charge of $+1/2$ is one such site.

The electron may sample many such traps before becoming more permanently trapped at a preferred site. Trapping of the electron occurs in less than 0.1 ns at room temperature.²¹ The shallowly trapped electron orbits about the trapping site in a large radius. At this stage the formal charge of the trap site becomes $-1/2$ and adjacent surface lattice ions relax, thereby increasing the depth of the trap.²² In octahedral AgBr emulsions this shallow-deep transition occurs within 10 ns at room temperature.²¹

The negative charge formally associated with the trapped electron attracts a mobile interstitial Ag^+ ion, which the trapped electron reduces to an Ag^0 atom. The site's charge reverts to $+1/2$. A second photoelectron is then trapped at the site and reacts with a second interstitial Ag^+ ion to form Ag_2^0 and so on as additional photons strike the crystal. Frenkel defect concentrations—interior plus surface—in the range of $10^{14}/\text{cm}^3$ have been reported for AgBr crystals.¹⁹ Latent image formation depends critically upon the existence of partially charged defects on the surface of the crystal.

Because the single-atom Ag^0 state is metastable and the Ag_2^0 state is not usefully detectable from gross fog by developing solutions (Chap. 4 of Ref. 3), a minimum of three photons must strike the crystal to form a detectable LI site, the second photon within the lifetime of the metastable trapped Ag^0 atom.* The transient existence of one or two silver atom sites has not been directly observed but is strongly inferred by indirect evidence.²⁰

The highest photoefficiencies are achieved after silver halide emulsions are heated with aqueous sulfur and gold salts to produce Ag_2S and AgSAu species on the surface of the crystal.²² Most of the evidence for sulfur sensitization suggests these sites improve electron trapping, perhaps by making trapping lifetimes longer at preexisting kink sites. Gold sensitization accomplishes at least two things: it reduces the size of the latent image center needed to catalyze development and it stabilizes silver atoms formed during the exposure process (Chap. 5 of Ref. 3).

Ideally only a single latent image site forms per exposed silver halide crystal. If more sites nucleate on a crystal, these can compete for subsequent photoelectrons, leading to losses in efficiency related to LI dispersity. One remarkable aspect of this process is that despite the large number of

*A metastable silver atom may dissociate back into an electron-hole pair, and the electron can migrate to another trapping site to form a new silver atom. This may happen many times in principle. The second electron must encounter the silver atom before electron-hole recombination or other irreversible electron loss takes place.

kink sites and chemically sensitized sites on a given crystal, in the most efficient silver halide emulsions only a single LI center forms per grain. The shallow-deep transition that occurs after the initial electron trapping selects one preferred defect out of the plethora of other possibilities for subsequent electron trapping.

The two predominant crystal faces that occur on photographically useful silver halide grains are [100] and [111]. Both surfaces have a negative charge²³ ranging from -0.1 to -0.3 V. A subsurface space charge layer rich in interstitial Ag^+ ions compensates for the charged surface.²⁴ The [100] surfaces are flat with steps containing jogs that are either positively or negatively charged kink sites. The positive kinks on the surface form shallow electron traps.

In contrast, the [111] surface is not well characterized and is believed to be sensitive to surface treatment. Calculations of surface energies suggest that several arrangements may coexist, including microfaceted [100] planes and half layers of all silver or all halide ions in arrangements with hexagonal symmetry.^{24,25}

All silver halides absorb light in the near-UV region of the spectrum. The absorption edge extends to longer wavelengths from AgCl to AgBr to AgI. AgCl and AgBr have indirect band gap energies of 3.29 and 2.70 eV, respectively.¹⁹ Absorption of light produces electrons in a conduction band whose minimum lies at the zone center and holes in the valence band whose maximum is at an L point. Carriers produced at excess energy rapidly thermalize at room temperature since electron mobility is limited by phonon scattering.

Electron mobility in AgBr is about $60 \text{ cm}^2/\text{Vs}$ at room temperature.¹⁹ In AgCl the hole mobility is low, but in AgBr it is substantial—only about a factor of 30 lower than electron mobility.²⁰ Carriers generated by exposure will explore the crystal in a random walk as they scatter off phonons and transiently trap at charged defects. It is expected that electrons can fully sample a $1\text{-}\mu\text{m}$ crystal within less than $1 \mu\text{s}$.

In most commercial photographic materials today, only about 25 percent to 50 percent of the electrons injected into the crystal's conduction band contribute to a developable LI site. The rest are wasted through electron-hole recombination, formation of internal LI that is inaccessible to the developing agent, or formation of multiple nucleation sites termed *dispersity*. The deliberate addition of dopants that act as shallow electron traps reduces the time electrons spend in the free carrier state and thereby limits their propensity to recombine with trapped holes.

Polyvalent transition metal ions are frequently doped into silver halide crystals to limit reciprocity effects, control contrast, and reduce electron hole recombination inefficiencies.²⁶ They act as electron or hole traps and are introduced into the crystal from aqueous hexa-coordinated complexes during precipitation. They generally substitute for $(\text{AgX}_6)^{5-}$ lattice fragments. Complexes of Ru and Ir have been especially useful. Because the dopant's carrier-trapping properties depend on the metal ion's valence state and the stereochemistry of its ligand shell, there are many opportunities to design dopants with specific characteristics. Dopants incorporating Os form deep electron traps in AgCl emulsions with an excess site charge of +3. An effective electron residence lifetime of 550 seconds has been measured for these dopants at room temperature.²⁰ They are used to control contrast at high-exposure regions in photographic papers.

Quantum sensitivity is a measure of the average number of photons absorbed per grain to produce developability in 50 percent of an emulsion population's grains (Chap. 4 in Ref. 27). This microscopic parameter provides a measure of the photoefficiency of a given emulsion; the lower the quantum sensitivity value, the more efficient the emulsion. The quantum sensitivity measurement gives a cumulative measure of latent image formation, detection, and amplification stages of the imaging chain.

Quantum sensitivity has been measured for many emulsions. The most efficient emulsions specially treated by hydrogen hypersensitization yield a quantum sensitivity of about three photons per grain.²⁸ Although hydrogen hypersensitization is not useful for general commercial films because it produces emulsions very unstable toward gross fog, this sensitivity represents an ambitious goal for practical emulsions used in commercial photographic products. The most efficient practical photographic emulsions reported to date have a quantum sensitivity of about five to six photons per grain.²⁹ The better commercial photographic products in today's market contain emulsions having quantum sensitivities in the range of 10 to 20 photons per grain.

30.4 THE STABILITY OF PHOTOGRAPHIC IMAGE DYES TOWARD LIGHT FADE

Introduction

Azomethine dyes are formed in most photographic products by reaction between colorless couplers and oxidized *p*-phenylenediamine developing agents to form high-saturation yellow, magenta, and cyan dyes (Chap. 12 in Ref. 3). Typical examples are shown in Fig. 4. The diamine structural element common to all three dyes comes from the developing agent, where R_1 and R_2 represent alkyl groups. The R group extending from the coupler side of the chromophore represents a lipophilic ballast, which keeps the dye localized in an oil phase droplet. In some dyes it also has hue-shifting properties.

Heat, humidity, and light influence the stability of these dyes in photographic films and papers.³⁰ Heat and humidity promote thermal chemical reactions that lead to dye density loss. Photochemical processes cause dyes to fade if the image is displayed for extended periods of time. Ultraviolet radiation is especially harmful to a dye's stability, which is partly why UV absorbers are coated in the protective overcoat layers of a color film or paper.

Stability toward light is especially important for color papers, where the image may be displayed for viewing over many years. It is less important in color negative film, which is generally stored in the dark and where small changes in dye density can often be compensated for when a print is made. Light stability is somewhat important for color reversal (slide and transparency) film, since a slide is projected through a bright illuminant, but projection and other display times are short compared to values for color papers. A similar situation exists for movie projection films, where each frame gets a short burst of high-intensity light but the cumulative exposure is low.

Evaluation of the stability of dyes toward light is difficult because the time scale of the photochemical reactions, by design, is very slow or inefficient. The quantum yields of photochemical fading of photographic dyes, defined as the fraction of photoexcited dyes that fade, are on the order of 10^{-7} or smaller.^{2,31} Accelerated testing using high-intensity illumination can sometimes give misleading results if the underlying photochemical reactions change with light intensity (p. 266 in Ref. 4).

