Kirk-Othmer Encyclopedia of Chemical Technology.

PHOTOGRAPHY, INSTANT

1. Introduction

The term instant photography originally referred to one-step film processes that provide finished photographs within a minute after exposure of a silver halide film. The processing of each film unit is initiated in the camera immediately after the film has been exposed. Such processing are outwardly dry, and the reagent is usually provided as part of the film unit. The technology of instant photography has been extended to include the application of similar chemistry to films wherein processing may be delayed for a time after exposure.

The advent of digital photography has further expanded the concept of instant photography. CCD cameras now make it possible to make an exposure, preview the resulting picture within seconds, and generate a corresponding color or black-and-white print within a few minutes. Furthermore, the major companies that provide instant films are now creating so-called hybrid systems that use both digital imaging and imaging on film to produce a variety of rapidly generated images. All such systems seek to enable the photographer to create a finished photograph under ambient conditions so as to view and judge the results quickly.

This article emphasizes the silver halide instant films and the cameras that expose and process these films. These were the predominant instant systems at the start of the twenty-first century. The term *instant photography* as used herein refers to these film-based systems. Also included in this article are examples of the rapidly emerging digital/film imaging systems. An incentive for such systems is the convenience of immediate hardcopy along with a digital record. Examples include digital/film imaging and digital camera/printer combinations.

The discussion will note relevant low speed reprographic systems, usually described as diffusion transfer reversal (DTR) processes, that utilize silver halide photosensitive layers and follow image-forming chemistry somewhat analogous to that of the instant processes.

Film systems using dye transfer based on microencapsulated dyes and photopolymerization (1), such as Cycolor, or photoinduced capsule rupture (2) to control image formation are outside the scope of this article. Similarly, dry-processed nonsilver black-and-white films, in which an image comprising fine carbon particles is formed by laser-induced imagewise phase transformation and resulting differential adhesion at the interface between the laser-sensitive layer and the carbon-bearing layer (3), are not included.

1.1. Historical Background

The first one-step photographic process, which produced sepia prints directly from the camera, was introduced by Land in 1947 (4). Land and co-workers (5) provided a comprehensive account of one-step photography detailing the development of instant black-and-white and color processes from 1944 through 1976. A monograph by Rott and Weyde (6) describes concomitant developments in silver diffusion transfer processes and includes a chronological list of selected DTR patents through 1972. Hill (7) reviewed DTR and web transfer processes in 1976. In 1978, the Sterckshhof Provinciaal Museum voor Kunstambachten provided a well-illustrated catalog

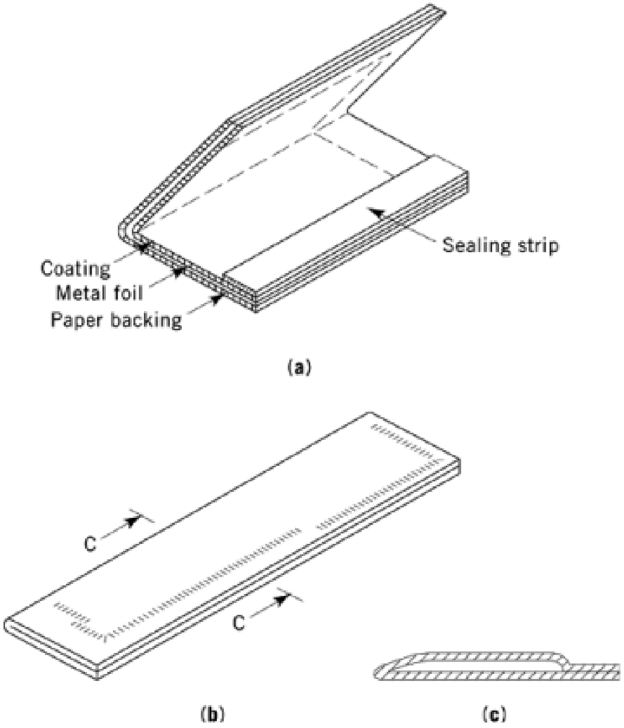


Fig. 1. Typical pod structure (14). (**a**) Unfilled pod; (**b**) filled, sealed pod; (**c**) cross section of filled pod along line C–C in (**b**).

of its exhibit documenting the first 40 years of developments in both one-step photography and DTR processes (8). Papers by Hanson (9) in 1976 and 1977 introduced a new instant camera and film. A 1983 paper by Van de Sande included a thorough discussion of instant color image formation (10).

