Kirk-Othmer Encyclopedia of Chemical Technology.

COLOR PHOTOGRAPHY

Color photography is a technology by which the visual appearance of a three-dimensional subject may be reproduced on a two-dimensional surface with a pleasing balance of brightness, hue, and color saturation. There are two essentials in the practice of color photography: the camera and the light-sensitive sensor. The task of the camera is to present an undistorted image to the plane of the sensor with an intensity level and exposure time appropriate to the sensitivity of the sensor being used. The sensor can either be silver-halide based photographic film or an electronic sensor such as a charge couple device (CCD). A digital record of the scene may also be obtained by scanning the processed film.

The technology of silver halide color photography is discussed herein. The physical record of the image is expected to have high permanence. The image may be viewed directly as a reflection color print, by projection as a color slide, or by back-illumination as a display transparency. In the case of a digital image, it may also be viewed on a video monitor. References 1–20 are general sources of information on the science and technologies supporting color photography (see also Photography; Color photography, instant). A detailed history of color photography may be found in References 1 and 2.

1. Color Vision and Three-Color Photography

Although color (qv) has been used for graphic purposes since prehistoric times, it was Isaac Newton's discovery of the solar spectrum in 1666 that led to an understanding of color with regard to the properties of light. From the observation that white light is not a pure entity, but consists of a mixture of colors, the idea developed that any color could be obtained by a mixture of three primary colors. A wide range of colors could be obtained by the mixing of red, green, and blue lights. At the start of the nineteenth century, the Young-Helmholtz theory of color vision proposed that there were three types of receptor in the human retina, each of which responded over a certain wavelength range in simple proportion to the amount of light absorbed. Because the concept of color is meaningless in the absence of an observer, the physiological basis of color is used as a starting point for trichromatic color reproduction.

Human vision is sensitive to electromagnetic radiation in the 400–700 nm range. Figure 1 is an illustration of the perceived colors over this wavelength range, together with the representative spectral sensitivities of human retinal receptors (21). There are no abrupt transitions between the spectral colors, as indicated by the vertical lines, but rather a gradual merging.

The human eye is known to contain two main types of light-sensitive cells: rods and cones. These names come from the shape of the outer segment of the cell. The rods are by far the most numerous, outnumbering the cones by a factor of nearly 20, and operate as the main sensors at low illumination levels. Scotopic (rod) vision as shown in Figure 1 centers at about 510 nm and extends from 400–600 nm. Because there is only one type of rod, it lacks the ability to discriminate colors and its electrical output varies as the integrated response over this wavelength range. Cones are the primary sensors of color vision, and there is strong evidence that there are three types, shown as ρ, γ, and β. Over most of the visible range any single wavelength stimulates

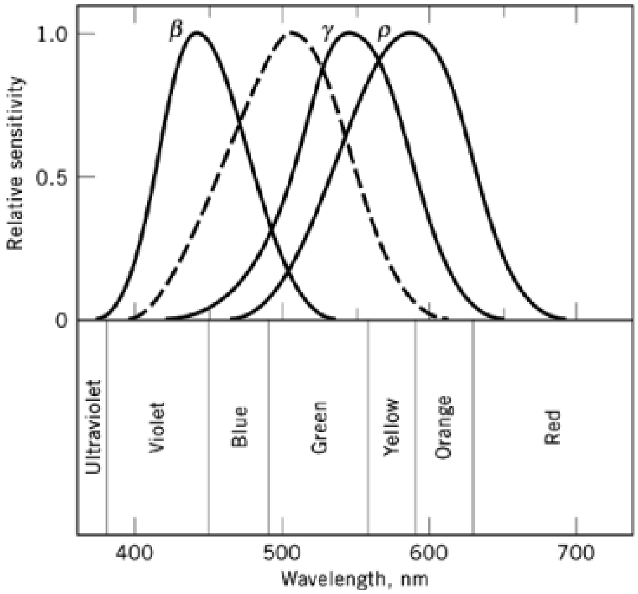


Fig. 1. Representative spectral sensitivities of the human retinal receptors, (- - -) scotopic (rod) vision, and β, γ, and ρ cone sensitivities. The wavelengths of the perceived colors are also shown. Reproduced with permission (21).

more than one receptor type. For example, the peak sensitivities of the ρ and γ receptors, at 580 nm and 540 nm, respectively, are quite close together.

The ability to distinguish small differences in spectral wavelength is believed to rely on the difference signals between the responses of the three cone detectors. For example, stimulation of the ρ and γ receptors by monochromatic light of 570 nm has no difference signal, and is thus interpreted by the brain as yellow light. However, for monochromatic light of 550 nm, stimulation of the γ receptor is increased, that of the ρ receptor is decreased, and the difference signal between the two is interpreted by the brain as greenish light. Most colors consist of many wavelengths of varying intensities; these signals are additive for each receptor.

This understanding of human color vision makes a definition of the characteristics of a perfect color reproduction system possible. For simplicity, assume a reproduction of any uniform patch of color, such that the original and the reproduction are indistinguishable under any illuminant, is desired. The first requirement is the selection of three sensors that match the cone sensitivity curves shown in Figure 1. The second requirement is that these sensors faithfully record the intensity or brightness of the stimulus. The third requirement is that in the viewing of the reproduction, the physical record of each sensor's response must be capable of stimulating only the cone receptor it is designed to mimic. This last requirement cannot be met in practice because even monochromatic light over most of the visible range stimulates more than one receptor type. Thus the construction in color vision that permits exquisite wavelength discrimination also makes perfect color reproduction using three-color mixing impossible. With this limitation, the design challenge of color photography is to reduce or correct for unwanted stimulations as much as possible.

In 1861, James Clerk Maxwell demonstrated that colored objects could be reproduced by photography, using three-color mixing (1). He produced three separate negative images in silver on glass plates, ostensibly taken through red, green, and blue filters. After the three negative plates were converted to positive plates, the positives were then loaded into three separate projectors, each of which had the corresponding filter used in the exposure in front of the lens, and the images were brought into registration on a white screen. A tolerable color reproduction was obtained. Although considered a landmark, the success of the experiment was fortuitous, because the silver halide crystals used as the light-sensitive element were sensitive only to ultraviolet and blue light. It was subsequently shown (22) that the green exposure resulted from the sensitivity of the silver halide tailing into the blue-green region of the spectrum, and the red exposure resulted from ultraviolet radiation passed by the red filter employed. Thus the ability to sensitize silver halide crystals to green and red light, in addition to the inherent blue sensitivity, is critical. Intrinsic sensitivity depends on the halide chosen: useful sensitivity does not extend beyond 410 nm for AgCl and 490 nm for AgBr.

It is axiomatic that only radiation that is absorbed can produce chemical action (Grotthus-Draper Law), in this case the promotion of an electron from the valence to the conduction band of silver halide. It was discovered in 1873 that certain organic dyes, when adsorbed to silver halide crystals, induce sensitivity to the longer wavelengths of the visible spectrum. In the course of testing photographic plates that contained a yellow dye to prevent back-reflection of light (halation), some sensitivity to green light was observed. Many thousands of dyes have been tested as spectral sensitizers, and materials exist for the selective sensitization of any region of the visible spectrum and the near infrared. As well as permitting better tone reproduction in black-and-white photography, this technology is the key to providing the red, green, and blue discrimination required in modern color photography.

Maxwell's demonstration was an example of an additive trichromatic process in that the final image was produced by combining red, green, and blue lights in registration, each light corresponding to its amount present in the original scene. The various colors produced by the additive combination of red, green, and blue lights are shown in Figure 2. To simplify the discussion, blue light is considered the 400–500 nm range of the spectrum, green the 500–600 nm range, and red the 600–700 nm range. White light is produced when all three colors are combined in equal amounts. The two-way combinations of red, green, and blue light produce three colors that each lack one-third of the spectrum. The color cyan is generated by the combination of blue and green lights, and lacks light in the red part of the spectrum. Similarly, the color magenta lacks light in the green part of the spectrum, and the color yellow lacks light in the blue part of the spectrum. For this reason cyan, magenta, and yellow are called subtractive primaries.

Early experimenters focused on the problem of converting the three separation positives produced by Maxwell's method into a form that could be printed with colored inks on a paper surface. The first clear statements of the basic principles underlying modern three-color photography are credited to two independent workers: du Hauron, who applied for a French patent in 1868, and Cros, who wrote an article in *Les Mondes* in 1869. Both noted that printing colors should be complementary or "antichromatic" to the red, green, and blue taking filters. The complementary colors are the subtractive primaries. Cyan is complementary to red, magenta is complementary to green, and yellow is complementary to blue. Each subtractive primary dye absorbs the color to which it is complementary. Figure 3 illustrates the superposition of equal amounts of the three subtractive primaries as dyes. The three possible two-way combinations yield red, green, and blue. The three-way combination yields black. Thus the three subtractive primary dyes used singly or together are capable of creating a wide variety of colors by selectively modulating the red, green, and blue components in white light.

2. The Light-Recording Element

The primary element for light capture in color photography is the silver halide crystal. By common usage, the term emulsion has come to denote in the photographic literature what is actually a dispersion of silver halide crystals (grains) in gelatin. Four discrete steps can be identified in the formation of a colored image: (*1*) light absorption by the crystal; (*2*) the solid-state processes leading to the formation of a latent image; (*3*) the reduction of all or part of a crystal-bearing latent image to metallic silver by a mild reducing agent; and (*4*) use of the by-products of the silver reduction to create a colored image in register by dye formation, dye destruction, or dye-transfer processes.

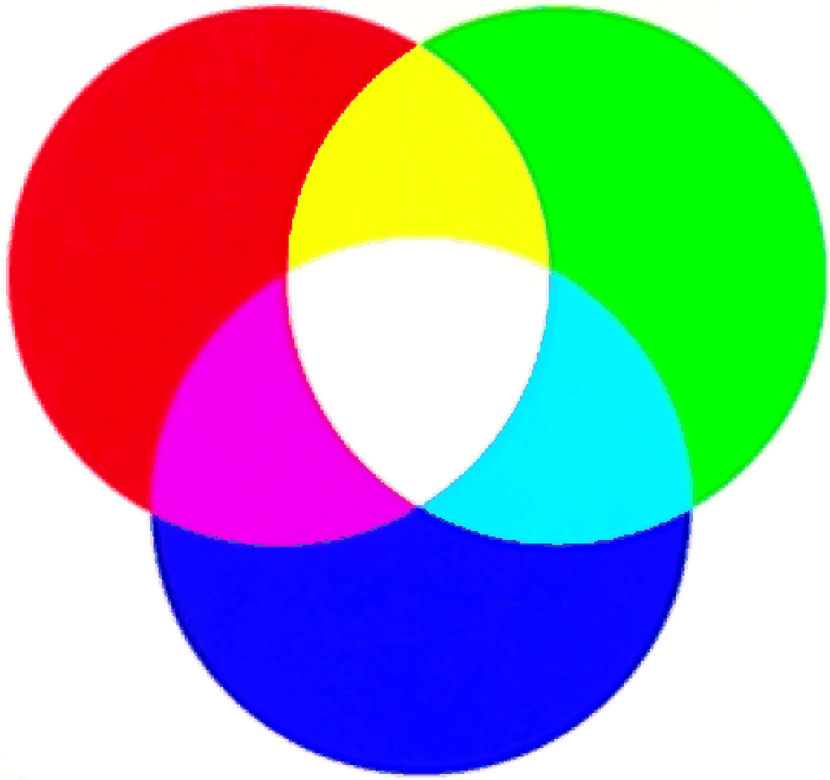


Fig. 2. Addition mixing of red, green, and blue lights.

Sensitivity, or photographic speed, is one of the most important attributes of the light-sensitive element. Practical color photography using a handheld camera is possible from conditions of bright sunlight to night street lighting. These conditions span a factor of about 10^5 in illuminance, and must be accommodated for by the combination of camera shutter speed, lens aperture, and choice of film speed. Most commercial emulsions contain a population of silver halide crystals varying widely in size and shape. Although the structure of the AgBr and AgCl lattice is simple face-centered cubic, an enormous variety of crystal shapes can be obtained, depending on the number and orientation of twin planes present in the crystal, the silver ion concentration during growth, and the presence of growth modifiers (23, 24). To add to this complexity, the crystals in commercial emulsions usually contain mixed-halide phases. Films suitable for a handheld camera generally contain silver bromoiodide, in which iodide ions are incorporated into the AgBr lattice during crystal growth.

The intrinsic sensitivity of silver halide is enhanced during manufacture by a heat treatment, usually in the presence of tiny amounts of sulfur and gold compounds, in a process known as chemical sensitization. This creates sub-developable chemical sensitization centers of mixed silver/gold sulfides on the grain surface. The gold incorporated into the latent image formed during exposure enhances the developability of the silver halide crystal, effectively increasing its light sensitivity, but without affecting the wavelength dependence of sensitivity. The key to efficient chemical sensitization is to effectively trap the photoelectron at a latent image site while minimizing loss processes such as electron-hole recombination. The important subject of chemical sensitization is dealt with more fully under Photography.

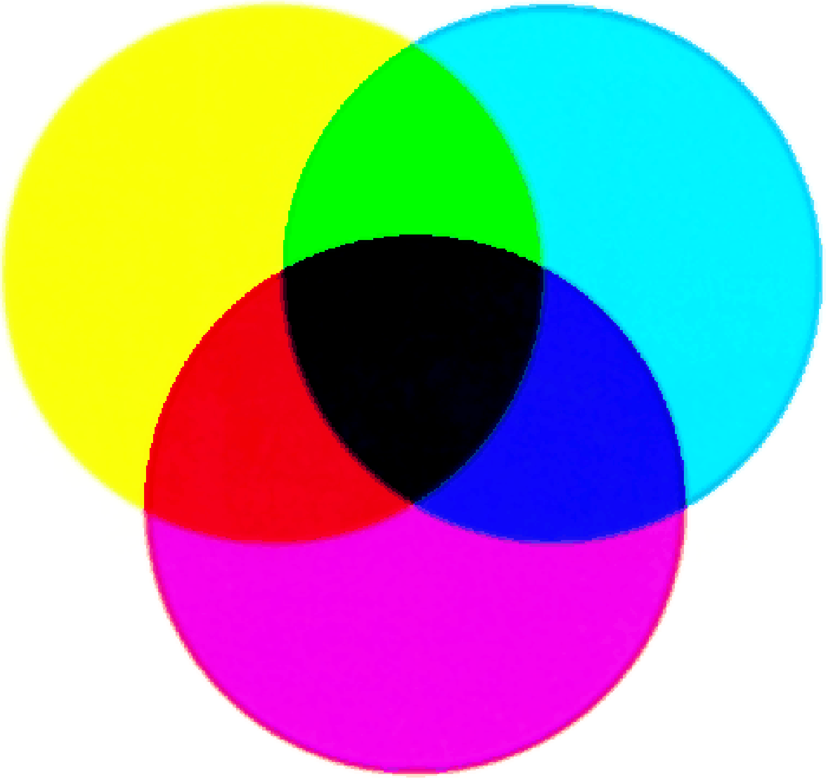


Fig. 3. Superimposed subtractive dyes.

Sensitizing dyes (25, 26) are essential to the practice of color photography. Although the initial discovery was made in 1873, it was not until the 1930s that photographic scientists began to develop a systematic series of dyes that could be adsorbed to the silver halide crystal and then transfer to it the energy of green and red light necessary to create a latent image. The most widely used of these materials are the cyanine dyes, which are heterocyclic moieties linked by a conjugated chain of atoms. More than 20,000 dyes of this class have been synthesized. In the example shown in Figure 4, when$n = 0$, the dye is yellow and provides sensitization to blue light. Dyes which sensitize in the blue are particularly important for AgCl emulsions, which lack intrinsic blue sensitivity. When $n = 1$, the dye, a carbocyanine, is magenta and absorbs green light. For $n = 2$, a dicarbocyanine, the dye appears cyan and sensitizes silver halide to red light. Extending the conjugation further produces dyes which absorb in the infrared, producing films useful for aerial photography and thermal analysis (see Cyanine dyes; Dyes, Sensitizing).

There are several requirements for a good sensitizing dye. A good dye is adsorbed strongly to silver halide. The dye molecules attach themselves to the surface of the silver halide crystals, usually up to monolayer coverage. This amount can be determined by measuring the adsorption isotherm for the dye. Dye in excess of this amount can cause the emulsion to lose sensitivity, so-called dye-induced desensitization. In color films, simple positively charged cyanine dyes can also dissolve in the organic phase used to solubilize the image-forming coupler, leading to a phenomenon known as unsensitization. This can be overcome by adding a negatively charged acidic group, such as sulfonate, to turn the dye into a zwitterion that is insoluble in organic media. Adsorption is also influenced by the composition and crystallographic surfaces of the silver halide crystal, and by the procedure of dye addition. The optical properties of the dye change on being attached to silver halide.