Given that dyes fade slowly over time, it is best if all three photographic dyes fade at a common rate, thereby preserving the color balance of the image (p. 267 in Ref. 4). This rarely happens. The perceived light stability of color photographic materials is limited by the least stable dye. Historically, this has often been the magenta dye, whose gradual fade casts a highly objectionable green tint to a picture containing this dye. This is most noticeable in images containing memory colors, such as neutral grays and skin tones.

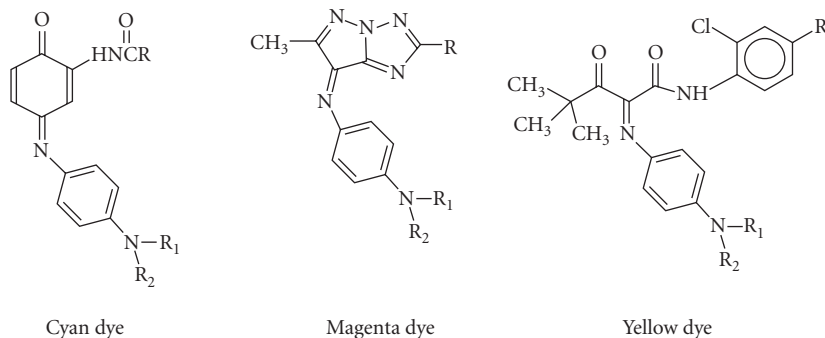


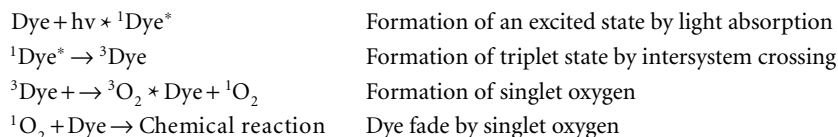
FIGURE 4 Typical examples of azomethine dyes used in photographic materials.

Photochemistry of Azomethine Dyes

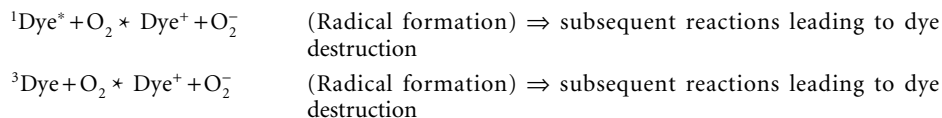
Upon absorption of a photon, a dye becomes reversibly excited to the singlet state. For azomethine dyes, the lifetime of the excited state is estimated to be on the order of picoseconds.^{32–39} Similarly, the lifetime of the triplet state of azomethine dyes, which is expected to form rapidly by intersystem crossing from the singlet excited state, has been estimated to be in the nanosecond range.³⁶ The short lifetime of these species seems to be at the basis of the observed low quantum yields of photochemical fading of azomethine dyes.

The nature of the initial elementary reactions involving excited or triplet states of dyes is not well understood. For some magenta dyes, the fading mechanism was reported to be photooxidative.³⁷ Cyan dye light fade appears to involve both reductive and oxidative steps³⁸ following photoexcitation of the dye.

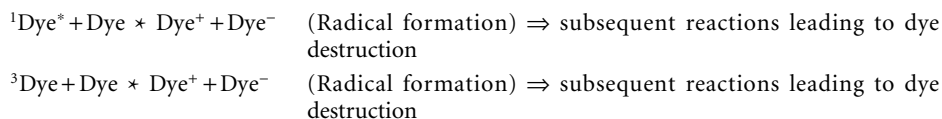
Singlet oxygen has been traditionally postulated to be involved in the oxidative pathway.³⁹ This high-energy species can, in principle, be formed by energy transfer between a triplet dye and molecular oxygen, and can subsequently induce dye destruction, although reaction with singlet oxygen does not always lead to decomposition.⁴⁰



Studies of the photophysical properties of photographic dyes, however, have shown that in general, azomethine dyes are good quenchers of singlet oxygen.⁴¹ This implies that the formation of singlet oxygen by the triplet state of the dyes should be inefficient. An alternative feasible role for molecular oxygen in dye fade involves electron transfer mechanisms.



The chemistry of dye fade may also be started by electron transfer between excited or triplet dye and a dye molecule in its ground state.



Excited State Properties

The few papers that have been published about excited singlet-state properties of azomethine dyes have mainly focused on pyrazolotriazole magenta dyes.^{32–35} These dyes have fluorescence quantum yields on the order of 10^{-4} at room temperature, but increase to ~ 1 in rigid organic glasses at 77 K.⁴⁰ The fluorescence quantum yield is the fraction of photoexcited molecules that emit a quantum of light by fluorescence from an excited state to the ground state having the same multiplicity (usually singlet to singlet). The results at room temperature imply singlet-state lifetimes of only a few picoseconds.⁴⁰

Room-temperature flash photolysis has identified a very short-lived fluorescent state plus a longer-lived nonfluorescent transient believed to be an excited singlet state whose structure is twisted compared to the ground state. This is consistent with the temperature-dependent results that allow rapid conformational change to the nonfluorescent singlet species at room temperature,

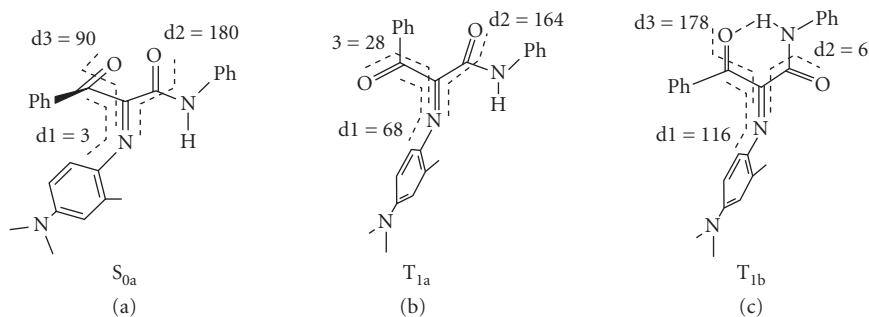


FIGURE 5 (a) Ground state conformation and (b and c) two conformations of the lowest triplet state.

in addition to intersystem crossing to the triplet excited state. But this conformational change is presumably restrained in a cold organic glass matrix, thereby allowing the excited singlet state time to fluoresce back to the ground state.

Investigation of the triplet states of azomethine dyes has proven difficult, and there are no definitive reports of direct observation of the triplet states. There are no reliable reports of phosphorescence from the triplet state of these dyes, although they have been studied by flash photolysis.^{32–35,41–45} Using indirect energy transfer methods, triplet lifetimes have been estimated to be less than 10 ns.³⁶ Similar studies⁴³ gave triplet energies of 166 to 208 kJ mol^{−1} for yellow dyes, 90 to 120 kJ mol^{−1} for magenta dyes, and about 90 kJ mol^{−1} for cyan dyes.

Computational studies have been carried out recently on the ground and lowest triplet states of yellow azomethine dyes.⁴⁵ Consistent with crystallographic studies,^{46,47*} the calculated lowest-energy ground state conformation S_0 is calculated to have the azomethine C=N bond coplanar with the anilide C=O carbonyl, but perpendicular to the C=O carbonyl of the ketone. The energy of the vertical transition triplet state having this conformation is quite high, calculated to be 230 kJ mol^{−1} above the ground state. Energy minimization on the lowest triplet energy surface starting with the geometry of S_0 results in a relaxation energy of 100 kJ mol^{−1} and leads to T_{1a} , characterized by a substantial twist around the C=N bond and by increased planarity of the keto carbonyl with the azomethine plane. These conformational changes offer an efficient mechanism for stabilizing the lowest triplet state in these dyes. A second triplet conformer T_{1b} with an energy 25 kJ mol^{−1} below T_{1a} was also calculated (see Fig. 5).

The low energy values calculated for T_{1a} and T_{1b} relative to S_{0a} (130 and 105 kJ mol^{−1}, respectively) have led to a new interpretation of the reported results⁴³ of energy transfer to S_{0a} . Using the nonvertical energy transfer model of Balzani,⁴⁸ it is shown that observed rates of energy transfer to S_{0a} can be consistent with formation of two distinct triplet states: one corresponding to a higher-energy excited triplet state (T_2) 167 kJ mol^{−1} above S_{0a} , and the second corresponding to one conformation of the lowest triplet state (T_1) with an energy of 96 kJ mol^{−1} above S_{0a} , in good agreement with the calculated T_{1b} configuration. The large structural differences between S_{0a} and the conformers of T_1 can explain the lack of phosphorescence in this system.