In 1987, Weyde and Land provided historical accounts of work in their respective fields as part of the conference "Pioneers of Photography", documented in the book bearing the same title (11). Articles by Thirtle and Zwick in the *Kirk-Othmer Encyclopedia of Chemical Technology* (*ECT*) 2nd ed., by Walworth in the *ECT* 3rd ed., and by Mervis and Walworth in the *ECT* 4th ed., detail developments in the chemistry of instant color processes. A later publication by Mervis and Walworth (12) describes developments in instant photography and related processes through 1996. McCann's 1993 compendium of Land's writings includes all of his papers on instant photography and a complete list of Land's more than 500 patents (13).

1.2. Contemporary Product Information

The instant films described herein, unless otherwise noted, were available in May 2001. For more comprehensive information on current products and applications, see the manufacturers' technical bulletins or visit their respective web sites: www.polaroid.com; www.polaroiddigital.com; www.fujifilm.com.

2. Principles of Instant Films and Processes

2.1. Film and Process Design

Handheld camera use requires a film of sufficient photographic speed to permit short exposures at small apertures. Silver halide emulsions have high sensitivity and, upon development, enormous amplification. In a one-step process a viscous reagent is spread between two sheets, one bearing an exposed silver halide emulsion and the other an image-receiving layer. Both sheets pass through a pair of pressure rollers, and a sealed pod (114) attached to one of the sheets ruptures to release the viscous reagent, which spreads to form a thin layer between the two sheets, bonding them together. The action of the reagent produces concomitantly a negative image in the emulsion layer and a visible black-and-white or color image in the image-receiving layer.

2.2. Film Configurations: Peel-Apart and Integral Films

In so-called "peel-apart" products, the two sheets are stripped apart to reveal the image. In "integral" films, the image-forming layers are located on the inner surfaces of the two sheets, at least one of which is transparent. The emulsion layers are exposed through a transparent support layer, and the processed print is viewed either through the same surface (15) or through the opposite surface (16, 17) of the film unit. A reflective white pigment layer within the film unit facilitates viewing by reflected light.

2.3. Reagents for Instant Photography; Pods

An essential component of each instant film is the reagent system. Essentially dry processing is realized by using a highly viscous fluid reagent and restricting the amount to just that needed to complete the image-forming reaction for a single picture.

The high viscosity of the reagent is provided by water-soluble polymeric thickeners (18). Suitable polymers include hydroxyethyl cellulose, the alkali metal salts of carboxymethyl cellulose, and carboxymethyl hydroxyethyl cellulose. The high viscosity of the reagent facilitates accurate metering to form a thin layer that also serves as an adhesive for the two sheets during processing. In peel-apart films, the reagent layer may remain on the surface of the print or it may be stripped away with the other sheet. In integral films, the reagent forms a new layer within the processed film unit.

A sealed pod of reagent for each picture permits the use of more highly reactive reducing agents and more strongly alkaline conditions than would be feasible in a tank or tray process. Sealing the pod protects the reagent from oxygen until it is used.

In addition to high molecular weight polymer, reducing agents, and alkali, the viscous reagent may contain reactive components that participate in image formation, deposition, and stabilization. Some reactants may also be incorporated in coatings on either of the two sheets. Such an arrangement may serve to isolate reactive components from one another before processing, facilitate sequential availability during processing, and provide each component with a stable and compatible environment.

The reagent-containing pod must be carefully designed for both containment and discharge of its contents. The pod lining must be inert to strong alkali and other components of the reagent, and the pods must be impervious to oxygen and water vapor over long periods. When the pod passes through processing rollers, the seal must rupture with a peeling separation, rather than explosive bursting, so that the reagent is released along one edge and spread uniformly, starting as a fine bead and forming a smooth, thin layer. The amount of reagent contained in each pod is particularly critical for integral film units that have limited capacity to conceal surplus reagent.