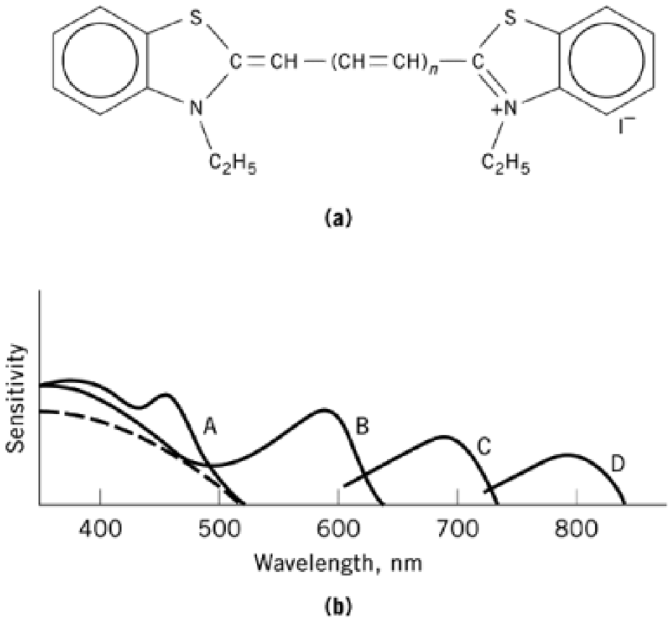


Fig. 4. Positive and negative-working integral tri-packs.

Typically the light absorption peak shifts by 30–50 nm to longer wavelengths. Frequently new absorption peaks occur as a result of different stacking arrangements of the dyes on the crystal surface.

A good sensitizing dye absorbs light of the desired wavelength range with high efficiency. The absorption spectrum of the sensitizing dye depends on a number of factors. Each heterocyclic nucleus has a characteristic color value associated with it which can be modified by chemical substitution. The chromophore length is another important variable. A useful empirical rule is that for each increment in *n,* the absorption peak of the eye shifts to longer wavelengths by 100 nm.

A good sensitizing dye sensitizes with high efficiency. Modern sensitizing dyes transfer an electron from the dye's excited singlet state to the conduction band of silver halide, which is subsequently able to participate in latent image formation. The ability of the dye to serve as an efficient sensitizer is often found to be proportional to the electrochemical reduction potential of the dye measured in solution. This has proved to be a useful tool in designing spectral sensitizers. A practical measure of dye efficiency is the relative quantum efficiency of sensitization (27) defined as the ratio of the number of quanta absorbed in the intrinsic region, usually 400 nm, of the silver halide to the number of quanta absorbed only by dye at a wavelength within its absorption band, both to produce the same specified developed density. For the best dyes this value is only slightly less than 1.0.

A good sensitizing dye does not interfere with other system properties. Sensitizing dyes can sometimes influence the intrinsic response of a chemically sensitized emulsion, leading to desensitization or additional sensitization. The dye can also interfere with development rate, increase or decrease unwanted fog density, and remain as unwanted stain in the film after processing. The dye should have adequate solubility for addition to the emulsion, but should not wander between layers in the final coating.

The relationship between crystal size and photographic speed can be understood using simple geometric arguments. For an individual crystal, sensitivity may be defined as the reciprocal of the minimum light absorption required to generate a developable latent image. For a silver halide crystal without sensitizing dye, blue light absorption is proportional to volume. If it is assumed that the crystal is a sphere and that the latent image can be formed with equal efficiency at all grain sizes, the relationship shown in Figure 5 is obtained. The

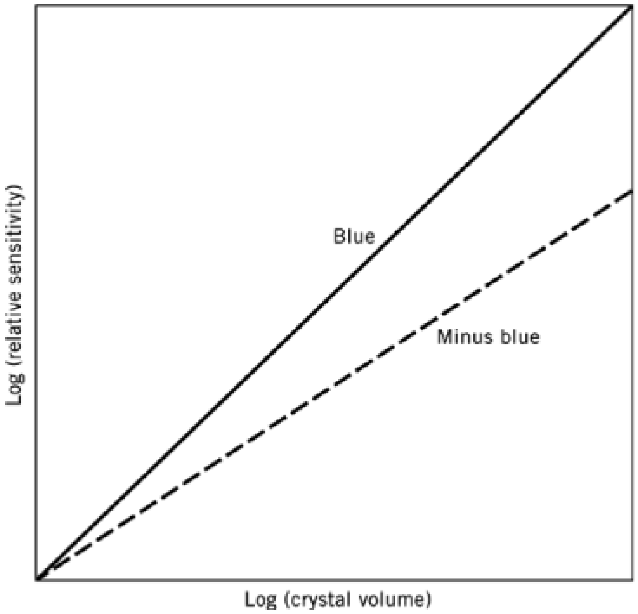


Fig. 5. Emulsions (**a**) traditional and (**b** hexagonal tabular crystals.

adsorption of sensitizing dyes is necessary to confer sensitivity to the green and red regions of the spectrum; this is frequently called "minus-blue" speed. To a first approximation, minus-blue speed depends on the surface area available for dye adsorption. Again, assuming sphericity, the line shown in Figure 5 is the expected change of minus-blue speed with crystal size. Even for the highest speed films, the crystals do not usually exceed 3 μm in linear dimension.

Over the years, emphasis has been placed on obtaining greater uniformity in silver halide crystal size and habit in the grain population, in the belief that the chemical sensitization process can then yield a higher average imaging efficiency. One way of doing this is to adjust the nucleation conditions so that untwinned crystals are favored, and then to ensure that no new crystals are formed during the growth of the starting population. Crystals containing twin planes grow anisotropically and it is more difficult to obtain a uniform population. Commercial materials are available that contain cubic and octahedral crystals of narrow size dispersity. Along with better control of the crystal size and shape in the population, the placement of iodide in the AgBr crystal has received a great deal of attention. Iodide incorporation increases blue light absorption, and its selective placement within the crystal allows control over the rate of the development reaction, since iodide also acts as a development inhibitor. In color negative films, the color image is formed by reducing less than one-quarter of the total silver available to metallic silver during development. This strategy is necessary so that the crystals are large enough to have the required sensitivity, yet each crystal by its partial reduction contributes only a small amount of dye to the final image, leading to an image of low graininess.

An approach has been devised (28) to break out of the surface-to-volume relationship imposed by crystal shapes that are nearly spherical. Conditions have been established to favor the growth of crystals having multiple parallel twin planes (29), and emulsions containing mostly hexagonal tabular crystals, such as those shown in Figure 6, can be prepared. Figure 6 compares the crystals of a newer emulsion to a more traditional one. Tabular thicknesses of around 0.1 μm are commonly employed. By adjustment of the projective area and thickness of these tabular crystals, it is possible to create a series of emulsions in which the surface area and hence minus-blue speed increases, but the crystal volume and hence blue speed remain constant. Because

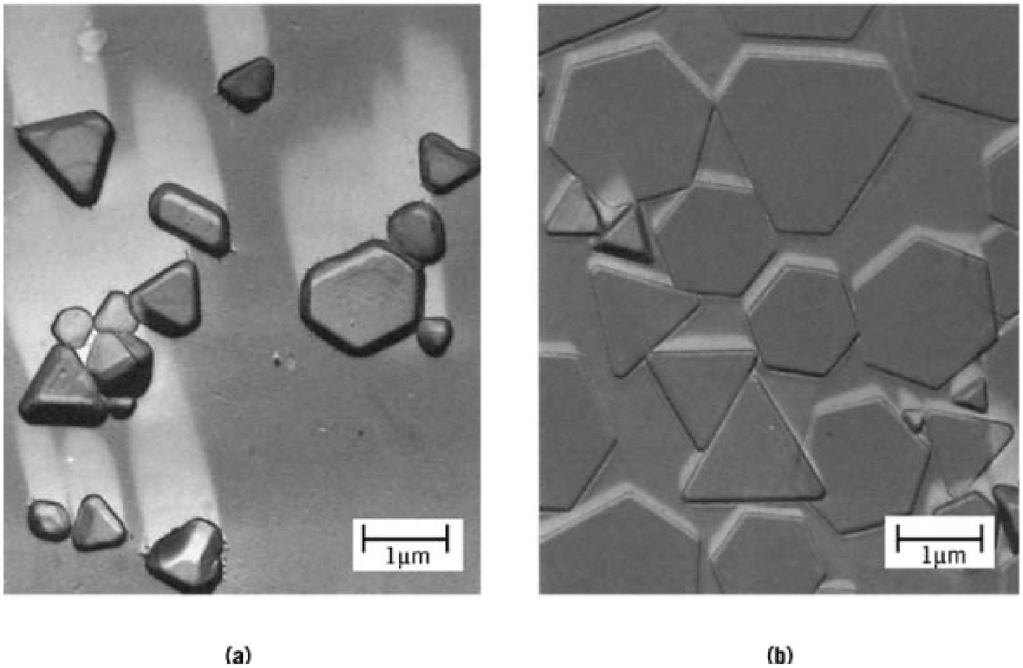


Fig. 6. (**a**) Cyanine sensitizing dye structure. (**b**) Sensitivity curves (- - -) intrinsic silver halide; and (—) for the dye in (**a**) where A corresponds to $n=0$; B to $n=1$; C to $n=2$; and D to $n=3$.

an emulsion that is dyed to be sensitive to green or red light still retains its intrinsic blue sensitivity, the greater minus-blue/blue sensitivity ratio afforded by tabular crystals reduces unwanted blue light sensitivity in those layers of the film designed to record green and red light. Another advantage cited for this technology is an improvement in the optical transmission properties of layers containing tabular emulsions. Because the crystals align themselves nearly parallel to the film support during the coating and drying operations, the transmitted light is less scattered sideways. This is advantageous for image sharpness in multilayer color films.

3. Color Processes

3.1. Additive Mixing

The first commercially successful color photographic systems used additive color mixing. Simultaneous recording of red, green, and blue components of an image was achieved in the chromoscope camera in 1898. The image beam was split into three using semitransparent mirrors and prisms, the three beams passing through red, green, and blue filters before striking the emulsion surface. One of the most serious practical difficulties encountered was nonuniformity of intensities at the film plane as a result of the optics of semireflecting mirrors.

If different colors are presented rapidly enough to the eye, they are additively fused by the visual system. This principle has been applied to the generation of moving color images, where successive frames contain the red, green, and blue records of the scene. Photography and projection is accomplished by having the appropriate colored filters move in synchronism with the image frames. This method places great mechanical demands on apparatus, however, requiring much higher than the normal projection rate of 24 frames per second. The results are often unsatisfactory because of color fringing of moving objects, and flicker from the different transmission characteristics of the filters used.

Mixing additive primaries as dyes by superposition does not work, because each primary absorbs two-thirds of the spectrum. The two difficulties of registration and additive superposition were overcome by what is known historically as the screen-plate process. The additive primaries are presented to the eye as a mosaic of very small colored dots in juxtaposition, as in pointillist painting. Although close inspection reveals a pattern of colored dots, additive blending occurs by increasing the viewing distance. The retina of the eye is itself a random mosaic of red, green, and blue receptors, and if the dot pattern is fine enough, the eye interprets the image as being smooth. The photographic record is obtained by exposing a silver halide emulsion which is sensitized throughout the visible spectrum, i.e., it is panchromatic, through a mosaic of very small red, green, and blue filters. The film is then processed to give a positive image in silver. When viewed or projected in registration with the original mosaic, a colored image is created. The amount of light transmitted through each filter is controlled by the developed silver optical density.

The first commercially successful screen-plate process was the Autochrome Plate made by the Lumiere Co. in France in 1907. The mosaic of filters was integral to the photographic plate, and consisted of starch granules about 15 μm in diameter that were dyed red, green, and blue. The individually dyed granules were mixed and pressed onto the plate so that their edges touched. The spatial distribution of red, green, and blue granules was random. Any gaps in the mosaic were filled by a carbon paste. This filter screen was then overcoated with the emulsion. Exposure was made through the reverse side so that the exposing light passed through the filters first. The final image was intended for direct viewing or projection. The relative surface areas of the three primary colors were such as to give a satisfactory neutral with the viewing illuminant. The Autochrome process survived commercially until the mid-1930s. Mottle sometimes appeared in the Autochrome image because of clumping of the starch granules. A regular grid of filters gave more satisfactory results, as in Dufaycolor (1908), which employed a very fine square grid of filter elements.

The lenticular method (30) was also commercially successful. The reverse side of a panchromatic black-and-white film was embossed with a very fine (about 25 per mm) pattern of cylindrical lenses or lenticules. The camera had a red filter over the top third of its lens, a green filter over the middle third, and a blue filter over the bottom third. During exposure, the lenticules were parallel to the camera filters. Light from any tiny area of the subject is focused onto the lenticular surface, which faces the lens. The lenticule then focuses a tiny image of the lens aperture with its three filters onto the panchromatic emulsion coated on the reverse side of the film. The relative intensities coming through each filter depend on the color of that tiny area of the subject. This process occurs for every point of the image, resulting in three horizontal bands for each lenticule. In this system, the variables to be optimized were line spacing, the thickness of the support, and the curvature of the lenticules. When the film is given a black-and-white reversal process, and the optical path reversed in a projector where the lens has the same arrangement of filters as the camera, a colored image is obtained. This system was introduced in 1928 by Eastman Kodak Company. as Kodacolor and was available until 1935 as a 16-mm motion picture film.

At present, the additive process is used in color television, in which light emitted from a tiny regular mosaic of red, green, and blue phosphors blends to give the colored image. Another modern additive color system is Polaroid's Polachrome 35-mm transparency film, which consists of a positive silver image overlying an additive screen having 394 triplets of red, green, and blue lines per centimeter of film. However, because additive photographic systems are inherently wasteful of light (each additive filter absorbs two-thirds of the light energy), most modern systems rely on the subtractive primaries.

3.2. Subtractive Mixing

There are mechanical difficulties in separating a photographic image into three images to record red, green, and blue information, only to recombine them later. Perfect registration of the color information can be preserved in a film if the three-color records are stacked on top of each other on the support. This film structure is known as an integral tri-pack. Photographic systems have been designed in which the three subtractive primary dyes - cyan, magenta, and yellow - can be formed in register, destroyed in register, or transferred in register to create the full-color image.

Dye destruction technology, Silver Dye-Bleach, is used in the Cibachrome process. After a black-and-white development step, the film is subjected to an acidic dye-bleach solution that destroys the incorporated azo dyes in proportion to the amount of developed silver, leaving a residual positive color image. Because the presence of light-absorbing dyes during exposure severely limits the photographic speed of these materials, they are used to make display transparencies and prints, usually from a camera transparency original. The azo dyes (qv) used in this process offer very good light and dark stability.

The first instant color photography system, introduced by the Polaroid Corp. in 1963 as Polacolor, used the transfer of subtractive dyes to a receiver sheet to produce a positive image. The incorporated dye-developers, containing a hydroquinone moiety, are soluble in the alkaline activator solution, except where silver development occurs, when they are immobilized as the quinone form.

Another dye diffusion method is the dye transfer system in which three-color separation negatives are prepared from an original positive color transparency. These are printed onto a special matrix film, which is processed in a tanning developer and washed in hot water to remove unhardened gelatin, giving three positive gelatin relief images. The depth of the gelatin relief is inversely proportional to the original camera exposure received. The corresponding subtractive primary dye is imbibed into each matrix and then transferred in register to a receiver sheet. Technicolor motion picture prints have been made by this process, which is used in situations that demand exceptional color quality and dye stability.

The first commercially successful film using the *in situ* formation of three subtractive dyes was Kodachrome film, introduced in 1935. The film has a multilayer structure in which red-sensitive, green-sensitive, and blue-sensitive emulsions are successively coated on the same support. Because the compounds necessary for dye formation are not incorporated in the film, an elaborate process is required to produce each dye in its correct layer. The first step is a conventional black-and-white development to give a silver image. In the first commercial Kodachrome process, the silver image was removed (bleached) to leave a reversal image in residual silver halide. As the initial step in color image formation, cyan dye was formed in all layers by the reduction of this (residual) silver halide. The film was then dried and subjected to a slowly penetrating bleach solution that decolorized the cyan dye and oxidized the silver in the blue- and green-sensitive layers. The process was repeated with magenta dye formation in the green- and blue-sensitive layers. The film was again dried, with subsequent selective bleaching of the magenta image and silver oxidation in the blue-sensitive layer. A final color-forming step generated yellow dye in the blue-sensitive layer. Removal of all image silver then left a positive three-color image. The modern Kodachrome process relies on selective layer exposure and dye formation steps, again using silver reduction to drive the dye formation reactions.

Subtractive dye precursors (couplers) that could be immobilized in each of the silver containing layers were sought, so that dye formation in all layers could proceed simultaneously rather than successively. The first of these to be commercialized were in Agfacolor Neue and Ansco Color films, introduced soon after Kodachrome film. These reversal working films contained colorless couplers that were immobilized (ballasted) by the attachment of long paraffinic chains. The addition of sulfonic or carboxylic acid groups provided the necessary hydrophilicity to make them dispersible as micelles in aqueous gelatin.