Light Stabilization Methods

Stabilization methods focus on elimination of key reactants (such as oxygen by various barrier methods), scavenging of reactive intermediates such as free radicals transiently formed during photodecomposition, elimination of ultraviolet light by UV absorbers, or quenching of photoexcited species in the reaction sequence.

*Other unpublished structures exhibiting the same conformation of S_{0a} have been solved at Kodak.

Stabilizer molecules⁴⁹ have been added to photographic couplers to improve the stability of their dyes toward light fade. Although the exact mode by which these stabilizers operate has not been disclosed, it is probable that some quench the photoexcited state of the dyes, thereby preventing further reaction leading to fading; some scavenge the radicals formed during decomposition steps; and some may scavenge singlet oxygen.

Polymeric materials added to coupler dispersions also stabilize dyes. These materials are reported to improve thermal dye decomposition⁵⁰ by physically separating reactive components in a semi-rigid matrix or at least decreasing the mobility of reactive components within that matrix. They may provide benefits for light stability of some dyes by a similar mechanism.

Photographic dyes sometimes form associated complexes or microcrystalline aggregates (p. 322 of Ref. 4). These have been postulated to either improve light stability by electronic-to-thermal (phonon) quenching of excited states, or to degrade light stability by concentrating the dye to provide more available dye molecules for reaction with light-induced radicals. Both postulates may be correct depending upon the particular dyes.

Modern photographic dyes have vastly improved light stabilities over dyes of the past. For example, the magenta dye light stability of color paper dyes has improved by about two orders of magnitude between 1942 and the present time.⁵¹ New classes of dyes^{52,53} have proved especially resistant to light fade and have made memories captured by photographic materials truly archival.

30.5 PHOTOGRAPHIC SPECTRAL SENSITIZERS

Introduction

Spectral sensitizing dyes are essential to the practice of color photography. In 1873, Vogel⁵⁴ discovered that certain organic dyes, when adsorbed to silver halide crystals, extend their light sensitivity to wavelengths beyond their intrinsic ultraviolet-blue sensitivity. Since then, many thousands of dyes have been identified as silver halide spectral sensitizers having various degrees of utility, and dyes exist for selective sensitization in all regions of the visible and near-infrared spectrum. These dyes provide the red, green, and blue color discrimination needed for color photography.

The most widely used spectral sensitizing dyes in photography are known as *cyanine dyes*. One example is shown in Fig. 6. These structures are generally planar molecules as shown.

A good photographic spectral sensitizing dye must adsorb strongly to the surface of the silver halide crystal. The best photographic dyes usually self-assemble into aggregates on the crystal's surface. Aggregated dyes may be considered partially ordered two-dimensional dye crystals.⁵⁵ Blue-shifted aggregates are termed *H-aggregates*, while red-shifted ones, which generally show spectral narrowing and excitonic behavior, are termed *J-aggregates*. Dyes that form J-aggregates are generally most useful as silver halide spectral sensitizers.

A good sensitizing dye absorbs light of the desired spectral range with high efficiency and converts that light into a latent image site on the silver halide surface. The relative quantum efficiency⁵⁶ of sensitization is defined as the number of quanta absorbed at 400 nm in the AgX intrinsic absorption region to produce a specified developed density, divided by the number of like quanta absorbed only by dye within its absorption band. For the best photographic sensitizing dyes this number is only slightly less than unity.

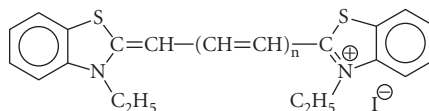


FIGURE 6 Typical cyanine spectral sensitizing dye used in photographic materials.

Adsorption isotherms for J-aggregated cyanine dyes on AgX follow Langmuir behavior with a saturation coverage that indicates closely packed structures.⁵⁷ The site area per molecule derived from the Langmuir isotherms implies dye adsorption along its long axis with heterocyclic rings perpendicular to the surface. Recent scanning tunneling microscope work^{58,59} has convincingly detailed the molecular arrangement within these aggregates, confirming general expectations.

The Photophysics of Spectral Sensitizers on Silver Halide Surfaces

Sensitizing dyes transfer an electron from the dye's excited singlet state to the conduction band of AgX. Evidence for this charge injection comes from extensive correlations of sensitization with the electrochemical redox properties of the dyes.^{22,60,61} In the adsorbed state a good sensitizing dye has an ionization potential smaller than that of the silver halide being sensitized. This allows the energy of the dye excited state to lie at or above the silver halide conduction band even though the energy of the photon absorbed by the dye is less than the AgX band gap. Dye ionization potentials are generally well correlated with their electrochemical oxidation potentials.

The triplet energy level of a typical cyanine dye lies about 0.4 to 0.5 eV (about 35 to 50 kJ mol⁻¹) below the radiationally excited singlet level.⁶² In most cases, this triplet state seems to have little effect on spectral sensitization at room temperature, although it may influence sensitization in special cases.⁶³

Electron transfer takes place by tunneling from the excited-state dye to the silver halide conduction band. Simple calculations verify that penetration of the potential barrier will compete favorably with de-excitation of the dye by fluorescence emission (p. 253 of Ref. 3). The interaction time between an excited spectral sensitizer and silver bromide appears to occur between 10⁻¹³ and 10⁻¹⁰ (p. 237 of Ref. 3). Factors favoring irreversible flow of electrons from dye to silver halide are delocalization within the conduction band, the negative space charge layer on the surface of the crystal, trapping by remote sites on the silver halide surface, and irreversible trapping to form a latent image.

Free electrons from dye sensitization appear in the silver halide conduction band having the same mobility and lifetime as those formed by intrinsic absorption. These electrons participate in latent image formation by the usual mechanism.

After electron transfer, the oxidized dye radical cation becomes the hole left behind. Because there is evidence that a single dye molecule may function repeatedly,⁶⁴ the dye cation "hole" must be reduced again. This can occur by electron tunneling from an occupied site on the crystal's surface, whose energy level is favorable for that process. A bromide ion at a kink is one such site. This leaves a trapped hole on the crystal surface that may be thermally liberated to migrate through the crystal. This hole can lead to conduction band photoelectron loss by recombination. A supersensitizer molecule (discussed later) may also trap the hole.

The formation of the J-aggregate exciton band has significant effects on the excited-state dynamics of the dye. There is the possibility of coherent delocalization of the exciton over several molecules in the aggregate.⁶⁵ The exciton is mobile and can sample over 100 molecules within its lifetime.⁶⁶ This mobility means that the exciton is sensitive to quenching by traps within the aggregate structure. The overall yield of sensitization generally increases to maximum, then decreases somewhat as the aggregate size increases. Optimum sensitizations usually occur below surface monolayer coverage.

Sometimes the spectral sensitivity of a dye is increased by addition of a second substance. If the added sensitivity exceeds the sum of both sensitizers individually, the increase is super-additive and the second substance is called a *supersensitizer*. Maximum efficiency of a supersensitizer often occurs in the ratio of about 1:20 where the supersensitizer is the dilute component.

The supersensitizer may increase the spectral absorption of the sensitizer by inducing or intensifying formation of a J-aggregate. In some cases these changes are caused by a mutual increase in adsorption to the grain surface, as when the sensitizer and supersensitizer are ions of opposite charge.⁶⁷ However, the most important supersensitizers appear to increase the fundamental efficiency of spectral sensitization as measured by the relative quantum yield.

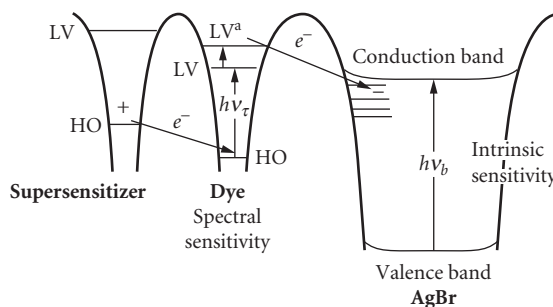


FIGURE 7 Simplified energy level diagram for a spectral sensitizer dye plus a supersensitizer dye adsorbed to a silver bromide surface.