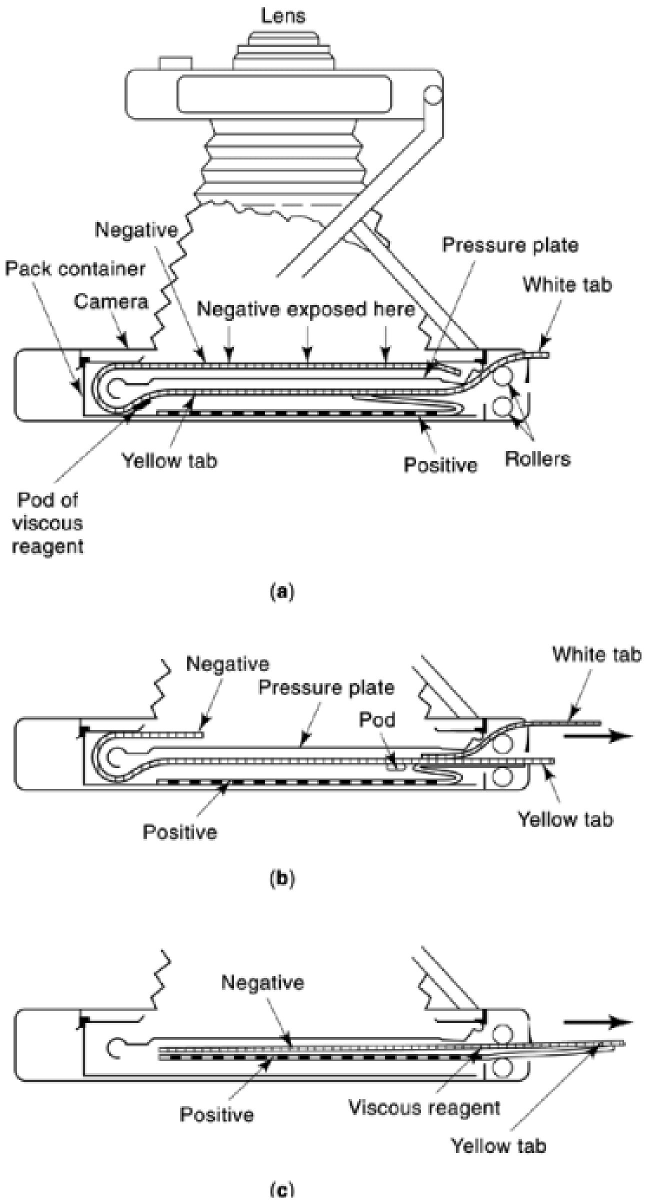
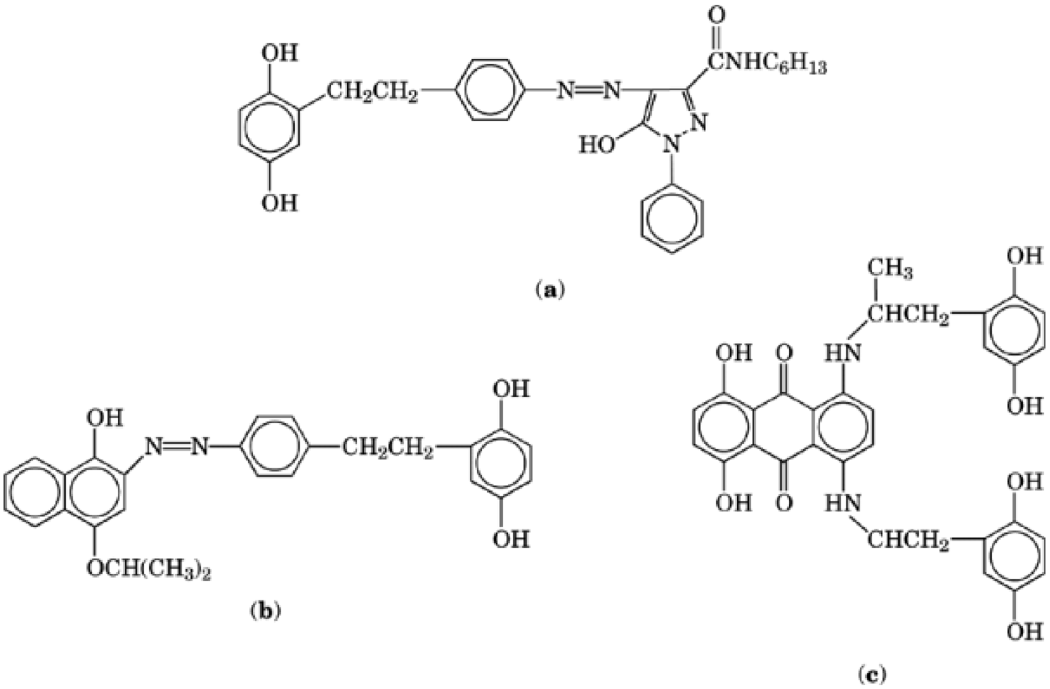