A different approach was taken in Kodacolor film, introduced by Eastman Kodak Company. in 1942. The couplers were ballasted but, instead of having hydrophilic functional groups, were dissolved in a sparingly water-soluble oily solvent. This oily phase was then dispersed by high agitation into a gelatin solution as fine droplets less than one micrometer in diameter. Kodacolor film is negative working, and was designed to be printed onto a companion color paper, which because it is also negative working, produces a positive color print. The whole system is known as the negative–positive process.

Figure 7 illustrates two ways in which the integral tri-pack can be processed. One leads directly to a positive image; the other leads to a negative image that can be subsequently printed on a negative-working paper. In the positive-working or “reversal” process, used in slide films, the first step is a black-and-white development to yield a negative silver image. After light or chemical fogging of the unexposed silver halide, subsequent development is carried out in a color developer that simultaneously reduces the unreacted silver halide and generates dye. Removal of all the silver leaves the positive color image. The negative-working process uses the initial silver development reaction to drive color formation. Because the camera negative is not the final image, the system is tolerant of underexposures and overexposures by as much as two stops (a factor of four), and density differences in the negative can be allowed for in the printing stage. The key process steps for color negative are develop/bleach/fix, which are carried out under carefully controlled temperature and agitation conditions. Water washes follow the bleach and fix steps.

The negative–positive system enjoys great commercial success. In 1949, color purity was improved by the introduction of colored masking couplers to the camera negative film, which partially corrects for the unwanted absorptions of the image dyes (31). Masking couplers account for the yellow-orange color seen in the unexposed parts of modern color negative films after processing. A later improvement was the introduction of development-inhibitor-releasing (DIR) couplers, in which a silver development inhibitor released as a function of exposure in one layer can influence the degree of development in adjacent layers (32). Using masking couplers and DIR couplers in concert can substantially improve the quality of color reproduction seen in the final print.

The principal features of an integral tri-pack are shown in Figure 8. The color records are stacked in the order shown, with the red record on the bottom, the green record next, and the blue record on the top. The blue record is on the top because it is necessary to interpose a blue light filter to remove blue light which would otherwise form latent images in the underlying red and green records. Silver halides, with the exception of AgCl, have an intrinsic blue light sensitivity even when spectrally sensitized to the green or red. The traditional filter material has been Carey Lea silver, a finely dispersed colloidal form of metallic silver, which removes most of the blue light at wavelengths $<$ca 500 nm. This material also filters out some green and red light, thus requiring additional sensitivity from the underlying emulsions. To alleviate this problem, organic solid particle filter dyes with better spectral characteristics may be used (33). In addition to a blue light filter, a green light filter may be employed under the green light record of the film. This is helpful in improving the spectral separation between the green and red records. Antihalation protection is required to prevent back-scatter of transmitted light from the air/support interface at the back of the film. This back-scattered diffuse light causes sharpness degradation and is most noticeable as a “halo” around bright objects. The antihalation underlayer is designed to prevent this. The required opacity is usually obtained by coating pre-developed filamentary silver, which is then easily removed in the normal film processing. Alternatively, an antihalation layer can be coated on the reverse side of the film. In motion picture films, a layer of finely divided carbon has been used for this purpose; it is physically removed by scrubbing before the film is processed.

Each color record is separated from its neighbor by a gelatin interlayer. This is required to prevent silver development in one record causing unwanted dye formation in another. It is also common practice to divide each color record into two or more separate layers, with the most sensitive emulsion of each record on the top. The optical screening of the underlying less sensitive layer allows a wider exposure latitude to be attained. A uv-filter layer is placed on top of the pack. Because silver halide is sensitive to ultraviolet light, this layer is designed to minimize transmission of wavelengths $<$ca 400 nm. Without this protection the film would record any uv radiation as blue light, leading to an unnatural bluish cast in the final image. The purpose of the overcoat layer is to give the film the desired combination of physical properties important in handling. These include adequate surface roughness to prevent sticking when the film is stored in roll form, lubrication for smooth transport in the camera, and the proper electrical conductivity to avoid static discharge.

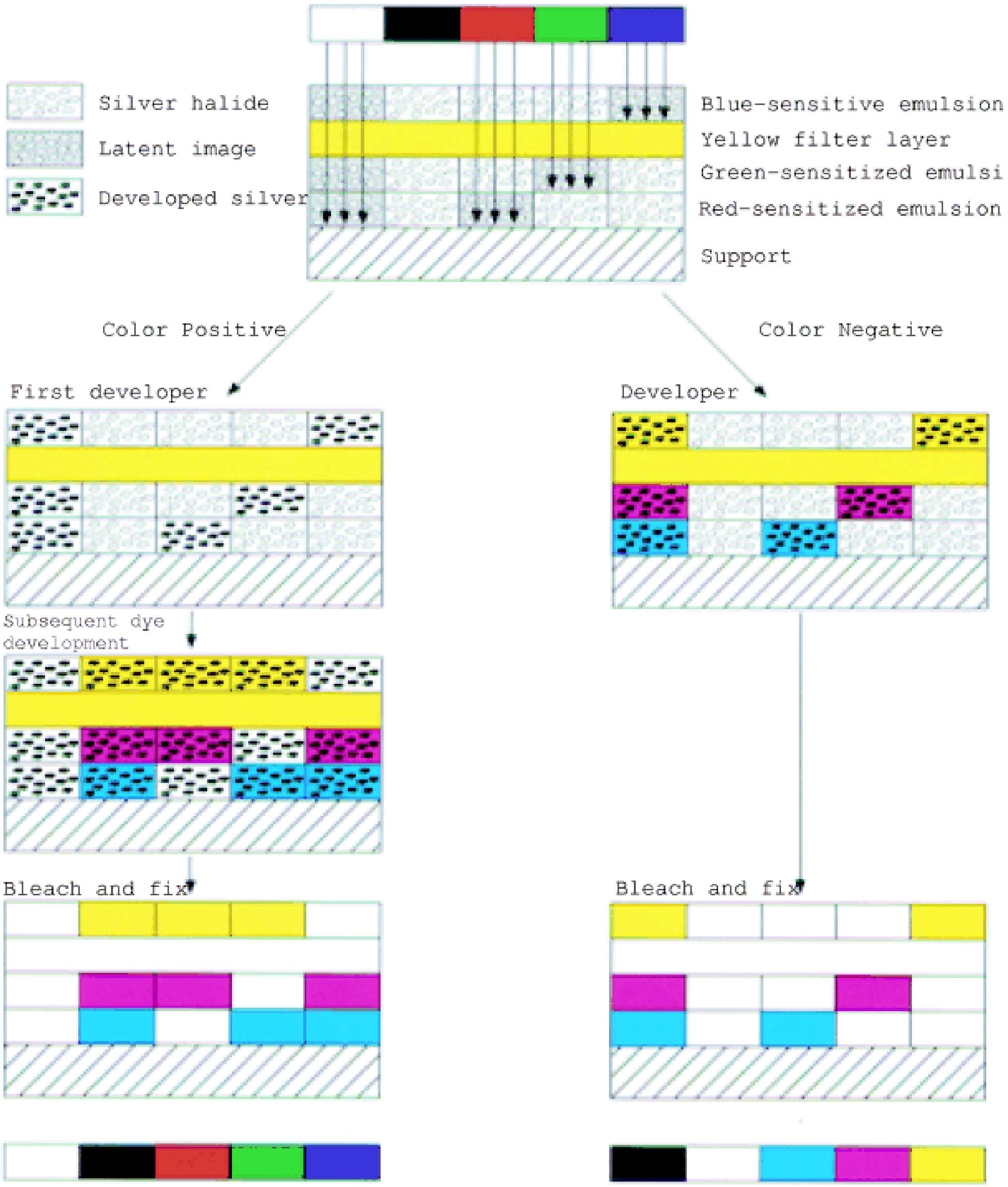


Fig. 7. Calculated relationship between log (relative sensitivity) and log (crystal volume) for (—) intrinsic response (blue) and (- - -) dyed response (minus blue), assuming crystals are spherical.

4. Chromogenic Chemistry

4.1. Developers

The detection and amplification of the latent image on the silver halide crystal occurs through the intervention of a mild reducing agent called a developer. In chromogenic development, this agent in its oxidized form has the further function of reacting with the dye-forming coupler to produce the color image.

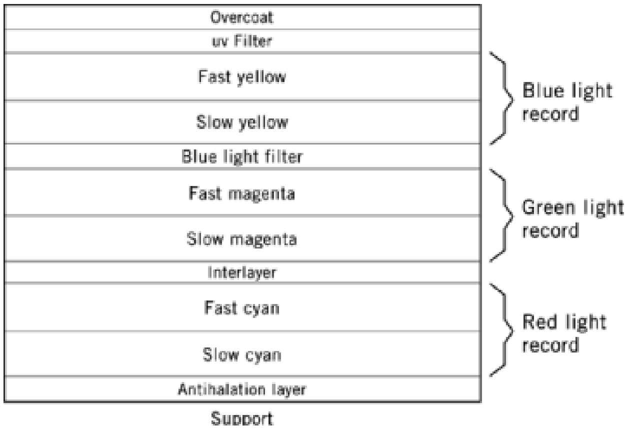


Fig. 8. Features of an integral tri-pack.

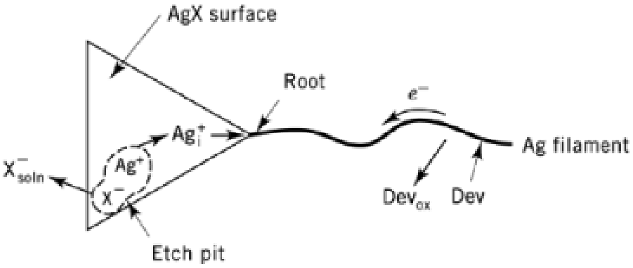
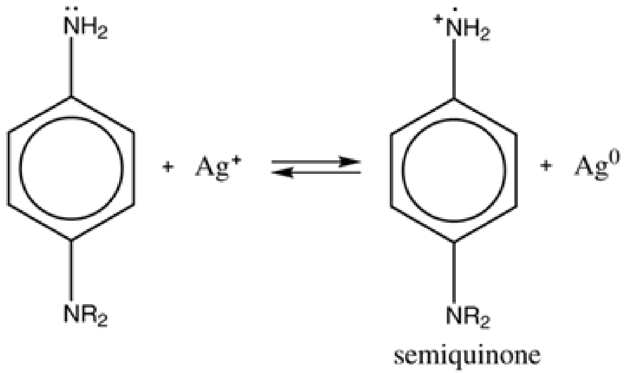
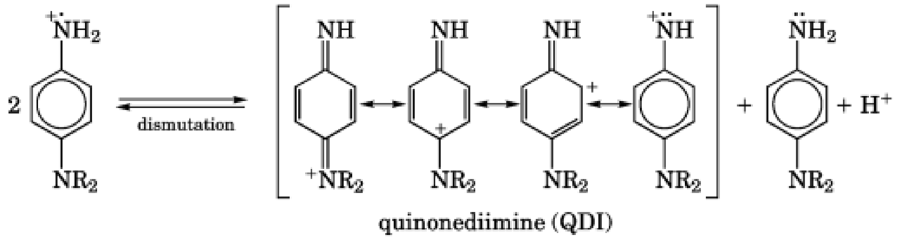


Fig. 9. Corrosion model of silver development. As the halide ion, X^-, is removed into solution at the etch pit, the silver ion, Ag^+, travels interstitially, Ag_i^+, to the site of the latent image where it is converted to silver metal by reaction with the color developer, Dev. Dev_{ox} represents oxidized developer.

In the corrosion model of silver development (35), the silver halide crystal may be viewed as an electrochemical cell where the latent image silver speck acts as both an anode and a cathode (Fig. 9). The silver metal that is exposed to the developer solution receives electrons from the developer, forming oxidized developer. The silver metal in contact with the silver halide crystal gives up electrons to silver ions from the crystal. The silver filament thus grows from its base, increasing the surface area for developer oxidation, accounting for the autocatalytic nature of the development process. This powerful amplification, on the order of 10^8 in commercial systems, of the latent image to the entire crystal is one of silver halide's unique imaging properties. As silver ions from the crystal are reduced to metallic silver, halide ions depart into solution to maintain electrical neutrality.

For modern color photographic systems, the developing agent of choice is an *N,N*-disubstituted *p*-phenylenediamine (PPD) (34, 36). In the initial heterogeneous reaction with silver halide, the PPD is oxidized by the loss of one electron to form the semiquinone (eq. **1**). Following desorption, two molecules of the semiquinone can undergo a fast dismutation reaction to produce the charged quinonediimine (QDI) and a molecule of the original reduced developer for an overall two-electron oxidation (eq. **2**). Alternatively, the adsorbed semiquinone can give up a second electron to the silver halide crystal to produce the QDI (37). It is this species that is the active dye-forming agent (37, 38). Because the overall development reaction produces protons, the process is favored by an alkaline environment and the developer solutions are often maintained around pH 10 by a carbonate buffer.

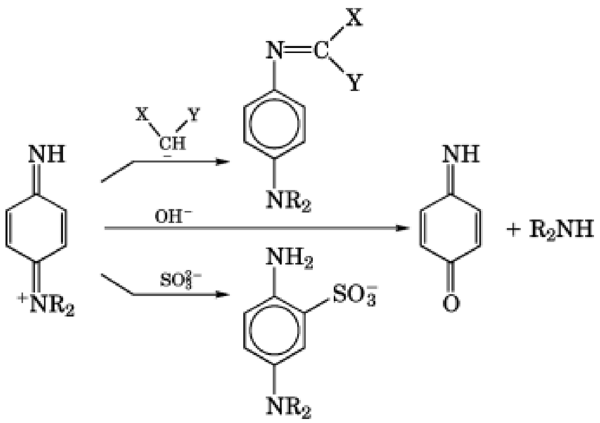




(2)

For most color photographic systems, development is the rate-determining step, and within that step the formation of semiquinone is the slow process (39). The fate of the highly reactive QDI is determined by the relative rates of a number of competing processes (40). The desired outcome is reaction with ionized coupler to produce dye (eq. **3**). Typically, the second-order rate constant for this process with ionized coupler is about 10^3 to 10^4 L/(mol·s) (41, 42). QDI is also attacked by hydroxide ion (eq. **4**) to produce a quinone monoimine (QMI), itself an oxidized developer derived from *p*-aminophenol. Such compounds can further react with coupler, albeit at a slower rate than QDI, to form a dye and were cited in the seminal patent as color developers (34). However, the dyes derived from this deaminated developer have different hues from the QDI dyes, and these hues are pH-dependent as a consequence of the phenolic group contributed by the developer. Although the deamination reaction to produce QMI is fast, the rate constant is 10^3 to 10^4 L/(mol·s) (42–44), its effect is somewhat offset by the redox reaction of the QMI with the reduced developer, present in large excess, to regenerate the desired QDI. The primary net effect of the deamination reaction is to enlarge the resulting dye cloud (45).

An even more potent nucleophile toward oxidized developer is the sulfite anion (eq. **5**) present in most developer formulations (44, 46). Sulfite is used to scavenge excess oxidized developer that otherwise would undergo a number of self-condensation reactions resulting in stain. Sulfite also serves to drive the redox reaction as well as acting as an antioxidant and mild silver halide solvent. Whereas the sulfite reaction is complicated, involving acid and base catalysis and a multiplicity of products, the half-life for oxidized color developer in a typical processing solution containing sulfite is only about 2 ms. This reaction with sulfite is the principal reaction limiting the size of the resulting dye cloud (47).



(3)

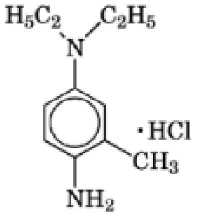
(4)

(5)

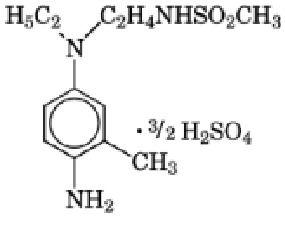
Practical developers must possess good image discrimination; that is, rapid reaction with exposed silver halide, but slow reaction with unexposed grains. This is possible because the silver of the latent image provides a conducting site where the developer can easily give up its electrons, but requires that the electrochemical potential of the developer be properly poised. For most systems, this means a developer overpotential of between -40 to +50 mV vs the normal hydrogen electrode.

Developing agents must also be soluble in the aqueous alkaline processing solutions. Typically such solutions are maintained at about pH 10 by the presence of a carbonate buffer. Other buffers used include borate and, less frequently, phosphate. Developer solubility can be enhanced by the presence of hydroxyl or sulfonamide groups, usually in the *N*-alkyl substituent. The solubilization also serves to reduce developer allergenicity by reducing partitioning into the lipophilic phase of the skin (48).