The low concentration of supersensitizer relative to sensitizer suggests trapping of an exciton moving through the quasicrystalline array of J-aggregated sensitizer molecules. One hypothesis is that the supersensitizer molecule traps the exciton, providing a site for facile electron transfer into the silver halide.⁶⁸

Gilman and coworkers^{69–72} proposed that the supersensitization of J-aggregating dyes takes place via hole trapping by the supersensitizer molecules. The exciton moving through the aggregate may be self-trapped at a site adjacent to a supersensitizer molecule. By hypothesis, the highest occupied (HO) electron energy level of the supersensitizer is higher than that of the partially empty HO level of the excited sensitizer molecule. An electron transfers from the supersensitizer to the sensitizer molecule. The sensitizer is reduced to an electron-rich, anion-free radical while the supersensitizer is oxidized to an electron-deficient cation radical of lower energy than the original hole, thereby localizing the hole on the supersensitizer (see Fig. 7).

Following electron transfer from the supersensitizer, the electron-rich free radical anion left on the sensitizer will possess an occupied electron level of higher energy than the excited level of the parent sensitizer. The reduction process thereby raises the level of the excited electron with respect to the conduction band of AgX, with a consequent increase in probability of electron tunneling into the silver halide conduction band.

The various proposed mechanisms of supersensitization are not mutually exclusive. Exciton trapping and hole trapping may operate together. Underlying all mechanisms are the roles of exciton migration throughout the aggregate, its interruption at or near the supersensitizer site, and a more facile transfer of the electron into the AgX conduction band at that localized state.

Spectral sensitizing dyes, especially at high surface coverage, desensitize silver halides in competition with their sensitization ability. Red spectral sensitizers generally desensitize more than green or blue spectral sensitizers do. Desensitization can be thought of as reversible sensitization. For example, a mobile conduction band electron can be trapped by a dye molecule to form a dye radical anion⁷³ or by reduction of a hole trapped on the dye.^{63,74–76} Under normal conditions of film use (not in a vacuum), a dye radical anion may transfer the excess electron irreversibly to an O₂ molecule with formation of an O₂^{•-} anion. Either postulate leads to irreversible loss of the photoelectron and consequent inefficiency in latent image formation.

Color Science of Photographic Spectral Sensitizers

Human vision responds to light in the range of 400 to 700 nm. The human eye is known to contain two types of light-sensitive cells termed *rods* and *cones*, so named because of their approximate shapes. Cones are the sensors for color vision. There is strong evidence for three types of cones sometimes termed long (L), middle (M), and short (S) wavelength receptors (Chap. 1 in Ref. 1). The normalized spectral responses of the human eye receptors (Chap. 26, Table 5 in Ref. 1) are

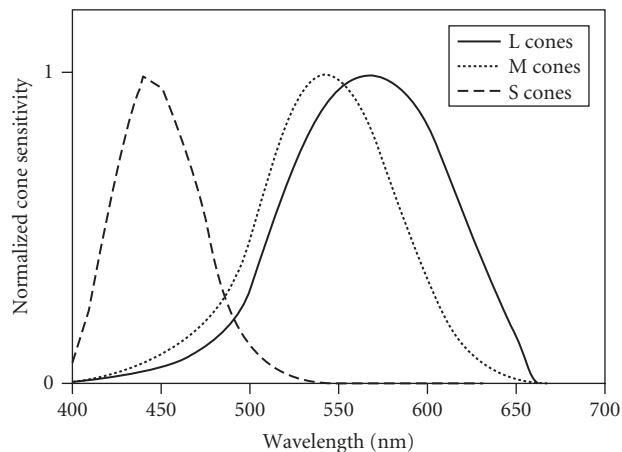


FIGURE 8 Normalized spectral sensitivity of the human eye.

shown in Fig. 8. The ability of humans to distinguish differences in spectral wavelength is believed to rely on difference signals created in the retina and optic nerve and interpreted by the brain from responses to light by the three cone detectors (Chap. 9 in Ref. 4).

The human eye's red sensitivity function peaks at around 570 nm and possesses little sensitivity at wavelengths longer than 650 nm. Also, there exists considerable overlap between red and green sensitivity functions, and to a lesser extent overlap between blue and green and blue and red sensitivity functions. This overlap in sensitivity functions, combined with signal processing in the retina, optic nerve, and brain, allows us to distinguish subtle color differences while simultaneously appreciating rich color saturation.

Photographic films cannot do this. The complex signal processing needed to interpret closely overlapping spectral sensitivity functions is not possible in a photographic material (Chap. 9 in Ref. 4). Some relief from this constraint might be anticipated by considering Maxwell's principle.⁷⁷

Maxwell's principle states that any visual color can be reproduced by an appropriate combination of three independent color stimuli called *primaries*. The amount of each primary per wavelength needed to reproduce all spectral colors defines three color-matching functions (Chap. 6 in Ref. 1) for those primaries. If there exists a set of color-matching functions that minimize overlap between spectral regions, a photographic film with spectral sensitivity like that set of color-matching functions and imaging with the corresponding primary dyes would faithfully reproduce colors.

The cyan, magenta, and yellow dye primaries used in photographic materials lead to theoretical color-matching functions (Chap. 19-II in Ref. 3; Ref. 78)* having more separation than human visual sensitivity, but possessing negative lobes as shown in Fig. 9. This is impossible to achieve in practical photographic films (Chap. 9 in Ref. 4), although the negative feedback from HE effects provides an imperfect approximation. Approximate color-matching functions have been proposed⁸⁰ that contain no negative lobes. But these possess a very short red sensitivity having a high degree of overlap with the green sensitivity, similar to that of the human eye.

It is therefore not possible to build a perfect photographic material possessing the simultaneous ability to distinguish subtle color differences, especially in the blue-green and orange spectral regions, and to render high-saturation colors. Compromises are necessary.

*The theoretical color-matching functions were calculated using the analysis described in Ref. 78, Eq. (9a-c) for block dyes having trichromatic coefficients in Table II, and using the Judd-Vos modified XYZ color matching functions in Chap. 26, Table 2 of Ref. 1.

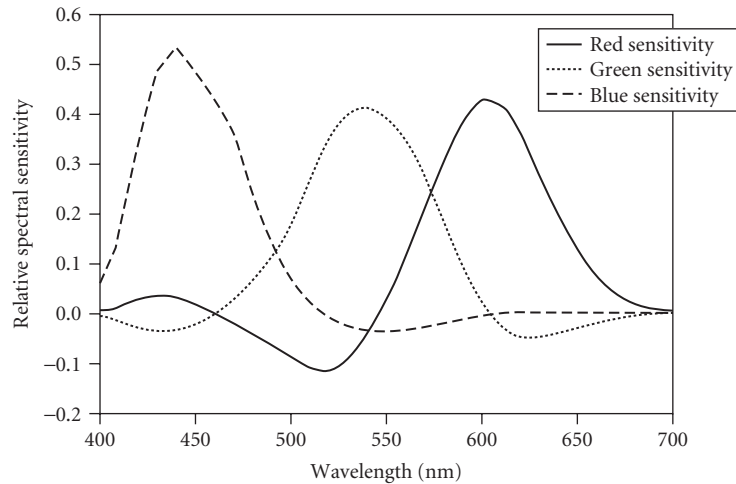


FIGURE 9 Spectral sensitivity for idealized photographic dyes. Note the large negative lobe around 525 nm.

Most photographic materials intended to image colors at high saturation possess spectral sensitivities having small overlap, and in particular possess a red spectral sensitivity centered at considerably longer wavelengths than called for by theoretical color-matching functions. This allows clean spectral detection and rendering among saturated colors but sacrifices color accuracy.

For example, certain *anomalous reflection colors* such as the blue of the lobelia flower possess a sharp increase in spectral reflectance in the long red region not seen by the human eye but detected strongly by a photographic film's spectral sensitivity (see Fig. 10). This produces a serious color

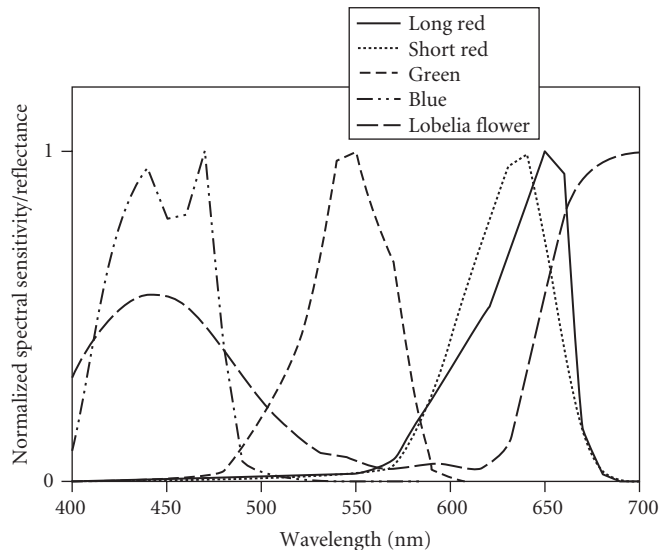


FIGURE 10 Spectral sensitivity for a real photographic film plus reflectance of the lobelia flower.

accuracy error (the flower photographs pink, not blue).⁸⁰ Among other such colors are certain green fabric dyes that image brown or gray. To correct for these hue errors, a special color reversal film was made whose general characteristic involves a short red spectral sensitivity.* This film does a considerably better job of eliminating the most serious hue errors, but unfortunately does not possess high color saturation. It is important in catalogue and other industries where accurate color reproduction is of paramount importance, but most consumers prefer saturated colors.