Fig. 2. Schematic section of Model 100 camera (1963), illustrating processing of pack film outside the camera. The outer surfaces of both negative and positive sheets are opaque. (**a**) Position of each element during exposure; (**b**) following exposure, pulling the white paper tab leads the negative into position for processing; (**c**) pulling the yellow paper tab draws the entire film unit between processing rollers, rupturing the pod and spreading the reagent, and leads the film unit out of the camera.



(a)

(b)

(c)

Fig. 3. Film holder for 4×5-in. sheet films, used with professional 4×5 cameras and in MP-4 industrial cameras. The external control arm controls retractable processing rollers inside the holder. The sequence of operations is as follows: (**a**) insertion of the light-tight film unit into the holder with the control arm in LOAD position causes engagement of the cap on the end of the packet by a spring-loaded retainer; (**b**) partial withdrawal of the outer envelope enables film exposure; (**c**) reinsertion of unit repositions the outer envelope; (**d**) pulling the unit out of the holder with the control arm in PROCESS position ruptures the pod and spreads its contents between negative and positive sheets to initiate processing. Processing reaches completion outside the film holder. Reprinted with permission of IS&T the Society for Imaging Science and Technology.

2.4. One-Step Cameras and Processors

The earliest one-step cameras used roll film and completed processing inside a dark chamber within the camera (19). Flat-pack film cameras (Fig. 2), introduced in 1963, provide for the film to be drawn between processing rollers and out of the camera before processing is completed (20). Film holders for instant film packets (Fig. 3) contain retractable rollers that enable the user to load the film unit without rupturing the pod (21). For 8 × 10-in. (20 × 25-cm) films, the rollers are part of a tabletop processor. The exposed film, contained in a protective black envelope, and a positive sheet with pod attached are inserted into separate slots of a tray that leads into the processor. The film passes through the rollers into a covered compartment within which processing is completed.

The Polaroid 20 × 24-in. (51 × 61-cm) camera uses separate negative and positive sheet films in continuous rolls. The pod is attached manually before the sheets enter motorized processing rollers. The 40 × 80-in. (102 × 203-cm) film used for Polaroid museum reproductions is also in continuous roll form. For this format, the reagent is applied from a flexible plastic “straw” that is drawn between rollers to extrude a bead of reagent along the nip between the sheets just before they enter the processing rollers.

In the 35-mm instant format, both negative and positive layers are coated on a single support (22). Processing of the film, following exposure in a conventional 35-mm camera, takes place in a tabletop processor, such as the Polaroid AutoProcessor, as illustrated in Figure 4. A processing pack provides a pod of reagent and a strip sheet. Processing is initiated as a thin layer of reagent applied to a strip sheet contacts the film surface. The strip sheet and film pass together between processing rollers and wind together onto a take-up spool. After a short interval, the strip sheet and film are rewound, separating so that the processed film goes back into its cartridge and the strip sheet, with adhered reagent, goes into the processing pack, which is then discarded.

Fully automatic processing was introduced in 1972 with the SX-70 camera, which ejects each exposed integral film unit automatically. Immediately after exposure a pick moves the uppermost film unit from the pack to the nip of motorized processing rollers, which spread the reagent and move the film unit out of the camera (23,24). Kodak instant cameras for integral films, introduced in 1976 and now discontinued, included both motorized and hand-cranked models. Fuji instant cameras for integral films are motorized. In several Polaroid instant cameras, pulling a handle out of the camera actuates the processing rollers, initiates processing, and ejects the developing film unit.

2.5. Formation of Instant Images

One or more of a series of complementary positive and negative images can serve as the starting point for a transfer process that leads to a useful final image. Candidate initial image pairs include exposed grains, unexposed grains; developed silver, undeveloped silver; oxidized developer, unoxidized developer; neutralized alkali, alkali not neutralized; and hardened gelatin, unhardened gelatin.