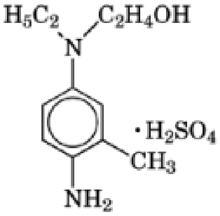
Some of the color developers in commercial use are CD-2(**4**) [2051-79-8], CD-3(**5**) [25646-71-3], and CD-4(**6**) [25646-77-9]. The various substituents control the rates of the various developer reactions as well as the hue, extinction, and stability of the resulting image dyes. The presence of an alkyl group ortho to the primary amino moiety serves several purposes, including steric minimization of the condensation reaction with reduced developer (49) and improved dye stability. Electron-donating groups either on the ring or on the tertiary amino group increase development rate while decreasing to a lesser extent the rate of reaction of oxidized developer with coupler (35, 42). Electron-donating groups on the developer also tend to shift the absorption of the dye that forms to longer wavelengths (50).



CD-2



CD-3



CD-4

In addition to the developer, sulfite, and pH buffer, commercial developer solutions often contain antifoggants or restrainers that reduce the rate of development of unexposed silver halide relative to exposed grains (51). A common restrainer is the halide ion of the same type as in the film's silver halide emulsion. The excess halide serves to control the silver ion concentration or pAg, where pAg = $-\log[\text{Ag}^+]$. Other antifoggants include organic materials like benzotriazoles, benzyltriazolium salts, and 3,5-dinitrobenzoic acid [99-34-3], $C_7H_4N_2O_6$. Developer solutions can also contain antioxidants (qv) such as hydroxylamine sulfate [10039-54-0], metal sequesterants (see Chelating agents), and materials to aid in sensitizing dye removal or to boost coupling rates.

4.2. Coupler Types

A photographic coupler is a weakly acidic organic compound that reacts with an oxidized *p*-phenylenediamine to produce a dye, usually one of the subtractive primaries, cyan, magenta, or yellow (52) (Fig. 10). In addition to the dye-forming portion of the molecule, most couplers also bear an organic ballast, a long aliphatic chain or combination of aliphatic and aromatic groups. This allows the coupler to be suspended in droplets of a high boiling organic liquid, called the coupler solvent, which serves to anchor the coupler in its appropriate film layer. In some recent formulations, the dye-forming portion of the coupler is attached to a polymeric backbone (53). In both cases such films are referred to as incorporated coupler systems. Kodachrome film is unique, however, because its couplers are not contained in the film, but diffuse in during the development steps. Although functionally similar to the incorporated couplers, couplers for Kodachrome films are water-soluble and do not contain an organic ballast.

Cyan dyes are derived typically from phenols or naphthols. These so-called indoaniline dyes absorb in the red, from 600 to 700 nm and beyond, and have unwanted absorptions in the blue-green. Magenta dyes are formed from pyrazolones, pyrazolotriazoles, and other species that have either an active methylene group as part of a conjugated ring or, less frequently, an active methylene flanked by electron-withdrawing groups. Magenta dyes are designed to absorb in the green between 500 and 600 nm, but often have additional absorbances in the blue. Yellow dyes are produced from couplers containing an active methylene group that is not part of a ring. These absorb blue light between 400 and 500 nm and typically have strong absorptions in the ultraviolet, which afford some protection to underlying layers from light-induced dye fade.

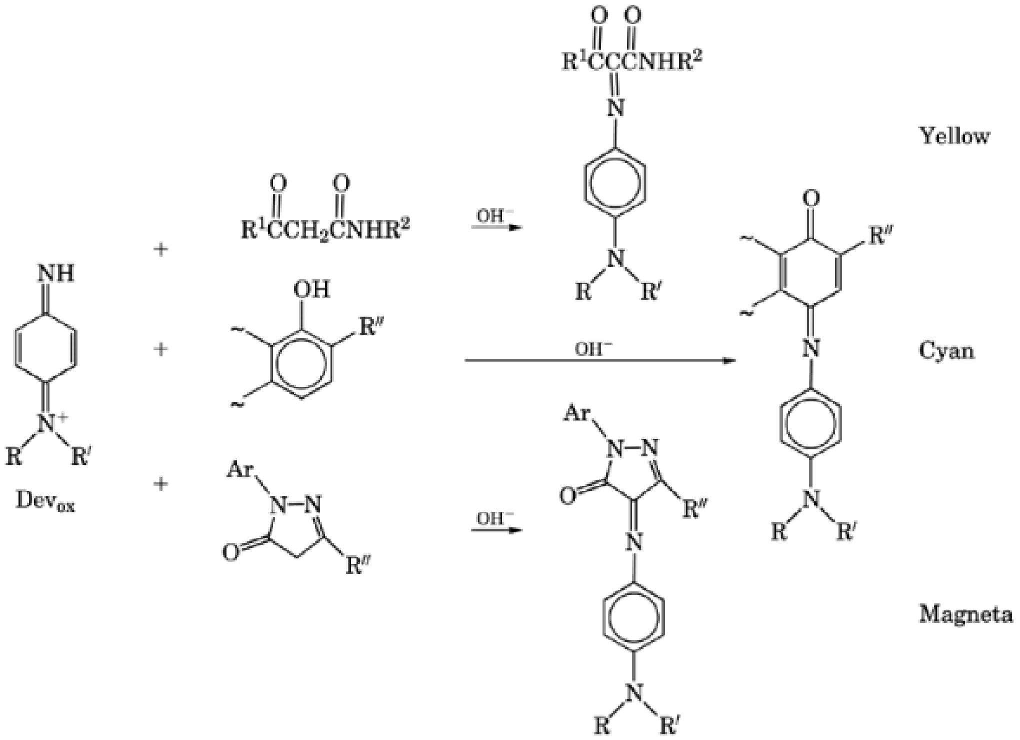


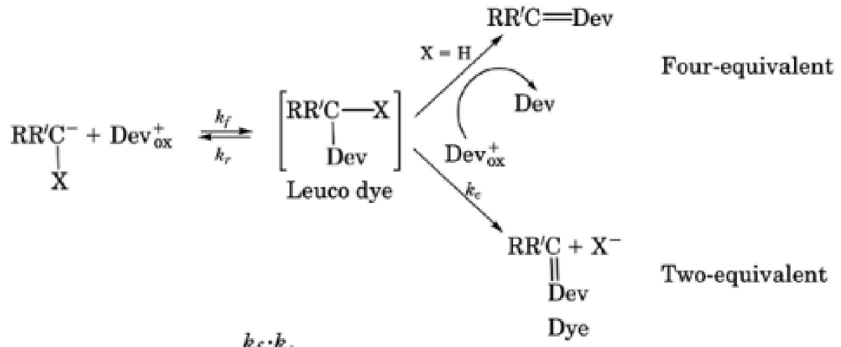
Fig. 10. In each image-forming layer, developer oxidized by the exposed silver halide (Dev_{ox}) reacts with the appropriate coupler to form the corresponding subtractive primary dye, yellow, cyan, or magenta. Ar represents an aryl group and the various R's are undefined organic segments.

4.3. Mechanisms of Coupling

Because the active coupling species is the ionized coupler (37, 54), the rate of the coupling reaction and hence its ability to compete for oxidized developer is dependent on the pH of the process, the pK_a or acidity of the coupler or less frequently the rate of coupler ionization, and the reactivity of the resulting coupler anion with the QDI (42).

For most cyan and magenta couplers, ionization is rapid and can be characterized by the pK_a of the coupler. For yellow couplers, which can exist as both keto (carbon acid) and enol (oxygen acid) tautomers, ionization can be measurably slow, even rate determining in some processes (55). This tautomeric equilibrium and hence the degree and rate of ionization can be both structure and environment dependent.

Once ionized, the coupler reacts with oxidized developer to produce an intermediate or leuco (colorless) dye (Fig. 11). If X is hydrogen, an oxidation involving a second molecule of QDI is required to produce the image dye. Because formation of each mole of QDI requires the reduction of two moles of silver ion (for a total of four moles), such couplers are referred to as "four-equivalent" couplers. If, however, X is a good leaving group, such as a halide, or a low pK_a phenol or heterocycle, departure of X as an anion to form the dye proceeds spontaneously, and the coupler is said to be "two-equivalent" (45). Although the final dye yield, i.e., the ratio of dye formed to silver reduced, can depend on the degree of competition in the system, two-equivalent couplers tend to be preferred because they undergo fewer side reactions with oxidized developer and require less silver halide to produce an equivalent amount of dye. Thus there is not only an obvious economic benefit, but it can lead to increased film sharpness by reducing optical scatter by the coated silver halide.



$$k_{e-} = \frac{k_f \cdot k_e}{k_r + k_e} \approx k_f \quad (\text{For } k_e \gg k_r)$$

Fig. 11. Reaction of ionized coupler and oxidized developer ($\mathrm{Dev}_{\mathrm{ox}}^{+}$) to produce the intermediate leuco dye. If X is a good leaving group, the reaction proceeds spontaneously to dye, and the coupler is said to be two-equivalent. If oxidation by a second molecule of oxidized developer is required, the coupler is four-equivalent.

For two-equivalent couplers where the conversion of the leuco dye to image dye is rapid, the experimentally observed second-order rate constant, k_{c^-}, can be equated with k_{f}, the rate of nucleophilic attack of coupler anion on oxidized developer. Thus when the pH of the process is specified, two parameters, $\mathrm{p}K_{\mathrm{a}}$ and k_{c^-}, can be conveniently used to characterize the molecular reactivity of a large variety of photographically well-behaved couplers (42, 56).

When couplers are grouped together in structurally similar families, such as the naphthols in Figure 12, it is found that a linear free-energy relationship of the form $\log kc_{-} = \alpha + \beta \mathrm{p}K_a$ often exists between the $\mathrm{p}K_{\mathrm{a}}$ of the coupler and the log k_{c^-} of its resulting anion (42). That is, a substituent X that raises the $\mathrm{p}K_{\mathrm{a}}$ of the coupler and thus reduces the concentration of active anion at a given pH also increases the activity of that anion. The constant β is a measure of the trade-off between those two opposing factors on coupler reactivity. For β greater than 1, increasing the electron-donating ability of the substituent leads to an increase in anion reactivity that more than compensates for the loss in anion concentration. For β less than 1, the opposite is true; overall reactivity results from decreasing the $\mathrm{p}K_{\mathrm{a}}$ of the coupler, until the $\mathrm{p}K_{\mathrm{a}}$ drops below that pH of the process. At that point, with the coupler fully ionized, changes in the molecule that lower $\mathrm{p}K_{\mathrm{a}}$ serve not to increase anion concentration, but only to decrease anion reactivity (56).

Studies on the naphthol and phenol couplers indicate that the field and resonance, but not steric, effects of the substituents are important in determining $\mathrm{p}K_{\mathrm{a}}$ and k_{c^-} suggesting that formation of the leuco dye proceeds through an early transition state where there is overlap between the electron-deficient *p*-orbitals of the developer ring and the electron-rich *p*-orbitals of the naphthol ring. This geometry is quite different from that of the product (57). For coupling reactions where conversion of the leuco dye to image dye is not fast, the rate constant of the reverse reaction, k_{r}, is important. If k_{r} is much less than k_{e}, dye formation is slow, but dye yield can still be high, although the leaving group may not be released in time to affect development. If, however, k_{r} is faster than k_{e}, much of the oxidized developer originally captured by the coupler is lost to other reactions, and dye yield is low (56).

Whereas the effect of the pH of the processing solution on coupling is most often considered in the context of the coupler, the structure of which can be varied, pH can also affect the activity of the oxidized developer (43, 56). In general, oxidized developers fall into three categories. The first, like CD-2, have a constant charge, either cationic or zwitterionic, at normal processing pH values, and coupling rates are little affected by pH changes. The second class exists in cationic or neutral forms as a function of pH. For example, the oxidized form of the commercially important CD-4 reacts reversibly with hydroxide ion to form a neutral pseudo-base,

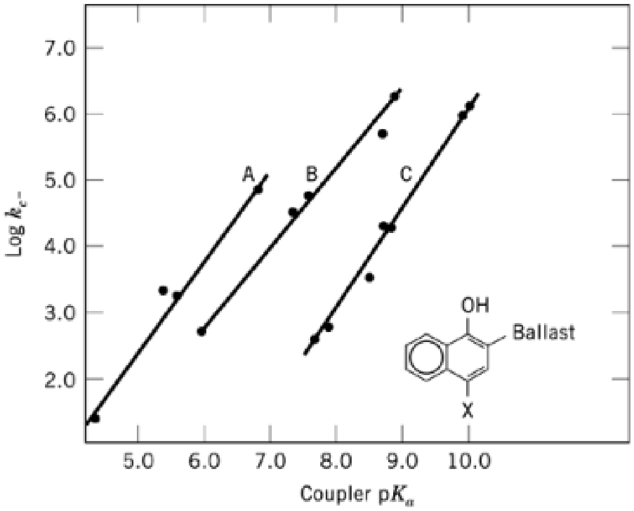


Fig. 12. The relationship between acidity and anion reactivity for naphthol couplers differing in the 2-position ballast where A is ballast 1; B, ballast 2; C, ballast 3. For each coupler data points represent different leaving groups, X.

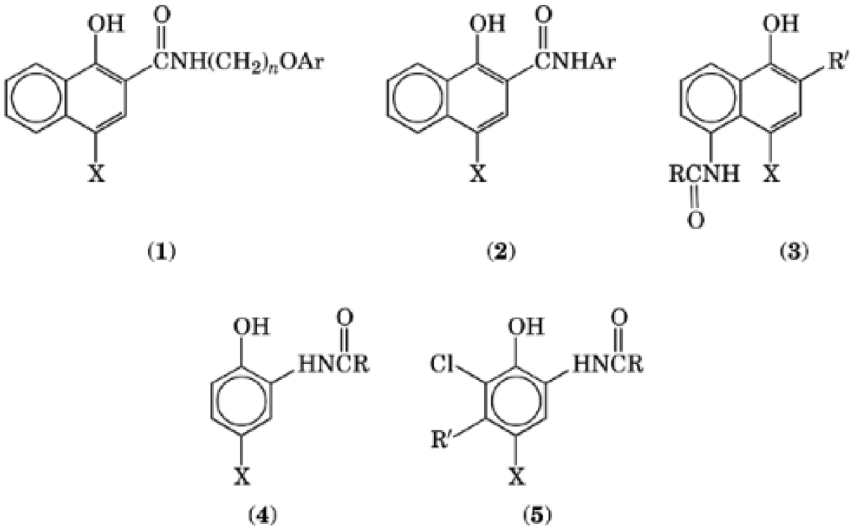
which is unreactive toward coupling (43). Finally, the quinonedimine derived from developers like CD-3 can exist in cationic and zwitterionic forms as a function of pH. Both forms can react with ionized coupler, but at different rates.

Though the molecular reactivities of the coupler and the developer are important, both can be severely constrained by the polyphasic nature of the film system, where the coupler is most often embedded in a lipophilic phase while the oxidized developer is generated in the aqueous gelatin phase (45). Because the organic solvent invariably has a lower dielectric constant than the aqueous phase, the effect is to suppress ionization of the coupler while slightly increasing the rate at which the positively charged QDI and coupler anion react with one another. The overall result is to reduce the rate of dye formation. In the case of some yellow couplers, the rate-determining step can change from coupling to ionization as a function of solvent or even substituent. The structure of the oxidized developer as well as its charge can also control its ability to partition into the organic phase (44, 58).

In some processes, development additives such as benzyl alcohol are added to the developer to increase the hydrophilic nature of the organic phase. More frequently, higher pK_a couplers are designed to have additional ionizable sites, such as carboxyl, sulfo, or phenolic groups, to accomplish the same end (59).

In any case, the kinetics of such systems can be very complex, depending not only on the identity of the coupler and developer, but also on the nature of the dispersed organic phase. Often, the rate of coupling is found to be proportional to the total surface area of the droplets containing the coupler. Less frequently, as when the droplet integrity is destroyed in the developer bath, the rate can be independent of droplet size. Surfactants (qv) and mechanical milling techniques are used to form these oil-in-water emulsions, or dispersions as they are called in the photographic literature, at highly controlled particle sizes and with the requisite stability for coating and storage.

In some cases, dye-forming moieties attached to a polymeric backbone, called a polymeric coupler, can replace the monomeric coupler in coupler solvent (53). In other reports, very small particles of coupler solubilized by surfactant micelles can be formed through a catastrophic precipitation process (60). Though both approaches have the potential to eliminate the need for mechanical manipulation of the coupler phase, as well as detrimental heating to effect coupler dissolution, in practice they have seen only limited application.



(1) (2) (3)

(4) (5)

Fig. 13. Cyan dye-forming couplers where X can be H, Cl, OAr, OR, or SAr. Ar is aryl. R and R′ are undefined organic segments.