More recently, color negative films possessing short red spectral sensitivities combined with powerful development inhibitor anchimeric releasing (DIAR) color correction chemistry and masking coupler technology have produced films[†] simultaneously having high color saturation plus accurate color reproduction, at least toward anomalous reflection colors. In addition, these films render improved color accuracy under mixed daylight plus (red-rich) incandescent lighting conditions. These films maintain the high color saturation capability important to consumers but also provide more accurate color hues—although they are not perfect.

A new type of color negative film has been described⁸¹ that possesses a fourth color record whose function approximates the large negative lobe in the theoretical red color-matching function of photographic dyes. Several embodiments have been described and are employed in modern films. The most practical utilizes a fourth color record containing silver halide emulsions sensitive to short green light plus a magenta DIR color correction coupler.[‡]

In simple terms, this special color record responds to short green light in the negative lobe region by releasing a development inhibitor that travels into the red-sensitive cyan color record, thereby reducing cyan dye in response to short green light, an effect opposite to that of normal red light exposure. This film's advantages reside in its ability to more accurately record colors in the blue-green spectral region, plus improved color accuracy under certain fluorescent lights that have a pronounced blue-green emission component.

Modern films are moving toward shorter-wavelength red spectral sensitivity. This allows improved color accuracy by shifting the red spectral sensitivity closer to that of the human eye. In addition, films have been designed to crudely approximate the principal negative lobe in the theoretical red color-matching function for photographic dye primaries, thereby producing a more accurate rendition of certain blue-green colors. Although not perfect, these techniques allow modern photographic films to record the world of color in all its richness and subtleties nearly as we ourselves see it.

30.6 GENERAL CHARACTERISTICS OF PHOTOGRAPHIC FILMS

Today there is available a large variety of films including different film speeds, types, and sizes. Many films are offered in both professional and consumer categories. This section describes some general characteristics of films as they relate to film speed and type. Some unique characteristics of professional films are contrasted to consumer films. Finally, color reversal, black-and-white, and color negative films are compared in more detail.

Low-Speed Films Compared to High-Speed Films

Higher granularity, higher sensitivity to ambient background radiation, and higher sensitivity to x rays are fundamental penalties that come with higher photographic speed. High-speed films often suffer additional penalties compared to their lower-speed counterparts, but these additional penalties

*Kodak Ektachrome 100 Film, EPN—a color reversal professional film.

†Kodak Gold 100, Kodak Gold 200, and Kodak Max 400 color negative films.

‡Fuji Reala 100 Film; Fuji Superia 200 and 400 film; Fuji Nexia 200 and 400 film; and Fuji 160 NPL, NPS, and NC professional films. These are all color negative films.

are not intrinsic. They represent conscious choices made by the manufacturer nearly always traceable to the desire to minimize granularity.

As one example, 400-speed color slide film generally has lower color saturation than its 100-speed counterpart. The reduced color saturation comes as a result of lower interlayer interimage effects (IIE) caused by higher iodide content in the mixed silver bromo-iodide crystals, which, in turn, is needed to achieve higher speeds from a smaller sized crystal and is ultimately done to reduce the photographic granularity penalty.

Photographic Speed and Photographic Granularity To understand the intrinsic connection between photographic speed and photographic granularity, recall that light quanta striking a flat surface follow Poisson statistics (Chap. 1 of Ref. 27). Therefore, a uniform light exposure given to a photographic film delivers photon hits Poisson-distributed across the plane of the film. Silver halide crystals are on the order of $1\ \mu\text{m}^2$ in projected area. On average in a film exposure (the product of the intensity of the radiation and the duration) appropriate for an EI100-speed film, the most sensitive silver halide crystals receive:*

E_q (red light; 650 nm)	~48 photons per square micrometer
E_q (green light; 550 nm)	~40 photons per square micrometer
E_q (blue light; 450 nm)	~33 photons per square micrometer

Because the most efficient practical photographic emulsions to date have a quantum sensitivity of about five photons per grain,²⁹ these approximate numbers suggest there is enough light (on average) striking a film during an EI100-speed film exposure to form latent image on efficient $1\text{-}\mu\text{m}^2$ silver halide grains. But an EI800-speed exposure at three stops down begins to push the limits of modern emulsion efficiency at five green photons per square micron.

Silver halide crystals within the film are light collectors. Just as large-area mirrors in telescopes collect more photons and are more sensitive detectors of starlight than smaller mirrors, all other things being equal, larger silver halide crystals likewise collect more photons to become more sensitive light detectors.

Strong correlates exist between silver halide surface area and photographic speed. Photographic speed often linearly follows the average surface area of the silver halide crystal population (p. 969 of Ref. 2): speed $\sim \bar{a}$.

According to the well-known Siedentopf formula (p. 60 in Ref. 27), the root-mean-square photographic granularity at density D is given by $G \sim D\hat{a}$. In this formula, the symbol \hat{a} represents the average cross-sectional area of the image particle projected onto the film plane. To a good approximation, this is proportional (not necessarily linear) to the mass of developed silver regardless of whether the image particle is a dye cloud or silver deposit.

These considerations demonstrate the intrinsic and well-known correlation between photographic speed and photographic granularity. For a given crystal morphology, as the size of the silver halide crystal increases, both surface area and mass increase, leading to a speed plus granularity increase.

At a fundamental level, to lower the granularity of a higher-speed photographic film the sensitivity to light of the silver halide crystals must improve. Then smaller silver halide crystals can be used to attain speed. Factors that contribute to this problem were discussed in Sec. 30.2.

In general, larger silver halide crystals suffer more inefficiencies in the latent-image-forming process because latent-image dispersity, electron-hole recombination, and other irreversible photon waste processes become more problematic as the grain size increases (p. 993 in Ref. 2). Overcoming these inefficiencies at all speeds, but especially at high photographic speeds, is a major challenge of modern photographic science.

Photographic Speed and Sensitivity to High-Energy Radiation High-energy subatomic particles induce developable latent image formation in photographic films. The process by which high-energy

*Analysis based on a typical EI100-speed color reversal film where the exposure falls near the photographically fastest, most sensitive part of the sensitometric curve. This analysis is described on p. 47 of Ref. 27.

charged particles produce latent image usually involves energy transfer to valence band electrons by inelastic scattering. Some of these scattered electrons are promoted into the silver halide conduction band and go on to produce latent image by the usual processes. Higher-speed films are more sensitive to this radiation because their larger silver halide crystals are hit (on average) more frequently and more collisions occur by passage through a larger crystal than through a smaller crystal.

Photographic films are slowly exposed by ambient background radiation (Chap. 23 in Ref. 3) caused by cosmic rays; ubiquitous stone and masonry building materials, which contain trace amounts of radioactive elements; and other low-level radiation sources. These radiation sources emit various types of charged and uncharged high-energy particles and photons including alpha particles, neutrons, γ rays, β particles, muons, and others. This results in a shorter ambient shelf life for very-high-speed films unless special storage precautions are taken.

Photographic emulsions are also sensitive to x rays. The formation of latent image silver by x rays (and γ rays) is due to the action of high-energy electrons emitted during the absorption or inelastic scattering of the electromagnetic radiation by matter (Chap. 23 in Ref. 3). These electrons may enter the conduction band of silver halide and proceed to latent image formation in the usual way. If the primary emitted electron is of sufficiently high energy, it may create secondary electrons of lower energy by inelastic scattering with other electrons. These secondary electrons enter the conduction band.

High-speed films have more sensitivity to x rays than do low-speed films. Some airline travelers ask airport security agents to hand-check their film rather than allowing it to pass through the baggage x-ray scanner. This precaution is prudent for higher-speed film because airport x-ray machines have become stronger emitters recently, especially at airports with special security concerns.