As an example, black-and-white instant print films utilize imagewise transfer of undeveloped silver halide, unoxidized developer, and unused alkali to an image-receiving layer, within which they react to form a positive silver image. In instant color processes that utilize dye developers, ie, molecules that are both image dyes and photographic developers, an image in terms of unoxidized dye developer transfers to form a positive image in the image-receiving layer. In dye release systems, either negative- or positive-working emulsions are used and dye release is effected by one or more of the initial images in terms of silver or developer.

3. Black-and-White Instant Imaging Processes

3.1. Chemistry of Silver Image Formation

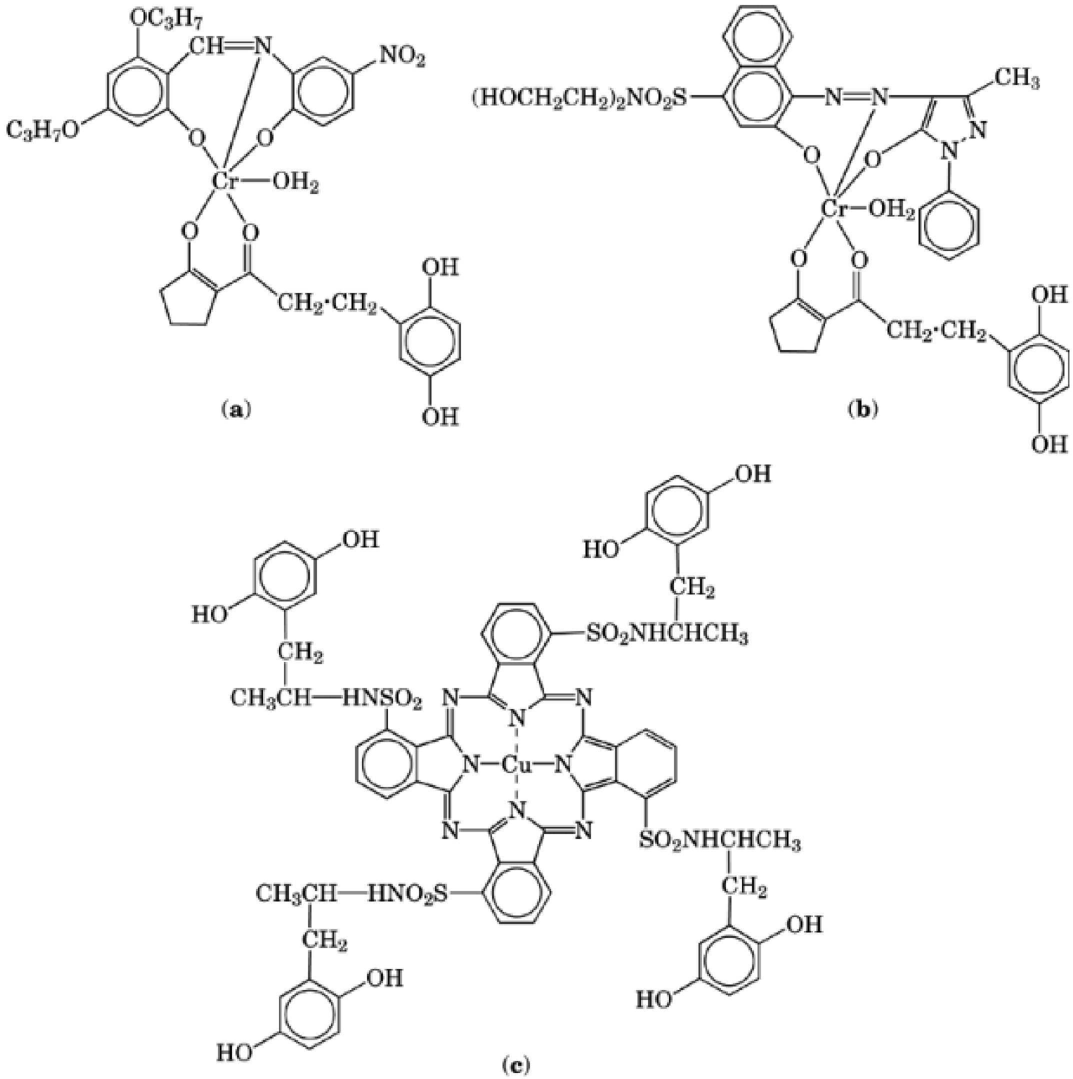
In the processing of a silver halide emulsion after camera exposure, a reagent containing developing agent, alkali, and a silver halide solvent reduces the exposed grains *in situ* (**1**). The solvent concomitantly dissolves the unexposed grains to form soluble silver complexes (**2**). These soluble complexes transfer from the emulsion (donor) layer to the image-receiving (receptor) layer. The developer reduces the complex silver salts to form an image comprising metallic silver, at the same time regenerating the solvent so that it may recycle to form additional soluble complex (**3**).