4.4. Cyan Couplers

Substituted phenols and α-naphthols are the primary classes of cyan dye-forming couplers (Fig. 13). Naphthols of structural types (**1**) and (**2**), the 1-hydroxy-2-naphthamides, have proved very useful and are easily and inexpensively prepared. Hydrogen bonding between the naphtholic oxygen and the hydrogen of the 2-amido group serves to shift the dye hue bathochromically (to longer wavelengths) while increasing its extinction and contributing to the dye's stability. Electron-withdrawing groups on the amide nitrogen also shift the hue bathochromically and increase the extinction coefficient (61). Substitution in the 4-position provides accessibility to image-modifying couplers of various types. However, some dyes of this class are prone to chemical reduction, which returns them to the colorless leuco form in the presence of ferrous ion during the bleaching step (62). Naphthols of type (**3**) are reported to show less fade to the leuco dye (63). probably due to stabilization of the dye by internal hydrogen bonding.

Phenols of structure (**4**) are also claimed to show markedly improved dye stability both in the presence of ferrous ion and, with a second carbonamido group in the 5-position, to simple thermal fade (64). Numerous substituent variations are described in the literature to adjust dye hue. A perfluoroacylamido in the 2-position shifts the hues bathochromically while maintaining thermal stability of the dyes (65). Phenols of structure (**5**) are said to show outstanding light stability, which makes them especially suitable for display materials like color paper (66).

Some cyan dyes derived from both naphthols and phenols are reported to show thermochromism, a reversible shift in the dye hue as a function of temperature. This can occur in a negative while prints are being made (67).

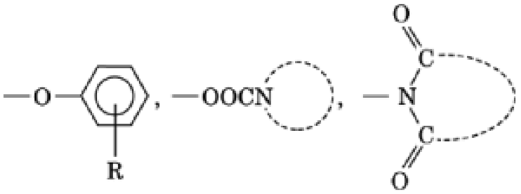
Derivatives of the pyrazolotriazole nucleus, more commonly used in magenta dye forming couplers (see below), and the related pyrrolotriazole ring, have recently been described as new parents for cyan couplers with the reported advantage of yielding dyes of very high extinction ($\epsilon > 60{,}000$). The hue of the dye is shifted into the cyan by the use of extended conjugation and electron-withdrawing groups (68).

4.5. Yellow Couplers

The most important classes of yellow dye-forming couplers are derived from β-ketocarboxamides, specifically the benzoylacetanilides **6** (69) and the pivaloylacetanilides **7** (70). Substituents Y and Z can be used to attach ballasting or solubilization groups as well as to alter the reactivity of the coupler and the hue of the resulting dyes. Typical coupling-off groups (X) cited in the literature are also shown.

(6)

(7)



For the widely studied benzoylacetanilides, coupler acidities can be correlated using a two-term Hammett equation involving substituents in either or both rings. As in the naphthols, there is a linear correlation of the log k_{c^-} and pK_a values, but β equals 0.55, suggesting that increased reactivity comes with reduced pK_a, until the coupler is nearly fully ionized (71). The hues of the resulting dyes can be shifted bathochromically by electron-withdrawing groups in either ring. Ortho substitution in the anilide ring increases the extinction coefficient while narrowing the bandwidth of the dyes. Both the couplers and their dyes have significant absorptions in the ultraviolet that offer protection to dyes in the underlying layers (72).

The relatively low pK_a values seen for the benzoylacetanilides, especially as two-equivalent couplers, minimize concerns over slow ionization rates and contribute to the couplers' overall reactivity. But this same property often results in slow reprotonation in the acidic bleach, where developer carried over from the previous step can be oxidized and react with the still ionized coupler to produce unwanted dye in a nonimage related fashion. This problem can be eliminated by an acidic stop bath between the developer and the bleach steps or minimized by careful choice of coupling-off group, coupler solvent, or dispersion additives.

The second widely used class of yellow couplers is the pivaloylacetanilides **7** and related compounds bearing a fully substituted carbon adjacent to the keto group. The dyes from these couplers tend to show significantly improved light stability and so these couplers have been widely adopted for use in color papers as well as many projection materials. In general, the dyes have more narrow bandwidths and less unwanted green absorptions (70).

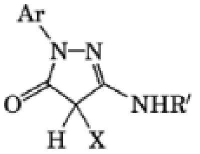
The lack of a second aryl group flanking the active methylene site, however, means that the pK_a values of the pivaloylacetanilides tend to be considerably higher than those of the benzoylacetanilides. As a result, these couplers are rarely used as their four-equivalent parents. Rather, the coupling site is substituted with electron-withdrawing groups to increase the acidity of the coupler or hydrophilic groups to aid in rate and extent of the oil-phase ionization. Both electron-withdrawing groups and hydrophilic groups can appear in the anilide ring as well. An interesting variation on this is the use of polarizable groups, such as C=O or S=O, in the ortho position of an aryloxy group attached to the coupling site. These groups reduce the pK_a of the coupler by increasing the rate of the ionization process (73). Another technique for increasing reactivity of these couplers is to reduce the steric hindrance of the tertiary-butyl group by constraining two of the pendant carbons in a cyclopropyl ring (74). The higher pK_a of the coupling site in the pivaloylacetanilides does mean that undesirable dye formation in bleach is minimized.

A deficiency of many yellow couplers is the relatively low extinction coefficient of the dyes they form, as low as about 15,000 and usually no higher than 22,000. This can be compared to typical cyan and magenta dyes with extinctions of greater than 30,000. To create a neutral in the film, this requires coating considerably more coupler and silver halide, resulting in a thicker, more expensive yellow layer with consequent reduced sharpness. One approach improved extinction has been to substitute an indolinyl or 2-aryl-3-indolyl group for the t-butyl group of the pivalolylacetanilides. These materials combine good reactivity with extinction coefficients as high as 27,000 (75). A second ingenious, albeit more complicated approach is to make the coupling-off group itself a pre-formed yellow dye whose hue does not manifest itself until the dye is released on coupling. Thus, each coupling event creates two dye molecules of dye, with a combined extinction of over 50,000 (76).

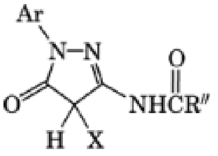
Other classes of yellow couplers reported in the literature include the indazolones (77) and the benzisoxazolones (78). Neither of these structures contains an active methylene group; dye formation is believed to occur through a ring-opening process.

4.6. Magenta Couplers

For many years the most widely used magenta couplers have been derived from the 1-aryl-2-pyrazolin-5-ones (79). Substituents in the aryl ring or at the 3-position have been used to alter dye hue and stability as well as to control coupler reactivity. Ballasting groups are usually attached through the 3-position as well. Electron-withdrawing groups at either site tend to shift the hue of the resulting dye bathochromically (80). Whereas the principal absorption of these dyes is in the region from 500 to 570 nm, most pyrazolinone dyes also show significant unwanted absorptions in the blue. Because these can be minimized by the use of 3-arylamino or 3-acylamino substituents (see structures **8**, **9**) while also increasing the extinction coefficient of the primary absorptions, such couplers have been extensively described in the literature (81). Ar represents an aryl group.

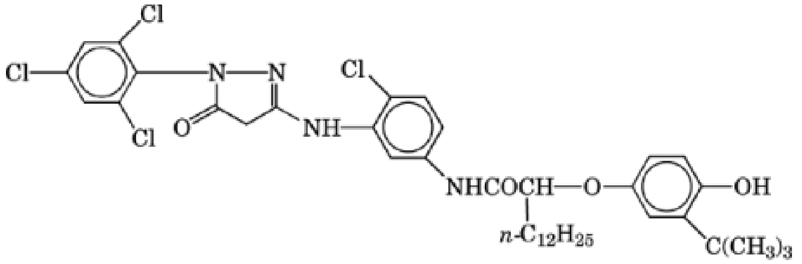


(8)



(9)

Although these pyrazolinone couplers can exist in several tautomeric forms, ionization of the couplers is rapid, and the four-equivalent parents have seen wide use for decades. The aryl ring is often trisubstituted in the 2,4,6-positions with one or more of the substituents being chlorine (82). The pK_a values for the 3-arylamino pyrazolinones **8** are higher than for their 3-acylamino **9** counterparts with dyes, the hues of which are shifted toward shorter wavelengths and show less unwanted blue absorption. Coupler **10** [61354-99-2] is unique because it carries its own stabilizer against photochemical dye fade in the form of the 4-alkoxyphenol ballast, making it especially suitable for color paper (83).

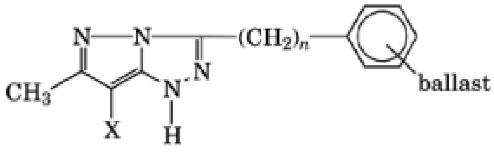


(10)

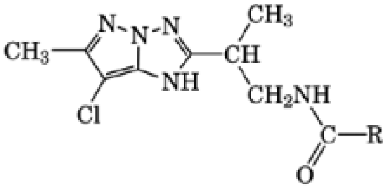
The four-equivalent pyrazolinones suffer from a number of disadvantages. Prior to processing, the couplers can react with ambient formaldehyde to yield a nondye-forming condensation product. Formaldehyde scavengers, such as ethyl enediurea, can be added to control this problem (84). After processing, the residual coupler can react with image dye to form colorless products (85). A formaldehyde stabilizer, which reacts with the residual coupler in the same fashion as the undesirable pre-process reaction, eliminates this problem. Finally, though these couplers react rapidly with oxidized developer, the intermediates undergo side reactions that result in reduced dye yields. Though the 3-acylamino pyrazolinones are more prone to these problems than the 3-arylamino couplers, both are susceptible (86).

The two-equivalent counterparts to these couplers are largely devoid of these problems. Both halogen and sulfo groups are unsatisfactory leaving groups because of various side reactions, whereas the otherwise attractive aryloxy moiety causes the coupler to undergo an often rapid radical chain decomposition process (87). Useful coupling-off groups cited in the literature include aryl, alkyl, and hetero thiol groups (88), nitrogen heterocycles (89), and arylazo groups (90). Because the thiols serve only to depress the reactivity of the already low pK_a acylamino pyrazolinones, they tend to be most useful on the arylamino couplers. Alkyl thiols, because of their high pK_a values, are generally reluctant leaving groups in the developer, but eventually form image dye in the low pH bleach (56, 91). Most of the arylthiol leaving groups cited in the literature show substitution at least in the 2-position. Bis-pyrazolinones, linked through the coupling site by methylene, substituted methylene, sulfide, and disulfide groups, have been reported to give two-equivalent couplers, but with only one of the couplers yielding dye (92).

A more recent class of magenta dye-forming couplers is the pyrazolo-(3,2,-*c*)-5-triazoles **11** and related isomers (93) where X can be Cl, SR, S-aryl, or O-aryl. Dyes from this class of couplers are exceedingly attractive, having good thermal stability and much lower unwanted blue and red absorptions than dyes from the pyrazolinones. However, the high pK_a values of the four-equivalent parents translate into unacceptably low reactivity. Two-equivalent analogues having chloro or aryloxy leaving groups and hydrophilic groups elsewhere in the molecule provide good reactivity and dye yield with resistance to ambient formaldehyde and dyes that do not require post-process stabilization (94). A related class of pyrazolotriazoles **(12)** is reported to yield dyes having improved light stability (95). The higher pK_a values of the pyrazolotriazole couplers have led to concerns over image variability induced by small changes in developer pH.



(11)



(12)

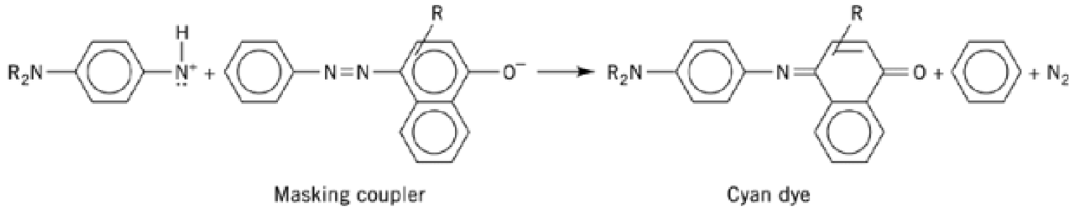
Other classes of magenta dye-forming couplers reported in the literature include the pyrazolobenzimidazoles (96) and the indazolones (97). The latter are unique because they do not contain an active methylene group and are proposed to form magenta dyes with a zwitterionic structure.

4.7. Colored Masking Couplers

The dyes produced in chromogenic development have unwanted absorptions. For example, the cyan dye is expected to control or modulate red light alone and thus should absorb only between 600 and 700 nm, but it shows lesser absorptions in the blue (400–500 nm) and green (500–600 nm) regions as well. Thus exposure of the red-sensitive layer of the film produces not only the desired density to red light in the negative, but also undesirable densities to blue and green light, resulting in desaturation or “muddying” of the color.

For materials that are not directly viewed, like a color negative film, masking couplers provide an ingenious solution (31, 98). Unlike a normal cyan dye-forming coupler, which is it colorless, a cyan masking coupler bears a colored, preformed (usually azo) dye in the coupling-off position. The hue of this dye is chosen to match the unwanted blue-green absorptions of the cyan dye that is generated. When coupling occurs, the preformed dye is released and washes out of the film or is destroyed. The result is a negative image formed by the cyan dye with its unwanted absorptions and an entirely complementary positive image left by the preformed dye remaining on the residual coupler (Fig. 14). This is equivalent to a perfect cyan image overlaid with a uniform blue-green density. Because the negative is printed onto color paper using separate cyan, magenta, and yellow exposures, a somewhat longer cyan exposure is required. Similar chemistry is employed to deal with the unwanted blue density of the magenta coupler (99).

The use of colored masking couplers does not come without a price, however. The pre-formed dye can absorb light on exposure, reducing effective film speed, and the background density of the masking dye can reduce the dynamic range of the negative. The first problem can be attacked by the use of process-removable group, which shifts the hue of the masking dye out of the visible region in the unprocessed film (100).



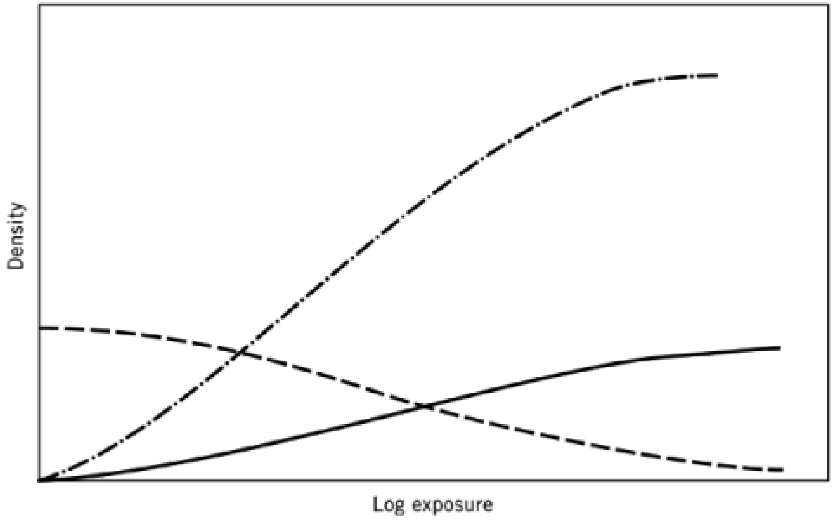
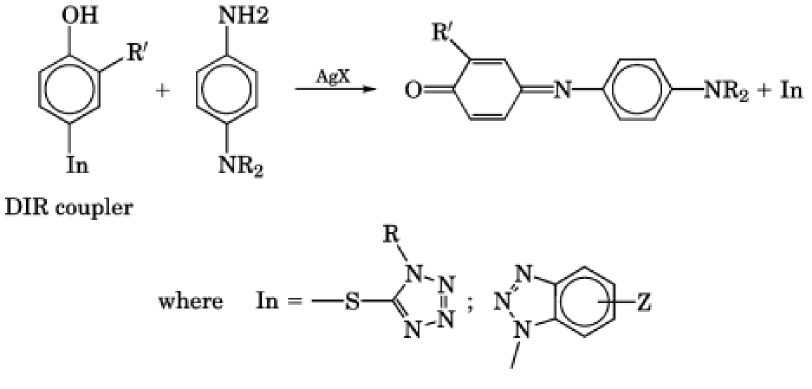


Fig. 14. Masking coupler used in the cyan layer showing (—) the unwanted density to blue-green light that accompanies cyan dye formation matched by (- - -) a complementary density to blue-green from the unreacted coupler, and (—·—·) density to red light.

4.8. DIR Couplers

Masking couplers cannot be used for directly viewed materials because of the objectionable color of the mask itself. But similar advantages and more can be achieved by using development-inhibitor-releasing (DIR) couplers (32, 101). These materials are usually image couplers that carry a silver development inhibitor (In) linked directly or indirectly to the coupling site (eq. **6**). When released as a function of dye formation, the development inhibitors migrate to the silver halide grain and either slow or stop further development. In addition to correction of unwanted dye absorptions, DIR couplers can be used to improve sharpness and reduce granularity of films (102).