Despite the higher price, inherent penalties, and willful compromises that characterize high-speed films, they offer access to more picture space under low-light conditions. Among the advantages a high-speed film offers are the following:

1. Pictures under low light where flash is not permitted, such as theaters and museums.
2. Pictures under low light using slower lenses such as zoom and telephoto lenses.
3. Pictures under low light when the subject lies beyond the reach of flash.
4. Pictures under low light taken in rapid sequence without waiting for a flash to recharge.
5. Pictures under low light when flash disturbs the subject, as in some nature photography.
6. Pictures of people without flash. Flash is responsible for a major defect known as *red-eye*, caused when light from a flash reflects off the retina of the eye.
7. Pictures using a stopped-down camera aperture for improved depth of field, so objects over a wider range of distance from the camera are imaged in focus.
8. Reduced dependence on flash for longer battery life.
9. Low-cost one-time-use cameras (OTUCs) when flash units are not needed.
10. Ability to freeze action using a rapid shutter speed.

For these and other reasons, a high-speed film may be the best choice for many film applications despite its shortcomings compared to lower-speed alternatives.

Professional Film Compared to Amateur Film

Most film manufacturers offer film in a professional category and an amateur (sometimes called *consumer*) category. These differ in many respects.

Consumer film is targeted for the needs of the amateur snap shooter. Drugstores, supermarkets, department stores, and other outlets frequented by nonprofessional photographers sell this film. Because most amateurs are price conscious, discount brands of film are available having some performance compromises that may not be important to some consumers.

To keep the price low, manufacturing tolerances for consumer film performance attributes are wider than those for professional film. In a well-manufactured film these departures from performance

aims are small enough to go unnoticed by most average consumers but large enough to be objectionable to highly discerning professionals.

People want pleasing color in their pictures that renders the main subject attractive to the eye. For most amateurs this means saturated colors enhanced to some extent beyond their true appearance in the original scene. However, this preference is highly selective since over-saturated skin tones are objectionable. Other *memory colors*—those that we recognize and know what they should be, such as green grass and blue sky—must also be rendered carefully to produce the most pleasing color appearance (Chap. 5 in Ref. 4). The best consumer films accommodate these color preferences.

Exposures on a roll of consumer film are sometimes stored for long times. It is not unusual for amateurs to take pictures spanning two successive Christmas seasons on the same roll of film. Thus, latent image stability under a wide range of temperature and humidity conditions is very important to a good consumer film. On the other hand professional photographers develop their film promptly, making this requirement far less demanding in a professional film.

Most amateurs are not skilled photographers. It is advantageous for consumer film to be easy to use and provide good-looking pictures under a wide variety of conditions. Consumer film incorporates more tolerance toward over- and underexposures.

Film for amateurs is offered in three standard formats. The most common format is the 35-mm cassette. Consumer cameras that accept this film have become compact, lightweight, and fully automatic. The camera senses the film speed through the DX coding on the film cassette and adjusts its shutter, aperture, and flash accordingly. Autofocus, autorewind, and automatic film advance are standard on these cameras, making the picture-taking experience essentially point and shoot.

The new Advanced Photo System (APS) takes ease of use several steps further by incorporating simple drop-in film loading and a choice of three popular print aspect ratios from panoramic to standard size prints. A magnetic coating on the film records digital data whose use and advantages are just beginning to emerge.

The third format is 110 film. Although not as popular as 35-mm and APS, it is often found in inexpensive cameras for gift packages. Film for this format comes in a cartridge for easy drop-in loading into the camera.

Professional photographers demand more performance from their film than do typical amateurs. These people shoot pictures for a living. Their competitive advantage lies in their ability to combine technical skill and detailed knowledge of their film medium with an artistic eye for light, composition, and the color of their subject.

Film consistency is very important to professionals, and they pay a premium for very tight manufacturing tolerances on color balance, tone scale, exposure reciprocity, and other properties. They buy their film from professional dealers, catalogues, and in some cases directly from the manufacturer. Professionals may buy the same emulsion number in large quantity, then pretest the film and store it in a freezer to lock in its performance qualities. Their detailed knowledge about how the film responds to subtleties of light, color, filtration, and other characteristics contributes to their competitive advantage.

Professional film use ranges from controlled studio lighting conditions to harsh and variable field conditions. This leads to a variety of professional films designed for particular needs. Some photographers image scenes under incandescent lighting conditions in certain studio applications, movie sets, and news events where the lights are balanced for television cameras. These photographers need a tungsten-balanced film designed for proper color rendition when the light is rich in red component, but deficient in blue compared to standard daylight.

Catalogue photographers demand films that image colors as they appear to the eye in the original scene. Their images are destined for catalogues and advertisement media that must display the true colors of the fabric. This differs from the wants of most amateurs, who prefer enhanced color saturation.

Some professional photographers use high color saturation for artistic effect and visual impact. These photographers choose film with oversaturated color qualities. They may supplement this film by using controlled light, makeup on models, lens gels, or other filtration techniques to control the color in the image.

Professional portrait photographers need film that gives highly pleasing skin tones. Their films typically image at moderate to low color saturation to soften facial skin blotches and marks that most people possess but don't want to see in their portraits. In addition, portrait film features highly

controlled upper and lower tone scale to capture the subtle texture and detail in dark suits and white wedding dresses and the sparkle in jewelry.

Professional photographers image scenes on a variety of film sizes ranging from standard 35-mm size to 120-size, and larger 4×5 to 8×10 sheet-film formats that require special cameras. Unlike cameras made for amateurs, most professional cameras are fully controllable and adjustable by the user. They include motor drives to advance the film rapidly to capture rapid sequence events. Professional photographers often take many pictures to ensure that the best shot has been captured.

Many specialty films are made for professional use. For example, some films are sensitized to record electromagnetic radiation in the infrared, which is invisible to the human eye. Note that these films are not thermal detectors. Infrared films are generally *false colored*, with the infrared-sensitized record producing red color in the final image, the red-light-sensitized record producing green color, and the green/blue-sensitized record producing blue color. Other professional films are designed primarily for lab use, such as duplicating film used to copy images from an original capture film.

Some film applications are important to a professional but are of no consequence to most amateurs. For example, professionals may knowingly underexpose their film and request *push processing*, whereby the film is held in the developing solution longer than normal. This brings up an underexposed image by rendering its midtone densities in the normal range, although some loss in shadow detail is inevitable. This is often done with color transparency film exposed under low-ambient-light conditions in the field. Professional films for this application are designed to provide invariant color balance not only under normal process times but also under a variety of longer (and shorter) processing times.

Multipop is another professional technique whereby film is exposed to successive flashes or *pops*. Sometimes the photographer moves the camera between pops for artistic effect. The best professional films are designed to record a latent image that remains nearly invariant toward this type of exposure.

Consumer film is made for amateur photographers and suits their needs well. Professional film comes in a wide variety of types to fit the varied needs of highly discerning professional photographers who demand the highest quality, specialized features, and tightest manufacturing tolerances—and are willing to pay a premium price for it.

Color Reversal Film

Color reversal films, sometimes called *color transparency* or *color slide* films, are sold in professional and amateur categories. This film is popular among amateurs in Europe and a few other parts of the world but has largely been replaced by color negative film among amateurs in North America. However, it is still very popular among advanced amateurs, who favor it for the artistic control this one-stage photographic system offers them, the ease of proofing and editing a large number of images, and the ability for large-audience presentations of their photographic work. Because the image is viewed by transmitted light, high amounts of image dye in these films can project intense colors on the screen in a dark auditorium for a very striking color impact.

Color reversal film is the medium of choice for most professional commercial photographers. It offers them the ability to quickly proof and select their most favored images from a large array of pictures viewed simultaneously on a light table. The colors are more intense compared to a reflection print, providing maximum color impact to the client. And professional digital scanners have been optimized for color reversal images, making it convenient to digitally manipulate color reversal images and transcribe them to the printed page. Today's professional imaging chain infrastructure has been built around color reversal film, although digital camera image capture is making inroads, especially for low-quality and low-cost applications.

Large-format color reversal film, from 120 size to large sheet formats, is often shot by professionals seeking the highest-quality images destined for the printed page. A larger image needs little or no magnification in final use and avoids the deterioration in sharpness and grain that comes from enlarging smaller images. Additionally, art directors and other clients find it easier to proof larger images for content and artistic appeal.