$$\mathrm{AgX_{exp}} + \mathrm{Developer_{red}} \longrightarrow \mathrm{Ag^0} + \mathrm{Developer_{ox}} \qquad (1)$$

$$\mathrm{AgX_{unexposed}} + 2\,(\mathrm{S_2O_3})^{2-} \longrightarrow \mathrm{Ag\,(S_2O_3)_2^{3-}} + \mathrm{X^-} \qquad (2)$$

$$\mathrm{Ag\,(S_2O_3)_2^{3-}} + \mathrm{Developer_{red}} \longrightarrow \mathrm{Ag^0} + \mathrm{Developer_{ox}} + 2\,(\mathrm{S_2O_3})^{2-} \qquad (3)$$

This sequence permits efficient silver transfer with minimum solvent. Further efficiency is realized by providing in each pod only the amounts of developer and solvent needed to process a single image (or strip of images, in the 35-mm films). The use of fresh reagent and the cyclic use of the solvent enable precise control of the competition between development and dissolution.



(a)

(b)

(c)

Fig. 4. Schematic diagram of the AutoProcessor for instant 35-mm films. (**a**) At the start of processing, the strip sheet (A) exits the processing pack and the viscous reagent (B) spreads onto the surface of the strip sheet. The coated strip sheet and the exposed film (D) pass together between the processing rollers (E) and wind onto the takeup spool (F); (**b**) After a timed interval the strip sheet and film are rewound. The strip sheet goes back into the processing pack (A) and the processed film goes back into its original cartridge (B). The used processing pack is discarded and the processed film is ready for viewing. Both hand-cranked and motorized AutoProcessors are available. Reprinted with permission of IS&T the Society for Imaging Science and Technology.

In equations (**2**) and (**3**), the silver solvent is sodium thiosulfate (hypo). The selection of developer and silver halide solvent depends on the nature of the image-receiving layer. With siliceous receptors, a typical reagent comprises a hydroquinone developer and sodium thiosulfate as solvent. With cellulosic receptors, typical developing agents are hydroxylamines and tetramethylreductic acid, and uracils serve as solvents.

Figure 5 is a schematic cross section of a black-and-white peel-apart instant film, such as Polaroid Type 667, before, during, and after processing.

3.2. Image-Receiving Layers

In addition to determining suitable composition of the reagent, the composition and structure of the image receiver control the tone of the silver image and the stabilization of that image.

3.2.1. Image Tone; Image Stabilization

The tone of the positive silver image depends on the nature of the receiving sheet and its effect on the particle size of the image silver. Particles that are very small produce a yellowish image silver deposit, and particles that are too large produce image silver with low covering power. For consistent tone throughout the density range, it is necessary to have well-controlled silver deposit size distribution. Means of achieving such control include limiting the deposition to a thin receiving layer, limiting the volume available within that layer, and providing nuclei that limit the number of sites available for deposition. Matrix materials that provide such controlled deposition include colloidal silica and several cellulosic polymers. Colloidal nucleating particles include metal sulfides and noble metals. The inclusion of certain mercaptans may also influence image tone by controlling silver particle and aggregate sizes.

In peel-apart films, even though the reagent adheres to the negative when the negative and positive are separated, the thin positive silver image, left unwashed, may be vulnerable to attack by residual reagent. The following sections discuss both image formation and the steps taken to ensure stability of the image.

3.2.2. Silica Receiving Layers

In the earliest one-step film (Polaroid Type 40, 1948), which produced sepia images, the image-receiving layer comprised a thin colloidal suspension of silica containing very fine particles of an insoluble metal sulfide precipitated within the suspension. This suspension was coated onto baryta paper. The sulfide particles formed fine aggregates in the interstices of the silica and served as nuclei for the deposition of image silver in aggregates 25–125 nm in diameter. These images were stabilized by incorporating within the support soluble salts that diffused into the image layer as the image neared completion, neutralizing the reagent and rendering the image highly stable.