(6)

Development inhibitors have long been used to control photographic processes, but the mechanism by which they work remains in dispute. In one model of the developing silver halide grain, the inhibitor reacts with the surface silver ions at the etch pit, a defect region on the crystal where halide ions depart into solution (Fig. 9). This complexation prevents these silver ions from migrating interstitially to the root of the developing silver filament and slows down or stops development (103). Another model views the inhibitor as complexing with the silver metal filament, where its insulating properties prevent electron injection by the oxidizing developer (104).

For color correction of, for example, the unwanted green absorptions of a cyan dye, a cyan DIR coupler is added to the imaging layer along with the cyan image coupler. The inhibitor is released in proportion to cyan dye formation and is designed to migrate into the adjacent magenta dye-forming layer, where it inhibits silver development and reduces the production of green density to the same degree that unwanted green density is produced by the cyan dye. This is sometimes referred to as a red-onto-green interlayer interimage effect and can occur only when the predominantly red image in the scene has some green component. Similar color correction can originate from the yellow and magenta dye forming layers, and the overall correction can be described using a 3-by-3 color matrix (101).

DIR couplers can also be used to control granularity, a measure of the visual nonuniformity of the dye image resulting from the random distribution of the dye clouds. Granularity is, in fact, the noise in the photographic signal, and is proportional to the density divided by the square root of the number of signal-generating centers, in this case, the silver halide grains. Increasing the amount of silver halide does not in itself reduce the granularity, however, because this also generates more oxidized developer and greater density. However, a DIR coupler can permit the coating of more silver halide centers without increased dye density by releasing an inhibitor that allows each grain to develop only partially.

Perhaps the most intriguing use of DIR couplers is the ability to improve the perceived sharpness of an image. If a sharp photographic edge or square wave signal is imposed on a piece of film, for example, by placing an opaque material over part of the film and exposing it to light, the resulting developed image shows some degradation of the edge, mostly because of light scatter, but also because of diffusion processes (Fig. 15**a**). This "softening" of the edge is perceived as a loss in sharpness. If, however, a DIR coupler is coated with the image coupler, it produces the inhibitor concentration profile of Figure 15**b.** The resulting inhibition of development leads to the final dye image of Figure 15**b,** where the density at the edge is enhanced relative to macro density. This increased rate of density change at the edge is seen as sharpness (102).

Although the varied uses for which DIR couplers are employed call for precise control over where the inhibitor diffuses, the very complexation mechanism by which inhibitors work would seem to preclude such control. The desired ability to target the inhibitor can be attained by the use of delayed release DIR couplers, which release not the inhibitor itself, but a diffusable inhibitor precursor or "switch" (Fig. 16) (105). Substituents (X, R) and structural design of the precursor permit control over both diffusivity and the rate of inhibitor release.

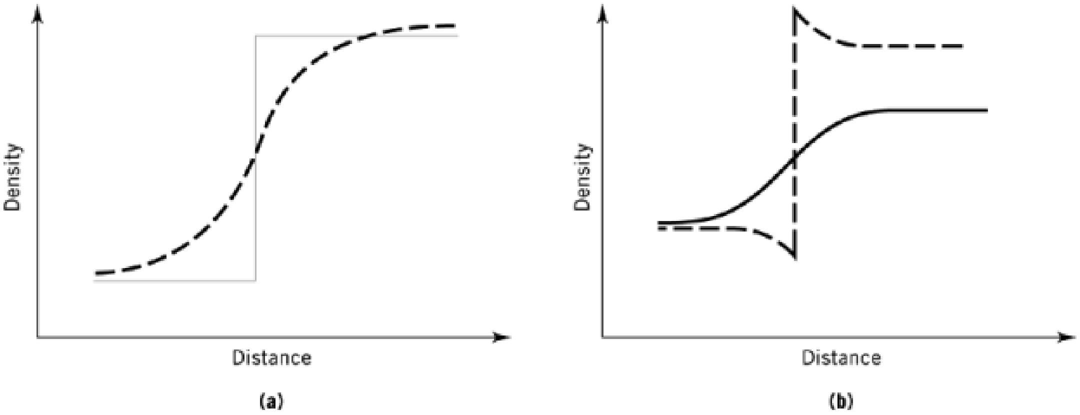


Fig. 15. Light scatter and chemical diffusion lead to a loss of sharpness at (**a**) a photographic edge where (—) represents the image and (- - -) the developed image. In the case of (**b**), an inhibitor modified edge, the sharpness to the (- - -) developed image can be restored by preferentially releasing a development inhibitor in image areas. (—) represents the inhibitor concentration profile. Diffusion of the inhibitor accentuates the edge relative to the macro portion of the image.

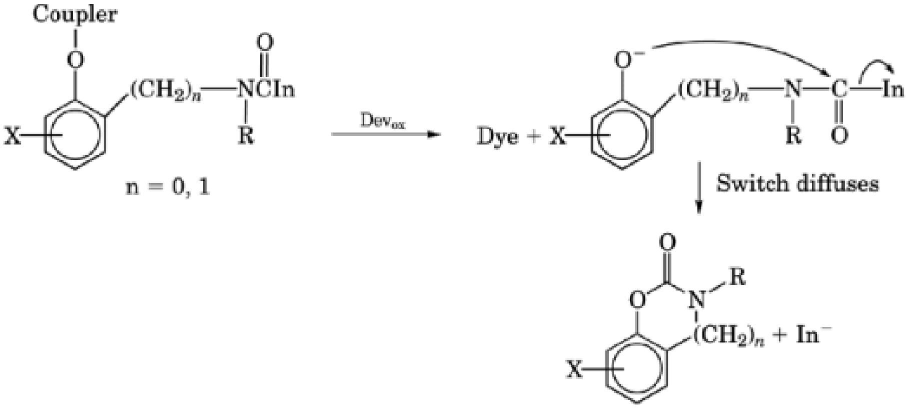
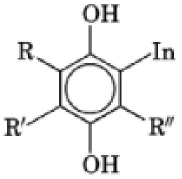


Fig. 16. Reaction of a delayed release DIR coupler and oxidized developer (Dev_{ox}). A delayed released DIR coupler permits fine-tuning of where and when the development inhibitor (In) is generated by releasing a diffusible inhibitor precursor or "switch" as a function of image formation. This permits control of inter- and intralayer effects.

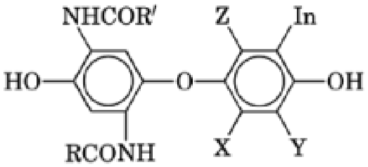
Increasing the effective diffusivity of the inhibitor, however, means that more of it can diffuse into the developer solution where it can affect film in an undesirable, nonimagewise fashion. This can be minimized by the use of self-destructing inhibitors that are slowly destroyed by developer components and do not build up or "season" the process (106).

Although most DIR couplers are based on image dye-forming parents, universal DIR couplers have appeared in the literature. These materials react with oxidized developer to produce the inhibitor (or precursor) and either a colorless dye, an unstable dye, or a washout dye (107). Universal DIR couplers could be used in any layer with a need to match only image-modifying properties, not hue, to the given layer.

In addition to inhibitors and masking dyes, similar coupling mechanisms have been used to release other photographically useful fragments, including development accelerators, image dyes, bleaching accelerators, development competitors, and bleaching inhibitors (108). Other mechanisms for imagewise release of inhibitors include inhibitor releasing developers (IRDs) **(13)** (109) and the related IRD-releasing couplers **(14)** (110). The former is of particular interest as a potential means of achieving image modification in reversal systems, where the image structure is determined in a black-and-white development step before chromogenic development.



(13)



(14)

4.9. Post-Development Chemistry

The silver and silver halide remaining in the film after color development must be removed, both to improve the appearance of the color image and to prevent the appearance from changing as silver halide is slowly photoreduced to silver metal. This is generally accomplished in two steps. The first, called bleaching, is an oxidation that converts silver metal back to silver salts. The second, called fixing, is the solubilization of the silver salts by complexation with a silver ligand. In some processes, particularly those used for color paper, the two steps can be combined in a single step called a bleach-fix or blix (62, 111).

The most common color film bleaches are of the rehalogenating type, that is, they contain halide ion, often bromide, to complex the silver ion being formed and drive the reaction to its conclusion. For many years the most common bleaching agent was ferricyanide, a powerful bleaching agent that also can convert residual leuco dye into image dye (62). However, the high oxidation potential, $E_0 = 356$ mV vs the hydrogen electrode (NHE), also makes ferricyanide capable of oxidizing the color developer carried over with the film. This can couple and form nonimagewise dye. For this reason, an intervening acidic “stop” bath must be used with ferricyanide bleaches.

Rehalogenating bleaches based on ferric ethylenediaminetetraacetic acid (ferric EDTA) are lower in potential, $E_0 = 117$ mV vs NHE, and do not require a stop bath, permitting a shorter and simpler process (112). The bleaching efficiency of ferric EDTA can be improved by lowering the solution pH below 6. However, as the pH is dropped, the propensity for reduction of indoaniline cyan dyes to the colorless leuco form increases. Thus most iron ligand bleaches are designed to operate in a window bounded by the pH of the bath and the oxidation potential of the bleaching agent.

The rates of most color bleaching processes are diffusion limited over at least part of the reaction. Color negative films tend to pass from a diffusion-limited regime into a chemically limited one as sensitizing dye and other passivating species accumulate on the remaining silver surfaces (113). Persulfate anion is used as a bleaching agent in some motion picture processes (114). Although it is thermodynamically attractive because of the very high ($E_0 = 2010$ mV vs NHE) oxidation potential, persulfate is a kinetically slow bleach in the absence of a catalyst. Commonly, a prebath containing dimethylaminoethanethiol [108-02-1] is used, although the use of bleach accelerator-releasing couplers or blocked bleach accelerators incorporated in the film has also been proposed (108, 115).

Thiosulfate, usually as its sodium or ammonium salt, is almost universally employed as the fixing agent for color films (111). Thiocyanate can be used as a fixing accelerator. Fixing performance is often defined by two parameters: the clearing time necessary to dissolve the silver halide and render the film optically transparent, and the fixing time required to remove the complexed silver from the film. Fixing must be complete and the fixing agents thoroughly washed from the film because thiosulfate can destroy image dye by reduction or by other reactions on long-term keeping. The complexation constants of thiosulfate with silver ion are sufficiently large to keep silver salts from being redeposited on the film on dilution in the wash.

5. Film Quality

5.1. Speed

Standards for photographic speed are now coordinated worldwide by the International Standards Organization (ISO) in Geneva, Switzerland. ISO speed is determined under specified conditions of exposure, processing, and measurement. Standards are published for color negative and color reversal films (116, 117). In amateur color photography, the most popular film speeds are in the ISO 100–400 range. For modern 35-mm cameras, these speeds offer a good compromise between image quality, depth of field, and ability to arrest motion, particularly when coupled with electronic flash. Several high speed color films of ISO 1000 or greater are now available from the primary manufacturers, recommended for conditions of low illumination or fast subject motion. The larger silver halide grains necessary for high speed become progressively less efficient in converting absorbed radiation into latent image, and in practice the linear relationship shown in Figure 5 rolls off at the larger sizes. Image graininess becomes objectionable if high magnification is required. Sensitivity to ambient ionizing radiation of both cosmic and terrestrial origin also increases with crystal size, resulting in a proportion of crystals being fogged during storage, causing graininess to increase (118, 119).

The human visual system has the ability to adapt to changes in the spectral balance of the scene illuminant. For example, a gray color appears gray both under daylight and tungsten illumination. However, a color film designed for use in daylight produces prints with a yellowish cast if used with tungsten illumination. This effect can be reduced by placing an appropriate filter over the camera lens, or by adjusting light filtration during printing in the case of a color negative. In practice, designing a film for a particular illuminant involves adjusting its sensitivity to blue, green, and red spectral light to account for the relative abundance of each in that illuminant. Most amateur films are balanced for optimum performance in daylight with a correlated color temperature of 5500 K (4, 21).

5.2. Color Reproduction

Color has three basic perceptual attributes: brightness, hue, and saturation. Saturation relates to how much of the hue is exhibited. The primary influences on the color quality of the final image are the red, green, and blue spectral sensitivities of the film or paper, and the spectral absorption characteristics of the image dyes. If the green record is designed to match the sensitivity of the eye's γ receptor and the red record the ρ receptor (Fig. 1), channel overlap is so severe that a satisfactory reproduction cannot be obtained. In practice, the peak sensitivity of the red record is moved to longer (ca 650 nm) wavelengths to reduce the overlap. A penalty is that colors having strong reflectances at 650 nm or longer appear excessively reddish in the reproduction.

Ideally, subtractive image dyes should exhibit no absorption outside the spectral ranges intended. In reality, considerable unwanted absorptions occur even using the best dyes, and colored masking couplers (see Fig. 14) are designed to alleviate this problem. However, to avoid serious speed losses, a colored coupler is normally only employed under layers in the film that absorb in a similar range. Thus a magenta-colored coupler, which absorbs green light, is used in the cyan pack; a yellow-colored coupler, which absorbs blue light, may be used in the magenta or cyan packs. Color correction may also be achieved by selectively suppressing dye generation in one color record as a function of exposure in another by using a diffusible development inhibitor generated by a development-inhibitor-releasing (DIR) coupler. Masking couplers and DIR couplers are the main tools to achieve the high color saturation of modern color negative films.

Because reversal films are designed so that the camera film is the film containing the final image, these are subject to additional constraints. The minimum densities in the image must be low to accommodate scene highlights and colored masking couplers cannot be used. In addition, because the color development step is exhaustive, i.e., develops all the residual silver halide, it is difficult to gain color correction from DIR couplers, which rely on influencing the relative development rates in a system that is only partially developed. Some degree of interlayer development inhibition can be obtained in the black-and-white developer by the migration of iodide released from the developing silver halide (120). Some of the factors important in the design of modern color reversal films are their ability to recover good quality images from underexposed film (push-processing), high emulsion efficiency for good speed and grain, and film technology for improved sharpness (121).

5.3. Dye Stability

The dyes used in photographic systems can degrade over time, both by thermal reactions and, if the image is displayed for extended periods, by photochemical processes. The relative importance of these two mechanistic classes, known as dark fade and light fade, respectively, depends on how the product is to be used (122).

Meaningful evaluations of dye stability on a practical time scale are difficult because the reactions themselves are by design either slow or inefficient. The $t_{1/10}$ value, defined as the time for a 0.1 density loss from a dye patch of 1.0 initial density, for dark fade ranges from 30 to greater than 100 years for chromogenically generated dyes, whereas the quantum yields of photochemical fading are often on the order of 1×10^{-7}. Accelerated testing conditions involving high temperature keeping or high intensity illumination must be used (123), although these are sometimes unreliable predictors of ambient fade (124). The perceived color stability of a photographic system is usually limited by the fading of its least stable dye, which can produce an undesirable shift in color balance. Whereas recovery of such faded images is often possible, a so-called neutral fade, in which all three color records lose density at approximately the same rate, is usually preferred.

For light fade the magenta dye has usually been limiting. Numerous studies support the hypothesis that the fading mechanism is photooxidative (125). Stabilization techniques have included exclusion of oxygen by barrier or encapsulation technologies; elimination of ultraviolet light by incorporated uv absorbers; quenching of one or more of the excited state species in the reaction sequence, i.e., dye singlet, dye triplet, or singlet molecular oxygen, via incorporated quenching agents; and the scavenging of reactive intermediates such as free radicals. Cyan light fade appears to include both reductive and oxidative components (126).

The dark fade of yellow dyes appears to be largely a hydrolytic process (127). Cyan dark fade results mostly from reduction of the dye to its leuco form. For the magenta record, dark keeping can be dominated by yellowing reactions from the residual coupler. A light-induced yellowing has also been observed. These problems have been successfully addressed by the design of new couplers and coupling-off groups.

Modern photographic products have stabilities vastly improved over those of the past. For example, the magenta light stability of color negative print papers has improved by about two orders of magnitude between 1942 and the present (128). Although such products offer very acceptable image stability in the vast majority of customer use situations, other processes, such as silver dye bleach and dye-transfer processes, can offer even greater stability, albeit at a significant cost in processing convenience.

5.4. Image Structure

Because the primary photographic sensors are a population of silver halide crystals having a random spatial distribution, the final image is also particulate. In black-and-white photography the image consists of opaque deposits of silver. In chromogenic photography using incorporated couplers, the image is formed by the coupler-containing hydrophobic droplets dispersed with the silver halide. The droplet size, typically 0.2 μm in diameter, is usually less than the crystal size. Dye is formed in a cloud of droplets around each developing crystal as oxidized developer is released. Individual droplets cannot be resolved under usual viewing conditions, but the dye clouds can be seen under magnification and convey a visual sensation of nonuniformity or graininess. The objective correlate of graininess is granularity, which is the spatial variation in density observed when numerous readings are taken on a uniformly exposed patch using a densitometer having a very small aperture. The distribution of such measurements approximates to Gaussian and can be characterized by its standard deviation, σ_{D}. This quantity, called root mean square (RMS) granularity, is published by film manufacturers as a figure of merit.