EI400-speed color reversal films generally possess low color saturation, low acutance, high grain, and high contrast compared to lower-speed color reversal films. The high contrast can lead to some loss in highlight and shadow detail in the final image. Except for very low-light situations, EI100 is

the most popular speed for a color reversal film. It offers the ultrahigh image quality professionals and advanced amateurs demand.

Modern professional color reversal films maintain good color balance under push processing conditions. They also perform very well under a variety of exposure conditions including multipop exposures and very long exposure times.

When professional photographers believe nonstandard push or pull process times are needed, they may request a “clip test” (sometimes also called a “snip test”) whereby some images are cut from the roll of film and processed. Adjustments to the remainder of the roll are based on these preprocessed images. Some photographers anticipate a clip test by deliberately shooting sacrificial images at the beginning of a roll.

Professional color reversal films can be segregated into newer modern films and older *legacy films*. Modern films contain the most advanced technology and are popular choices among all photographers. Legacy films are popular among many professional photographers who have come to know these films’ performance characteristics in detail after many years of experience using them.

Legacy films continue to enjoy significant sales because the huge body of personal technical and artistic knowledge about a film accumulated by a professional photographer over the years contributes to his or her competitive advantage. This inertia is a formidable barrier to change to a new, improved, but different film whose detailed characteristics must be learned.

In some cases, the improved features found in modern films are not important to a particular professional need. For example, a large 4×5 sheet film probably needs little or no enlargement, so the poorer grain and sharpness of a legacy film may be quite satisfactory for the intended application. The detailed knowledge the professional has about how the legacy film behaves in regard to light and color may outweigh the image structure benefits in a modern film. Also, all films possess a unique tone scale and color palette. A professional may favor some subtle and unique feature in the legacy film’s attributes.

Kodachrome is a special class of color reversal legacy films. Unlike all other types of color reversal films, this film contains no dye-forming incorporated couplers. The dyes are imbibed into the film during processing so the film’s layers are coated very thin. This results in outstanding image sharpness. Moreover, many photographers prefer Kodachrome’s color palette for some applications.

Kodachrome dyes are noted for their image permanence. Images on Kodachrome film have retained their colors over many decades of storage, making this film attractive to amateurs and professionals alike who want to preserve their pictures. However, modern incorporated coupler color reversal films also have considerably improved dark storage image stability compared to their predecessors.

Table 1 lists some color reversal films available today. This is not a comprehensive list. Most film manufacturers improve films over time, and portfolios change frequently.

TABLE 1 Color Reversal Capture Films

Modern Films	Legacy Films	Kodachrome Films	Tungsten Films
Kodak Ektachrome 100VS (very saturated color)	Fuji Velvia 50 RVP (very saturated color)	Kodachrome 25 PKM	Kodak Ektachrome 64T EPY
Kodak Ektachrome E100S (standard color, good skin tones)	Kodak Ektachrome 64 EPR (standard color)	Kodachrome 64 PKR	Fujichrome 64T RTP
Fuji Astia 100 RAP (standard color, good skin tones)	Kodak Ektachrome 100 Plus EPP (standard color)	Kodachrome 200 PKL	Agfachrome 64T
Fuji Provia 100 RDPII (standard color)	Kodak Ektachrome 100 EPN (accurate color)		Kodak Ektachrome 160T EPT
Agfachrome 100 (standard color)	Kodak Ektachrome 200 EPD (lower color saturation)		Kodak Ektachrome 320T EPJ
Kodak Ektachrome E200 (can push 3 stops)	Agfachrome 200		
	Kodak Ektachrome 400 EPL		
	Fuji Provia 400		
	Agfachrome 400		

Unless a photographer has some particular reason for choosing a legacy color reversal film, the modern films are generally a better overall choice. More detailed information about these films' uses and characteristics can be found in the film manufacturers' Web pages on the Internet.

Black-and-White Film

Black-and-white (B&W) films and papers are sold through professional product supply chains. Color films and papers have largely displaced B&W for amateur use, with the exception of advanced amateurs who occasionally shoot it for artistic expression.

The image on a B&W film or print is composed of black metallic silver. This image has archival stability under proper storage conditions and is quite stable even under uncontrolled storage. Many remarkable and historically important B&W images exist that date from 50 to over 100 years ago. This is remarkable considering the primitive state of the technology and haphazard storage conditions.

Pioneer nature photographer Ansel Adams reprinted many of his stored negatives long after he stopped capturing images in the field. This artistic genius recreated new expressions in prints from scenes captured many years earlier in his career because his negatives were well preserved.

Ansel Adams worked with B&W film and paper. Many photographic artists work in B&W when color would distract from the artistic expression they wish to convey. For example, many portraits are imaged in B&W.

B&W films pleasingly image an extended range of tones from bright light to deep shadow. They are panchromatically sensitized to render colors into grayscale tones. A B&W film's tone scale is among its most important characteristics.

Photographers manipulate the contrast of a B&W image by push- or pull-processing the negative (varying the length of time in the developer solution) or by printing the negative onto a select contrast paper. Paper contrast grades are indexed from 1 through 5, with the higher index giving higher contrast to the print. Multigrade paper is also available whereby the contrast in the paper is changed by light filtration at the enlarger.

It is generally best to capture the most desired contrast on the negative because highlight or shadow information lost on the negative cannot be recovered at any later printing stage. Paper grades are designed for pleasing artistic effect, not for highlight or shadow recovery.

Legacy films are very important products in B&W photography. Although typically a bit grainier and less sharp than modern B&W films, their tone scale characteristics, process robustness, and overall image rendition have stood the test of time and are especially favored by many photographers. Besides, the B&W photographic market is small so improvements to this line of films occur far less frequently than do improvements to color films.

Unlike the case with color films, which are designed for a single process, a photographer may choose among several developers for B&W films. Kodak Professional T-Max developer is a good choice for the relatively modern Kodak T-Max B&W film line. Kodak developer D-76 is also very popular and will render an image with slightly less grain and slightly less speed. It is a popular choice for legacy films. Kodak Microdol-X developer is formulated to give very low grain at the expense of noticeable speed loss. Kodak developer HC110 is popular for home darkrooms because of its low cost and ease of use, but it renders a grainier image compared to other developers. Other manufacturers, notably Ilford Ltd., carry similar types of B&W developers.

A new type of B&W film has emerged that is developed in a standard color negative process. This incorporated-coupler 400-speed film forms a black-and-white image from chemical dyes instead of metallic silver. Among its advantages are very fine grain at normal exposures in the commonly available color negative process. Its shortcomings are the inability to control contrast on the negative by push or pull processing and its objectionable high grain when underexposed compared to a comparably underexposed 400-speed legacy film. And many photographers prefer the tone scale characteristics found in standard B&W films.

Table 2 lists some B&W films available today. This is not a comprehensive list. Modern films generally feature improved grain and sharpness compared to legacy films. However, the legacy films are favorite choices among many photographers because of their forgiving process insensitivity, the

TABLE 2 Black and White Films

Modern Films	Legacy Films	Specialty Films
Kodak T-Max 100 Professional (fine grain, high sharpness)	Ilford Pan F Plus 50	Kodak Technical Pan 25 (fine grain and very high sharpness)
Ilford Delta 100 Pro (fine grain, high sharpness)	Kodak Plus-X 125	Kodak IR (infrared sensitive)
Kodak T-Max 400 Professional (finer grain compared to legacy films)	Ilford FP4 Plus 125	Ilford SFX 200 (extended long red sensitivity but not IR)
Ilford Delta 400 Pro (finer grain compared to legacy films)	Kodak Tri-X 400	Ilford Chromogenic 400 (incorporated couplers, color negative process)
Fuji Neopan 400 (finer grain compared to legacy films)	Ilford HP5 Plus 400	Kodak Professional T400 CN (incorporated couplers, color negative process)
Kodak T-Max P3200 Professional (push process to high speed, high grain)		
Ilford Delta P3200 Pro (push process to high speed, high grain)		

experience factor of knowing their detailed behavior under many conditions, and the characteristic look of their images. More detailed information about these films' uses and characteristics can be found in the film manufacturers' Web pages on the Internet.

Color Negative Film

Today's color negative film market is highly segmented. It can be most broadly divided into consumer films and professional films. The consumer line is further segmented into 35-mm film, 110 format film (a minor segment whose image size is 17×13 mm), single-use cameras, and the new Advanced Photo System (APS). Each segment serves the needs of amateur photographers in different ways. The basic films are common across segments, with the main difference being camera type.