In 1950, Polaroid initiated the use of silica-based receiving layers that produce black silver images. Larger aggregates form in a very thin layer of silica/metal sulfide, $\sim 0.5\ \mu m$ thick, coated over a layer of poly(vinyl butyral). The image aggregates so constrained are 100–160 nm in diameter, and each aggregate comprises fine particles 10–30 nm in diameter. Because the underlying layer is impervious, diffusion of neutralizing components from beneath the image-receiving layer is not feasible. Instead, each print is stabilized after processing by swabbing with a *print coater*, a disposable swab saturated with an acidic solution of a basic polymer. The print coater removes residual reagent and deposits a thin polymeric layer that dries quickly to form a tough, impermeable coating. Typical *print-coater* films include Polaroid Types 611, 51, 52, 57, and 55P/N (positive/negative).

3.2.3. Cellulosic Receiving Layers

Coaterless films were introduced by Polaroid in 1970. These films utilize image-receiving layers produced by hydrolyzing a cellulose acetate layer containing nuclei (25). Suitable nuclei include colloidal metals and colloidal metal sulfides and selenides. The depth of hydrolysis determines the depth of the image-forming stratum. The silver aggregates form between 0.04 and 0.40 below the surface. The reagents for coaterless black-and-white films utilize nonstaining developing agents and silver halide solvents. The developing agents are substituted hydroxylamines (26), and the silver halide solvents are colorless, sulfur-free compounds, such as cyclic imides (27). An immobile layer of an acidic polymer underlying the image-receiving layer neutralizes residual alkali,

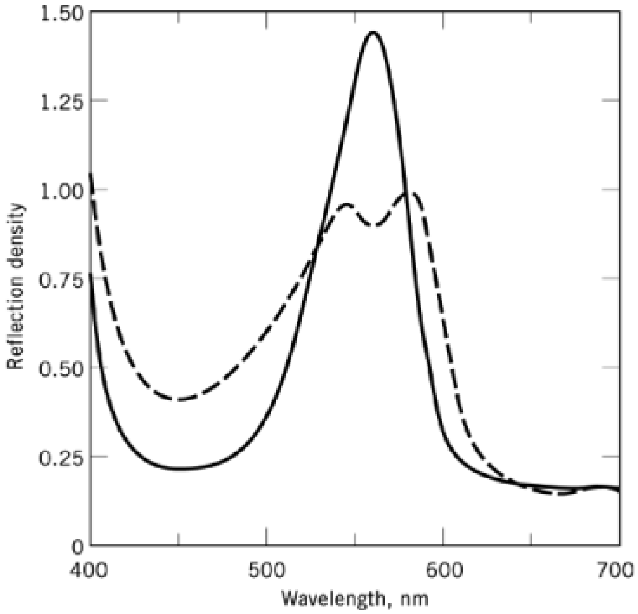


Fig. 5. Schematic cross section of a black-and-white peel-apart film, eg, Polaroid Type 667. (**a**) Negative and positive sheets and pod before processing; (**b**) The same components during processing. The pod has ruptured, and the viscous reagent has spread between the sheets to form a temporary lamination. In exposed areas (left), silver halide grains develop *in situ*. At the same time grains in unexposed areas (right) dissolve and transfer as a soluble complex to the image-receiving layer and undergo reduction there to form the positive image; (**c**) The sheets stripped apart after processing. The reagent has adhered to the negative sheet and the positive print is ready for viewing. Reprinted with permission of IS&T the Society for Imaging Science and Technology.

and the onset of neutralization is controlled by a polymeric *timing layer* between the image-receiving layer and the acidic polymer layer.Stabilization of this type was first developed for the Polacolor color print process, and similar mechanisms are used in integral black-and-white and color films. Coaterless black-and-white print films with hydrolyzed cellulose acetate image-receiving layers include many of Polaroid's peel-apart films. Fuji coaterless black-and-white films also use hydrolyzed cellulose acetate receiving layers. Polaroid's integral black-and-white films print and instant black-and-white slide films utilize hydroxyethyl cellulose receiving layers containing noble metal nuclei (28).