The features that differentiate a color image from a black-and-white image are the transparency of the dyes and the spreading of the dye cloud around the developing crystal. Dye clouds continue to grow during development as the oxidized developer diffuses farther to find unreacted coupler. Overlapping of adjacent dye clouds leads to a granularity reduction as more and more of the voids are filled in. The size of the dye clouds can be controlled by reducing the amount of silver development per crystal using development-inhibitor-releasing couplers, or by having a soluble coupler in the developer which competes with the incorporated coupler for oxidized developer (129), the dye formed being subsequently washed out.

Sharpness is the ability to discriminate edge detail in the final image. There are many opportunities to lose sharpness in the photographic system. Camera focus, depth of field, subject movement, camera movement during exposure, and the optical properties of the film all contribute to image sharpness. In the negative-positive system, printer focus and the optics of the color paper stock are also important. Modern multilayers of the type illustrated in Figure 8 are typically 20–25 μm thick. As light penetrates the front surface, it is subject to scatter by the imbedded silver halide crystals, which differ in refractive index from the supporting gelatin medium. This optical spread increases with depth and thus the uppermost blue-sensitive layer records the sharpest image and the lowest red-sensitive layer the least sharp image. Over the years, film manufacturers have reduced coated thickness both to improve sharpness and reduce material costs. Absorbing dyes may also be included in the film to reduce sideways light scatter, although at some cost in speed. These are generally removed by the processing solutions. Another method of improving sharpness is to change the layer order. Motion picture theatrical print film, for example, has the green record on top to improve sharpness, because the eye is most sensitive to differences in mid-spectrum light.

The sharpness of a film is often assessed by the modulation transfer function (MTF), which measures how sinusoidal test patterns of different frequencies are reproduced by the photographic material (130). A perfect reproduction would have a MTF of 100% at all frequencies. In practice, a decrease of MTF with increasing frequency occurs because of optical degradation. Films having couplers that release development inhibitors can display MTF values above 100% at low frequencies, because of edge effects that increase the output signal amplitude beyond that of the reference signal. The transport of inhibitor fragments across image boundaries leads to development suppression or enhancement on the microscopic scale (Fig. 15). Such edge effects are particularly useful in boosting the apparent sharpness of the lower layers of the film most degraded by optical scatter. However, if chemical enhancement of edges is carried too far, the effects appear unnatural.

6. Environmental Aspects

Photographic processing, i.e., photofinishing, is a geographically dispersed chemical industry. With an increasing proportion of images being processed in minilabs, rather than large, centralized photofinishers, manfacturers have responded to the need for more environmentally benign chemistry. Processing machines are rarely emptied and refilled with fresh solutions, but do require replenishment because of chemical use, evaporation, and overflow. New films have been designed that make more efficient use of coated silver and thus require less in terms of the chemicals for processing. The solution overflow that does occur is usually chemically regenerated and returned to the tank.

Silver is most commonly recovered by electrolysis or metallic replacement from the processing solutions or by ion exchange (qv) from the wash water (131). Loss of chemicals from one tank into the next has been minimized. The color paper process has progressed from five chemical solutions, three washes, and a replenishment rate of 75 μL/cm^2 (70 mL/ft^2) of film for each of the five solutions to two chemical solutions, one wash, and replenishment rates of 6 μL/cm^2 (6 mL/ft^2) and less than 3 μL/cm^2 (3 mL/ft^2). For color negative films, developer replenishment has dropped from over 300 to 43 μL/cm$_2$ (40 mL/ft^2). Regeneration of the now reduced overflow has decreased chemical discharge by as much as 55% (132).

The new chemistry of the RA-4 paper process permits the elimination of benzyl alcohol from the developer and a 50% reduction of the biological or chemical oxygen demand (BOD/COD) of the film/paper effluent. Substitution of the more powerful ferric 1,3-propylenediaminetetraacetic acid (ferric 1,3-PDTA) bleaching agent for ferric EDTA allowed for 60% reduction in both iron and ligand concentrations as well as total elimination of ammonia from the bleaching formulation (133). Although ferric EDTA and related materials are rapidly photo-degraded in the environment (134), concerns over the potential for persistent chelating agents to translocate heavy metals have led to the development of photobleaches based on biodegradable chelating agents such as methyliminodiacetic acid (MIDA) and ethylenediaminodisuccinic acid (135). During the period 1985 through 1998, some components in the effluent have been reduced to near zero and an overall reduction in effluent concentration of as much as 80% has been obtained (132). Some of these reductions have been achieved by using solutions of highly concentrated, precisely metered chemicals, culminating in a system that uses dry tablets to deliver the replenishment chemistry, adding plain water as the only liquid (136).

7. Economic Aspects

At the present time, more than 3 billion rolls of film are processed worldwide every year. In spite of its great size, there is still a tremendous opportunity for growth in the consumer photographic business. The countries with the highest consumption (US and Japan) average 7-8 rolls of film per household per year, whereas in developing markets such as China and Russia, film use averages less than $\frac{1}{2}$ roll per household per year. The last two decades have seen an increasing dominance of 35-mm color negative at the expense of color slide, because of its greater exposure latitude, the convenience of viewing reflection prints, and the ease of obtaining duplicate prints. The growth in popularity of picture-taking has been fueled by the increasing sophistication of 35-mm point-and-shoot cameras. These offer features such as auto-exposure, auto-focus, motor drive, and built-in flash, all within a very compact camera body. The single-use camera, in which the film box itself is equipped with a lens and shutter has also been very successful.

In 1996, a camera-film format called the Advanced Photo System (APS) was introduced as a new industry standard. This has smaller negative size than 35-mm film, but offers advantages to the customer such as easy loading, smaller camera size, a choice of three print formats including panoramic, and an index print with each order. APS negatives are returned in their original cassette, providing a convenient interface to a film scanner and therefore images in digital form. Looking at how the relative volumes of different film speeds have changed over the years, there is a trend towards higher speeds, because of the photographic flexibility that higher speed offers in improved ability to arrest motion, better zoom capability, and better depth of field. For example, dividing the color negative population into two categories - those of 400 speed and higher and those of 200 speed and lower - the relative volume of the higher speed films has increased by about 50% from 1995 to 1999.

The photofinishing industry has been growing at more than 5% annually. Since the mid-1970s, a shift has occurred to favor local minilabs over large centralized processing laboratories. Although minilabs are generally more expensive, consumers appreciate the convenience, rapid-access, and personal service. It has become clear in the 1990s that the photographic business is going through a period of transition, driven both by the threats and opportunities provided by digital technology. Digital still imaging is starting to reach the consumer through digital still cameras based on charge couple device (CCD) sensors, and while the price for an equivalently featured digital camera is still considerably higher than a film camera, the prices are declining rapidly. An advantage of digital photography is that the image can be modified and transmitted easily, and the public is becoming aware that there is more they can do with their pictures. However, high-resolution scanning puts silver halide film on the same playing field as electronic capture for image manipulation and re-use for different purposes. The scanning or "digitization" of conventional films and papers is becoming an increasingly important pathway in the industry. In the future, every film may be scanned as a matter of course after processing. Stand-alone "kiosks" provide a way to scan, copy or enhance conventional photographic prints. There are now more than 20,000 such kiosks in the US. With the growth of the Internet, many new businesses have started up offering photographic services including storage of customers' pictures. It is too early to judge the long-term viability of their business models. However, it is clear that convenient hard copy output will be even more important in the future as people learn they can use their images for different purposes. There will be more options for getting high quality prints - through wholesale photofinishing, minilabs, inkjet printing at home, and the Internet.

The professional segment of color photography includes portrait and wedding photography, advertising photography, and photojournalism. Films tailored to these markets are offered by the major photographic manufacturers. Most photojournalists now use digital still cameras because of their need for rapid access to the image. The motion picture industry has enjoyed continued growth in the last two decades. In spite of video-cassette recorders, there continues to be strong demand for the theatrical experience of first-run movies. This experience is enhanced by the improved picture quality of 70-mm origination and projection. Color negative film is often the preferred medium for pre-recorded television shows and advertising; telecine transfer converts the images to electronic form for transmission.

BIBLIOGRAPHY

"Color Photography" under "Photography" in *ECT* 1st ed., Vol. 10, pp. 577–584, by T. H. James, Eastman Kodak Company; "Color Photography" in *ECT* 2nd ed., Vol. 5, pp. 812–845, by J. R. Thirtle and D. M. Zwick, Eastman Kodak Company; in *ECT* 3rd ed., Vol. 6, pp. 617–646, by J. R. Thirtle and D. M. Zwick, Eastman Kodak Company; "Color Photography" in *ECT* 4th ed., Vol. 6, pp. 965–1002, by Jon Kapecki and James Rodgers, Eastman Kodak Company; "Color Photography" in *ECT* (online), posting date: December 4, 2000, by Jon Kapecki and James Rodgers, Eastman Kodak Company

Cited Publications

1. E. J. Wall, *History of Three-Color Photography*, American Photographic Publishing Company, Boston, Mass., 1925.
2. J. S. Friedman, *History of Color Photography*, 2nd ed., Focal Press, London, 1968.
3. R. M. Evans, W. T. Hanson, and W. L. Brewer, *Principles of Color Photography*, John Wiley & Sons, Inc., New York, 1953.
4. R. W. G. Hunt, *The Reproduction of Colour* 4th ed., Fountain Press, UK, 1987.
5. T. H. James, ed., *Theory of the Photographic Process*, 4th ed., Macmillan Publishing Co., New York, 1977.
6. J. Sturge, V. Walworth, and A. Shepp, eds., *Imaging Processes and Materials—Neblette's Eighth Edition* Van Nostrand Reinhold, New York, 1989.
7. J. M. Eder, *History of Photography*, Columbia University Press, New York, reprinted by Dover, New York, 1978.
8. W. T. Hanson, *Photogr. Sci. Eng.* **21**, 293–296 (1977).
9. A. Weissberger, *Am. Sci.* **58**, 648–660 (1970).
10. P. Glafkides, *Photographic Chemistry*, Vol. **II**, Fountain Press, London, 1960.
11. G. F. Duffin, *Photographic Emulsion Chemistry*, Focal Press, London, 1966.

12. G. Haist, *Modern Photographic Processing*, John Wiley & Sons, Inc., New York, 1979.
13. L. F. A. Mason, *Photographic Processing Chemistry*, Focal Press, London, 1966.
14. F. W. H. Mueller, *Photogr. Sci. Eng.* **6**, 166 (1962).
15. J. Pouradier, in E. Ostroff, ed., *Pioneers of Photography*, SPSE, Springfield, Va., 1987, Chap. 3.
16. T. J. Dagon, *J. Appl. Photogr. Eng.* **2**, 42 (1976).
17. R. L. Heidke, L. H. Feldman, and C. C. Bard, *J. Imag. Technol.* **11**, 93 (1985).
18. P. Krause, *Modern Photogr.* **48**(4) (1984) *ibid.* **49**(11), (1985.
19. R.D. Theys and G. Sosnovsky, *Chem. Rev.*, **97**, 83 (1997).
20. T. Tani, *Photographic Sensitivity*, Oxford University Press, (1995).
21. R.W.G Hunt, *Measuring Color*, Ellis Horwood Ltd., Chichester, UK, 1987, p. 21.
22. R. M. Evans, *J. Photogr. Sci.* **9**, 243 (1961).
23. C. R. Berry, in Ref. 5, p. 98.
24. J. E. Maskasky, *J. Imag. Sci.* **30**, 247 (1986).
25. B. H. Carroll, *Photogr. Sci. Eng.* **21**, 151 (1977).
26. S. Dahne, *Photogr. Sci. Eng.* **23**, 219 (1979).
27. J. Spence and B. H. Carroll, *J. Phys. Colloid Chem.* **52**, 1090 (1948).
28. J. T. Koran and R. E. Booms, *J. Soc. Photogr. Sci. Technol. Jpn.* **49**(6), 499 (1986).
29. U.S. Pat. 4,439,520 (1984), J. T. Kofron and Co-workers (to Eastman Kodak Company).
30. C. E. K. Mees, *J. Chem. Ed.* **6**, 286 (1929).
31. W. T. Hanson, *J. Opt. Soc. Am.* **40**, 166 (1950).
32. C. R. Barr, J. R. Thirtle, and P. W. Vittum, *Photogr. Sci. Eng.* **13**, 214 (1969).
33. U.S. Pat. 4,923,788 (1990), L. Shuttleworth, P.B. Merkel, G.M. Brown (to Eastman Kodak Company).
34. Ger. Pat. 253,335 (1912), R. Fischer; R. Fischer and H. Siegrist, *Photogr. Korresp.* **51**, 18 (1914).
35. L. E. Friedrich and J. E. Eilers, in F. Granzer and E. Moisar, eds., *Progress in Basic Principles of Imaging Systems*, Vieweg & Sohn, Wiesbaden, Germany, 1987, p. 385.
36. R. L. Bent and co-workers, *J. Am. Chem. Soc.* **73**, 3100 (1951).
37. L. K. J.Tong and M. C. Glesmann, *J. Am. Chem. Soc.* **79**, 583, 592 (1957).
38. J. Eggers and H. Frieser, *Z. Electrochem.* **60**, 372, 376 (1956).
39. L. K. J. Tong, M. C. Glesmann, and C. A. Bishop, *Photogr. Sci. Eng.* **8**, 326 (1964) L. K. J. Tong and M. C. Glesmann, *Photogr. Sci. Eng.* **8**, 319 (1964) R. C. Baetzold and L. K. J. Tong, *J. Am. Chem. Soc.* **93**, 1347 (1971).
40. J. C. Weaver and S. J. Bertucci, *J. Photogr. Sci.* **30**, 10 (1988).
41. E. R. Brown, in S. Patai and Z. Rappoport, eds., *The Chemistry of Quinonoid Compounds*, Vol. **2**, Wiley-Interscience, New York, 1988.
42. L. K. J. Tong and M. C. Glesmann, *J. Am. Chem. Soc.* **90**, 5164 (1968).
43. L. K. J. Tong, M. C. Glesmann, and R. L. Bent, *J. Am. Chem. Soc.* **82**, 1988 (1960).
44. J. Texter, D. S. Ross, and T. Matsubara, *J. Imag. Sci.* **34**, 123 (1990).
45. L. K. J. Tong, in Ref. 5, 345–351.
46. E. R. Brown and L. K. J. Tong, *Photogr. Sci. Eng.* **19**, 314 (1975).
47. J. Texter, *J. Imag. Sci.* **34**, 243 (1990).
48. U.S. Pat. 2,108,243 (1938), B. Wendt (to Agfa Ansco Corp.) U.S. Pat. 2,193,015 (1940), A. Weissberger (to Eastman Kodak Company) Brit. Pat. 775,692 (1957), D. W. C. Ramsay (to Imperial Chemical Ind.) Fr. Pat. 1,299,899 (1962), W. Pelz and W. Puschel (to Agfa-Gevaert), for examples.
49. C. A. Bishop and L. K. J. Tong, *Photogr. Sci. Eng.* **11**, 30 (1967).
50. R. Bent and co-workers, *Photogr. Sci. Eng.* **8**, 125 (1964).
51. F. W. H. Mueller, in S. Kikuchi, ed., *The Photographic Image*, Focal Press, London, 1970, p. 91.
52. J. R. Thirtle, *Chemtech.* **9**, 25 (1979), for a tutorial.
53. Brit. Pat. 701,237 (1953), (to DuPont) U.S. Pat. 3,767,412 (1973), M. J. Monbaliu, A. Van Den Bergh, and J. J. Priem (to Agfa-Gevaert) Brit. Pat. 2,092,573 (1982), M. Yagihara, T. Hirano, and K. Mihayashi (to Fuji Photo Film) U.S. Pat. 4,612,278 (1986), P. Lau and P. W. Tang (to Eastman Kodak Company).
54. F. Sachs, *Berichte* **33**, 959 (1900).
55. C. A. Bishop and L. K. J. Tong, *J. Phys. Chem.* **66**, 1034 (1962).