Consumer color negative film is a highly competitive market with many film and camera manufacturers offering products. In general, films for this marketplace offer bright color saturation that is most pleasing to amateurs. The higher-speed films show progressively more grain than do the lower-speed films. The highest-speed films are less often used when enlargement becomes significant, such as in APS and 110 format, but are prevalent in single-use cameras.

Consumer 35-mm Films Films in 35-mm format form the core of all consumer color negative products. These same basic films are also found in single-use cameras, 110 format cameras, and APS cameras. Film speeds include 100, 200, 400, and 800. All manufacturers offer films at 100, 200, and 400 speed, but only a few offer films at speeds of 800 and above.

The 400-speed film is most popular for indoor shots under low light and flash conditions. Lower-speed films are most often used outdoors when light is plentiful.

The best consumer films feature technology for optimized color rendition including the high color saturation pleasing to most consumers, plus accurate spectral sensitization for realistic color rendition under mixed lighting conditions of daylight plus fluorescent and incandescent light, which is often present inside homes. Technology used for accurate spectral sensitization was briefly described for Fujicolor Superia and Kodak Gold films in Sec. 30.5.

Kodak consumer films segment into Kodak Gold and Kodak Royal Gold films. Kodak Gold consumer films emphasize colorfulness, while Kodak Royal Gold films emphasize fine grain and high sharpness.

Films made in 110 format generally fall into the 100- to 200-speed range because the enlargement factors needed to make standard-size prints place a premium on fine grain and high sharpness.

Single-Use Cameras The single-use camera marketplace is extremely competitive because of the high popularity of this film and camera system among amateurs. These low-cost units can be bought at all consumer outlets and are especially popular at amusement parks, theme parks, zoos, and similar family attractions. After the film is exposed, the photographer returns the entire film plus camera unit for processing. Prints and negatives are returned to the customer while the camera body is returned to the manufacturer, repaired as needed, reloaded with film, and repackaged for sale again. These camera units are recycled numerous times from all over the world.

Single-use cameras come in a variety of styles including a waterproof underwater system, low-cost models with no flash, regular flash models, an APS style offering different picture sizes, and a panoramic style. Single-use cameras typically contain 800-speed film, except for APS and panoramic models, which usually contain 400-speed film due to enlargement demands for finer grain.

Advanced Photo System (APS) APS is the newest entry into consumer picture taking. The size of the image on the negative is 29×17 mm, about 60 percent of the image size of standard 35-mm film (image size 36×24 mm). This puts a premium on fine grain and high sharpness for any film used in this system. Not all film manufacturers offer it. Speeds offered are 100, 200, and 400, with the higher speeds being the most popular.

Some manufacturers offer a B&W film in APS format. The film used is the incorporated-coupler 400-speed film that forms a black-and-white image from chemical dyes and is developed in a standard color negative process.

The APS camera system features simple drop-in cassette loading. Unlike the 35-mm cassette, the APS cassette contains no film leader to thread into the camera. When loaded, the camera advances the film out of the cassette and automatically spools it into the camera, making this operation mistake-proof. Three popular print sizes are available; panoramic, classic, and high-definition television (HDTV) formats. These print sizes differ in their width dimension.

A thin, nearly transparent magnetic layer is coated on the APS film's plastic support. Digital information recorded on this layer, including exposure format for proper print size plus exposure date and time, can be printed on the back of each print. Higher-end cameras offer prerecorded titles—for example, "Happy Birthday"—that can be selected from a menu and placed on the back of each print. Additional capabilities are beginning to emerge that take more advantage of this magnetic layer and the digital information it may contain.

The APS system offers easy mid-roll change on higher-end cameras. With this feature, the last exposed frame is magnetically indexed so the camera "remembers" its position on the film roll. A user may rewind an unfinished cassette to replace it with a different cassette (different film speed, for example). The original cassette may be reloaded into the camera at a later time. The camera will automatically advance the film to the next available unexposed frame.

Markings on the cassette indicate whether the roll is unexposed, partially exposed, fully exposed, or developed. There is no uncertainty about whether a cassette has been exposed or not. Unlike the 35-mm system, where the negatives are returned as cut film, the negatives in the APS system are rewound into the cassette and returned to the customer for compact storage. An index print is given to the customer with each processed roll so that each numbered frame in the cassette can be seen at a glance when reprints are needed.

Compact film scanners are available to digitize pictures directly from an APS cassette or 35-mm cut negatives. These digitized images can be uploaded into a computer for the full range of digital manipulations offered by modern photo software. Pictures can be sent over the Internet, or prints can be made on inkjet printers. For the best photo-quality prints, special photographic ink cartridge assemblies are available with most inkjet printers to print onto special high-gloss photographic-quality paper.

Table 3 summarizes in alphabetical order many brands of 35-mm consumer film available today worldwide. Some of these same basic films appear in single-use cameras, APS format, and 110 format, although not all manufacturers listed offer these formats. This is not a comprehensive list. Because this market is highly competitive, new films emerge quickly to replace existing films. It is not unusual for a manufacturer's entire line of consumer films to change within three years. More detailed information about these films' uses and characteristics can be found in the film manufacturers' Web pages on the Internet.

TABLE 3 Consumer 35-mm Color Negative Films

Manufacturer and Brand Name					
Agfacolor HDC Plus	100	200	400		
Fujicolor Superia	100	200	400	800	
Ilford Colors	100	200	400		
Imation HP	100	200	400		
Kodak Gold	100	200	Max400	Max800	
Kodak Royal Gold	100	200	400		1000
Konica Color Centuria	100	200	400	800	
Polaroid One Film	100	200	400		

Professional Color Negative Film Professional color negative film divides roughly into portrait and wedding film and commercial and photojournalism film. Portrait and wedding films feature excellent skin tones plus good neutral whites, blacks, and grays. These films also incorporate accurate spectral sensitization technology for color accuracy and excellent results under mixed lighting conditions. The contrast in these films is about 10 percent lower than in most consumer color negative films for softer, more pleasing skin tones, and its tone scale captures highlight and shadow detail very well.

The most popular professional format is 120 size, although 35-mm and sheet sizes are also available. Kodak offers natural color (NC) and vivid color (VC) versions of Professional Portra film, with the vivid color having a 10 percent contrast increase for colorfulness and a sharper look. The natural color version is most pleasing for pictures having large areas of skin tones, as in head and shoulder portraits.

Commercial films emphasize low grain and high sharpness. These films offer color and contrast similar to those of consumer films. Film speeds of 400 and above are especially popular for photojournalist applications, and the most popular format is 35 mm. These films are often push processed.

Table 4 summarizes in alphabetical order many brands of professional color negative film available today worldwide. This is not a comprehensive list. Because this market is highly competitive, new films emerge quickly to replace existing films. More detailed information about these films' uses and characteristics can be found in the film manufacturers' Web pages on the Internet.

Silver halide photographic products have enjoyed steady progress during the past century. This chapter has described most of the technology that led to modern films. Most noteworthy among these advances are

1. Efficient light management in multilayer photographic materials has reduced harmful optical effects that caused sharpness loss and has optimized beneficial optical effects that lead to efficient light absorption.
2. Proprietary design of silver halide crystal morphology, internally structured halide types, transition metal dopants to manage the electron-hole pair, and improved chemical surface treatments has optimized the efficiency of latent image formation.

TABLE 4 Professional Color Negative Films

Manufacturer and Brand Name (Commercial Film)					
Agfacolor Optima II Prestige	100	200	400		
Fujicolor Press			400	800	
Kodak Professional Ektapress	PJ100		PJ400	PJ800	
Konica Impresa	100	200			3200 SRG
Manufacturer and Brand Name (Portrait Film)					
Agfacolor Portrait		160 XPS			
Fujicolor		160 NPS	400 NPH	800 NHGII	
Kodak Professional Portra		160 NC	400 NC		Pro 1000
		160 VC	400 VC		
Konica Color Professional		160			

3. Transition metal dopants and development-modifying chemistry have improved process robustness, push processing, and exposure time latitude.
4. New spectral sensitizers combined with powerful chemical color correction methods have led to accurate and pleasing color reproduction.
5. New image dyes have provided rich color saturation and vastly improved image permanence.
6. New film and camera systems for consumers have made the picture-taking experience easier and more reliable than ever before.

Photographic manufacturers continue to invest research and product development resources in their silver halide photographic products. Although digital electronic imaging options continue to emerge, consumers and professionals can expect a constant stream of improved silver halide photographic products for many years to come.

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