56. J. A. Kapecki, D. S. Ross, and A. T. Bowne, *Proceedings of the International East-West Symposium II* The Society for Imaging Science and Technology, Springfield, Va., 1988, p. D-11.
57. L. E. Friedrich, unpublished data, 1983.
58. T. Matsubara and J. Texter, *J. Colloid Sci.* **112**, 421 (1986) J. Texter, T. Beverly, S. R. Templar, and T. Matsubara, *Ibid.*, **120**, 389 (1987).
59. U.S. Pat. 4,443,536 (1984), G. J. Lestina (to Eastman Kodak Company).
60. Brit. Pat. 1,193,349 (1970), J. A. Townsley and R. Trunley (to Ilford, Ltd.) W. J. Priest, *Res. Discl.* **16468**, 75–80 (1977) U.S. Pat. 4,957,857 (1990), K. Chari (to Eastman Kodak Company).
61. C. Barr, G. Brown, J. Thirtle, and A. Weissberger, *Photogr. Sci. Eng.* **5**, 195 (1961).
62. K. H. Stephen, in Ref. 5, 462–465.
63. U.S. Pat. 4,690,889 (1987), N. Saito, K. Aoki, and Y. Yokota (to Fuji Photo Film).
64. U.S. Pat. 2,367,531 (1945), I. L. Salminen, P. Vittum, and A. Weissberger (to Eastman Kodak Company) U.S. Pat. 2,423,730 (1947), I. L. Salminen and A. Weissberger (to Eastman Kodak Company) U.S. Pat. 4,333,999 (1982), P. T. S. Lau (to Eastman Kodak Company).
65. U.S. Pat. 2,895,826 (1959), I. Salminen, C. Barr, and A. Loria (to Eastman Kodak Company).
66. U.S. Pat. 2,369,929 (1945), P. Vittum and W. Peterson (to Eastman Kodak Company) U.S. Pat. 2,772,162 (1956), I. Salminen and C. Barr (to Eastman Kodak Company) U.S. Pat. 3,998,642 (1976), P. T. S. Lau, R. Orvis, and T. Gompf (to Eastman Kodak Company).
67. E. Wolff, in *Proceedings of the SPSE 43rd Conference*, The Society for Imaging Science and Technology, Springfield, Va., 1990, 251–253.
68. Eur. Pat. Apps. 744,655 and 717,315 (1996), S. Ikesu, V. B. Rudchenko, M. Fukuda, Y. Kaneko (to Konica Corp.)
69. U.S. Pat. 2,407,210 (1946), A. Weissberger, C. J. Kibler, and P. W. Vittum (to Eastman Kodak Company) Brit. Pat. 800,108 (1958), F. C. McCrossen, P. W. Vittum, and A. Weissberger (to Eastman Kodak Company) Ger. Offen. 2,163,812 (1970), M. Fujiwhara, T. Kojima, and S. Matsuo (to Konishiroku KK.) Ger. Offen. 2,402,220 (1974), A. Okumura, A. Sugizaki, and A. Arai (to Fuji Photo Film) Ger. Offen. 2,057,941 (1971), I. Inoue, T. Endo, S. Matsuo, and M. Taguchi (to Konishiroku KK.) Eur. Pat. 296793 A2 (1988), B. Clark, N. E. Milner, and P. Stanley (to Eastman Kodak Company) Eur. Pat. 379,309 (1990), S. C. Tsoi (to Eastman Kodak Company).
70. U.S. Pat. 3,265,506 (1966), A. Weissberger and C. Kibler (to Eastman Kodak Company) U.S. Pat. 3,770,446 (1973), S. Sato, T. Hanzawa, M. Furuya, T. Endo, and I. Inoue (to Konishiroku KK.) Fr. Pat. 1,473,553 (1967), R. Porter (to Eastman Kodak Company) U.S. Pat. 3,408,194 (1968), A. Loria (to Eastman Kodak Company) U.S. Pat. 3,894,875 (1975), R. Cameron and W. Gass (to Eastman Kodak Company).
71. E. Pelizzetti and C. Verdi, *J. Chem. Soc. Perkin II*, 806 (1973) E. Pelizetti and G. Saini, *J. Chem. Soc. Perkin II*, 1766 (1973) D. Southby, R. Carmack, and J. Fyson, in Ref. 67, 245–247.
72. G. Brown and co-workers, *J. Am. Chem. Soc.* **79**, 2919 (1957).
73. J. A. Kapecki, unpublished data, 1981; U.S. Pat. 4,401,752 (1981), P. T. S. Lau (to Eastman Kodak Company).
74. U.S. Pat. 5,359,080 (1984), Y. Shimura, H. Kobayashi, Y. Yoshioka (to Fuji Photofilm Co.)
75. U.S. Pat. 5,213,958 (1993), M. Motoki, S. Ichijima, N. Saito, T. Kamio and K. Mihayashi (to Fuji Photofilm Co.) U. S. Pat. 6,083,677 (2000), T. Welter and J. Reynolds (to Eastman Kodak Company).
76. U.S. Pat. 5,457,004 (1995), J. B. Mooberry, J. J. Siefert, D. Hoke, D. T. Southby and F. D. Coms (to Eastman Kodak Company) D. Hoke, J. B. Mooberry, J. J. Siefert, D. T. Southby and Z. Z. Wu, *J. Imaging Sci. and Tech.*, **42**, 528 (1988).
77. Brit. Pat. 875,470 (1961), E. MacDonald, R. Mirza, and J. Woolley (to Imperial Chemical Ind.).
78. Brit. Pat. 778,089 (1957), J. Woolley (to Imperial Chemical Ind.).
79. U.S. Pat. 2,600,788 (1952), A Loria, A. Weissberger, and P. W. Vittum (to Eastman Kodak Company) U.S. Pat. 2,369,489 (1945), H. D. Porter and A. Weissberger (to Eastman Kodak Company) U.S. Pat. 1,969,479 (1934), M. Seymour (to Eastman Kodak Company).
80. G. Brown, B. Graham, P. Vittum, and A. Weissberger, *J. Am. Chem. Soc.* **73**, 919 (1951).
81. U.S. Pat. 2,343,703 (1944), H. Porter and A. Weissberger (to Eastman Kodak Company) U.S. Pat. 2,829,975 (1958), S. Popeck, and H. Schulze (to General Aniline and Film) U.S. Pat. 2,895,826 (1959), I. Salminen, C. Barr, and A. Loria (to Eastman Kodak Company) U.S. Pat. 2,691,659 (1954), B. Graham and A. Weissberger (to Eastman Kodak Company) U.S. Pat. 2,803,544 (1957), C. Greenhalgh (to Imperial Chemical Ind.) Brit. Pat. 1,059,994 (1967), C. Maggiulli and R. Paine (to Eastman Kodak Company).

82. U.S. Pat. 2,600,788 (1952), A. Loria, A. Weissberger, and P. Vittum (to Eastman Kodak Company) U.S. Pat. 3,062,653 (1962), A. Weissberger, A. Loria, and I. Salminen (to Eastman Kodak Company).
83. U.S. Pat. 3,127,269 (1964), C. W. Greenhalgh (to Ilford, Ltd.) U.S. Pat. 3,519,429 (1970), G. Lestina (to Eastman Kodak Company).
84. U.S. Pat. 3,582,346 (1971), F. Dersch (to Eastman Kodak Company) U.S. Pat. 3,811,891 (1974), R. S. Darlak and C. J. Wright (to Eastman Kodak Company).
85. P. W. Vittum and F. C. Duennebier, *J. Am. Chem. Soc.* **72**, 1536 (1950).
86. A. Wernberg, unpublished data, 1986.
87. L. E. Friedrich, in Ref. 65, p. 261.
88. U.S. Pat. 3,227,554 (1966), C. R. Barr, J. Williams, and K. E. Whitmore (to Eastman Kodak Company) U.S. Pat. 4,351,897 (1982), K. Aoki and co-workers (to Fuji Photo Film) U.S. Pat. 4,853,319 (1989), S. Krishnamurthy, B. H. Johnston, K. N. Kilminster, D. C. Vogel, and P. R. Buckland, (to Eastman Kodak Company).
89. U.S. Pat. 4,241,168 (1980), A. Arai, K. Shiba, M. Yamada, and N. Furutachi (to Fuji Photo Film).
90. U.S. Pat. 3,519,429 (1970), G. J. Lestina (to Eastman Kodak Company).
91. N. Furutachi, *Fuji Film Res. Dev.* **34**, 1 (1989).
92. U.S. Pat. 2,213,986 (1941), J. Kendall and R. Collins (to Ilford, Ltd.) U.S. Pat. 2,340,763 (1944), D. McQueen (to DuPont) U.S. Pat. 2,592,303 (1952), A. Loria, P. Vittum, and A. Weissberger (to Eastman Kodak Company) U.S. Pat. 2,618,641 (1952), A. Weissberger and P. Vittum (to Eastman Kodak Company) U.S. Pat. 3,834,908 (1974), H. Hara, Y. Yokota, H. Amano, and T. Nishimura (to Fuji Photo Film).
93. U.S. Pat. 3,725,067 (1973), J. Bailey (to Eastman Kodak Company) U.S. Pat. 3,810,761 (1974), J. Bailey, E. B. Knott, and P. A. Marr (to Eastman Kodak Company).
94. U.S. Pat. 4,443,536 (1984), G. J. Lestina (to Eastman Kodak Company) Eur. Pat. 284,240 (1990), A. T. Bowne, R. F. Romanet, and S. E. Normandin (to Eastman Kodak Company) Eur. Pat. 285,274 (1990), R. F. Romanet and T-H. Chen (to Eastman Kodak Company).
95. U.S. Pat. 4,540,654 (1985), T. Sato, T. Kawagishi, and N. Furutachi (to Fuji Photo Film).
96. K. Menzel, R. Putter, and G. Wolfrum, *Angew. Chem.* **74**, 839 (1962) Brit. Pat. 1,047,612 (1966), K. Menzel and R. Putter (to Agfa-Gevaert).
97. J. Jennen, *Chim. Ind.* **67**(2), 356 (1952).
98. W. T. Hanson, Jr. and P. W. Vittum, *PSA J.* **13**, 94 (1947) U.S. Pat. 2,449,966 (1948), W. T. Hanson, Jr. (to Eastman Kodak Company) K. O. Ganguin and E. MacDonald, *J. Photogr. Sci.* **14**, 260 (1966).
99. Ref. 4, pp. 270 ff, 320–321.
100. U.S. Pat. 5,364,745 (1994), J. B. Mooberry, S. P. Singer, J. J. Seifert, R. J. Ross and D. L. Kapp (to Eastman Kodak Company)
101. U.S. Pat. 3,227,554 (1966), C. R. Barr, J. Williams, and K. E. Whitmore (to Eastman Kodak Company) C. R. Barr, J. R. Thirtle, and P. W. Vittum, *Photogr. Sci. Eng.* **13**, 74, 214 (1969).
102. M. A. Kriss, in Ref. 5, 610–614; P. Kowaliski, *Applied Photographic Theory*, John Wiley & Sons, UK, 1972, 466–468.
103. L. E. Friedrich, unpublished data, 1985 K. Liang, in Ref. 35, p. 451.
104. T. Kruger, J. Eichmans, and D. Holtkamp, *J. Imag. Sci.* **35**, 59 (1991).
105. U.S. Pat. 4,248,962 (1981), P. T. S. Lau (to Eastman Kodak Company) Brit. Pat. 2,072,363 (1981), R. Sato, Y. Hotta, and K. Matsuura (to Konishiroku KK.).
106. Brit. Pat. 2,099,167 (1982), K. Adachi, H. Kobayashi, S. Ichijima, and K. Sakanoue (to Fuji Photo Film) U.S. Pat. 4,782,012 (1988), R. C. DeSelms and J. A. Kapecki (to Eastman Kodak Company).
107. U.S. Pat. 3,632,345 (1972), P. Marz, U. Heb, R. Otto, W. Puschel, and W. Pelz (to Agfa-Gevaert) U.S. Pat. 4,010,035 (1977), M. Fujiwhara, T. Endo, and R. Satoh (to Konishiroku Photo) U.S. Pat. 4,052,213 (1977), H. H. Credner, and co-workers (to Agfa-Gevaert) U.S. Pat 4,482,629 (1984), S. Nakagawa, H. Sugita, S. Kida, M. Uemura, and K. Kishi (to Konishiroku KK.).
108. T. Kobayashi, in *Proceedings of the 16th Symposium of Nippon Shashin Kokkai, Japan*, 1986 U.S. Pat. 4,390,618 (1983) H. Kobayashi, T. Takahashi, S. Hirano, T. Hirose, and K. Adachi (to Fuji Photo Film) U.S. Pat. 4,859,578 (1989), D. Michno, N. Platt, D. Steele, and D. Southby (to Eastman Kodak Company) U.S. Pat. 4,912,025 (1990), N. Platt, D. Michno, D. Steele and D. Southby, (to Eastman Kodak Company) Eur. Pat. 193,389 (1990), J. L. Hall, R. F. Romanet, K. N. Kilminster and R. P. Szajewski (to Eastman Kodak Company).

109. Brit. Pat. 1,097,064 (1964) C. R. Barr (to Eastman Kodak Company) Belg. Pat. 644,382 (1964), R. F. Porter, J. A. Schwan and J. W. Gates, Jr. (to Eastman Kodak Company).
110. K. Mihayashi, K. Yamada and S. Ichijima, in Ref. 67, p. 254.
111. G. I. P. Levenson, in Ref. 5, 437–461.
112. K. H. Stephen and C. M. MacDonald, *Res. Disclosure* **240**, 156 (1984) J. L. Hall and E. R. Brown, in Ref. 33, p. 438.
113. S. Matsuo, *Nippon Shashin Gak.* **39**(2), 81 (1976).
114. *Manual for Processing Eastman Color Films*, Eastman Kodak Company, Rochester, New York, 1988.
115. U.S. Pat. 4,684,604 (1987), J. W. Harder (to Eastman Kodak Company) U.S. Pat. 4,865,956 (1989), J. W. Harder and S. P. Singer (to Eastman Kodak Company) U.S. Pat. 4,923,784 (1990), J. W. Harder (to Eastman Kodak Company).
116. ISO 5800:1987(E), Photography—Color Negative Films for Still Photography—Determination of ISO Speed.
117. ISO 2240:1982(E), Photography—Color Reversal Camera Films—Determination of ISO Speed.
118. A. F. Sowinski and P. J. Wightman, *J. Imag. Sci.* **31**, 162 (1987).
119. D. English, *Photomethods*, 16 (May 1988).
120. W. T. Hanson, Jr. and C. A. Horton, *J. Opt. Soc. Am.* **42**, 663 (1952).
121. J.D. Baloga, “Factors in Modern Color Reversal Films,” Proceedings, P.I.C.S. Conference (Society for Imaging Science and Technology), Portland, Oregon, May 17-20, 1998, p. 299; J.D. Baloga and P.D. Knight, *J. Soc. Photogr. Sci. Technol. Jpn.* **62**, 111 (1999).
122. R. J. Tuite, *J. Appl. Photogr. Eng.* **5**, 200 (1979).
123. K. O. Ganguin, *J. Photogr. Sci.* **9**, 172 (1961) D. C. Hubbell, R. G. McKinney, and L. E. West, *Photogr. Sci. Eng.* **11**, 295 (1967).
124. Y. Seoka and K. Takahashi, *Second Symposium on Photographic Conservation, Society of Scientific Photography*, Japan., Tokyo, July 1986, 13–16.
125. P. Egerton, J. Goddard, G. Hawkins, and T. Wear, *Royal Photographic Society Colour Imaging Symposium*, Cambridge, UK, Sept. 1986, p. 128.
126. K. Onodera, T. Nishijima, and M. Sasaki, in *Proceedings of the International Symposium: The Stability and Conservation of Photographic Images*, Bangkok, Thailand, Nov. 1986.
127. E. Hoffmann and A. Bruylants, *Bull. Soc. Chim. Belges* **75**, 91 (1966) K. Sano, *J. Org. Chem.* **34**, 2076 (1969).
128. R. L. Heidke, L. H. Feldman, and C. C. Bard, *J. Imag. Technol.* **11**(3), 93 (1985).
129. U.S. Pat 2,689,793 (1954), W. R. Weller and N. H. Groet (to Eastman Kodak Company).
130. J. C. Dainty and R. Shaw, *Image Science*, Academic Press, Inc., London, 1974 M. Kriss, in Ref. 5, Chapt. 21, p. 596.
131. *CHOICES—Choosing the Right Silver-Recovery Method for Your Needs* Kodak Publication J-21, Rochester, New York, 1989.
132. T. Cribbs, *Sixth International Symposium on Photofinishing Technology, The Society for Imaging Science and Technology*, Springfield, Va., 1990, p. 53; Kodak Publication Z130, revision of July, 1998 at www.kodak.com.
133. D. G. Foster and K. H. Stephen, in Ref. 132, p. 7.
134. F. G. Kari, S. Hilger and S. Canonica, *Environmental Science and Technology*, **29**, 1008 (1995) F. G. Kari and W. Giger, ibid, **29**, 2814 (1995).
135. U.S. Pat. 4,294914 (1981), J. Fyson (to Eastman Kodak Company) U.S. Patents 5,652,085 and 5,691,120 (1997), D. A. Wilson, D. K. Crump and E. R. Brown (to Eastman Kodak Company) Eur. Pat. 532,003B1 (1998), Y. Ueda
136. S. Koboshi, M. Hagiwara, Y. Ueda, IS&T Tenth International Symposium on Photofinishing Technology Paper Summaries, p. 17, The Society for Imaging Science and Technology, Springfield, VA.

JON KAPECKI
JAMES RODGERS
Eastman Kodak Company