3.3. Black-and-White Instant Films

3.3.1. Polaroid Pack and Sheet Films

Continuous-tone peel-apart print films provided by Polaroid fall into several speed classes, ranging from ISO 100 to ISO 3000 and 3200. Most pack films produce $3\frac{1}{4} \times 4\frac{1}{4}$-in. prints with image area 7.3 × 9.5 cm ($2\frac{7}{8}$; × $3\frac{3}{4}$ in.). Professional 4 × 5 pack films provide prints with image area 9 × 11.7 cm ($3\frac{1}{2} \times 4\frac{5}{8}$; in.), and prints from professional 4 × 5 sheet films have 9 × 11.4 cm ($3\frac{1}{2} \times 4\frac{1}{2}$-in.) image area. Most of the black-and-white films are coaterless. The 100-speed Polapan Pro films are professional proofing films characterized by medium contrast and long tonal range. The faster print films are for general use.

P/N positive–negative films, Type 655 pack film and Types 55 and Type 55 HC (high-contrast) sheet films, provide from each exposed film unit both a print for immediate viewing and a fully developed and fixed negative of high resolution and very fine grain. The negatives require aftertreatment in a clearing bath to remove residual reagent. With the pack films, this treatment also removes a temporary black opacifying back coat.

A peel-apart transparency film for X-ray imaging, TPX, is available in 8 × 10-in. format. Type 611, a specialty low-contrast ISO 200 film, provides extended dynamic range and exposure latitude for recording cathode ray tube (CRT) images. An ISO 400 sepia print film is used to simulate old-time photographs.

Integral black-and-white films include 600 Classic (600 Extreme in Europe, 600 B&W in Japan) and 600 Copy&Fax, which incorporates a halftone screen. These ISO 640 square format films, provide prints 7.9 × 7.9 cm ($3\frac{1}{8} \times 3\frac{1}{8}$-in.) image area. Autofilms, which provide 10.2 × 7.6-cm (4 × 3-in.) image area, are Type 331 print film, ISO 400, and Type 337 high speed print film, ISO 3200.

3.3.2. Polaroid 35-mm Transparency Films

Instant slide films in 35-mm cartridges fit into standard 35-mm cameras and camera backs. The films are processed in the tabletop processor described in Fig. 4. The black-and-white positive transparency films are Polapan CT continuous tone slide film and PolaGraph HC high contrast slide film, both ISO 125.

3.3.3. Fuji Print Films

In 1984, Fuji introduced a series of black-and-white and color peel-apart films. Most of the black-and-white films are available in both pack and sheet formats. Equipment provided for these films includes camera backs and film holders in each format and the Fuji UP-L camera, which has interchangeable backs in both formats. The Fuji films are compatible with corresponding format Polaroid cameras, camera backs, and film holders.

The products include general purpose films, with speeds ranging from ISO 100 to 3000, and a low-contrast ISO 400 film for medical imaging and CRT screen imaging. Films available in the United States are FP-100B, FP-100C, and FP-3000B. The Fuji black-and-white prints require no coating or other aftertreatment.

4. Black-and-White Diffusion Transfer Reversal (DTR) Processes

The tank processing of black-and-white DTR materials involves silver halide reduction, complex formation, and image transfer steps, as in the instant films. Unlike the instant films, the light-sensitive emulsions are of low speed, designed for use in copy equipment under ambient room light. In DTR processing, donor and receptor sheets pass through separate aligning feed trays into an activator bath comprising developing agent, silver halide solvent, and an organic base. The sheets exit the activator through rollers that temporarily laminate the two sheets. Stripping the two apart reveals the positive image on the receptor sheet. It is also possible to have both donor and receptor on the same support, so that just one sheet passes through the activator. Other variations incorporate some or all of the processing components in the sheet materials. If all components are so incorporated, the bath may be only water.

DTR products current in 2001 include Agfa's Copyproof negatives, receiving films and papers, chemicals, equipment, and accessories. The processes provide film and paper reproductions of both continuous tone and high contrast originals. Principal applications are in graphic arts. Panchromatic materials are also used for color separations. A specialty sepia "antique" receiving paper is used with continuous tone negatives and processed in a dedicated activator bath. Kodak's diffusion transfer products, identified as PMT materials, have been discontinued.

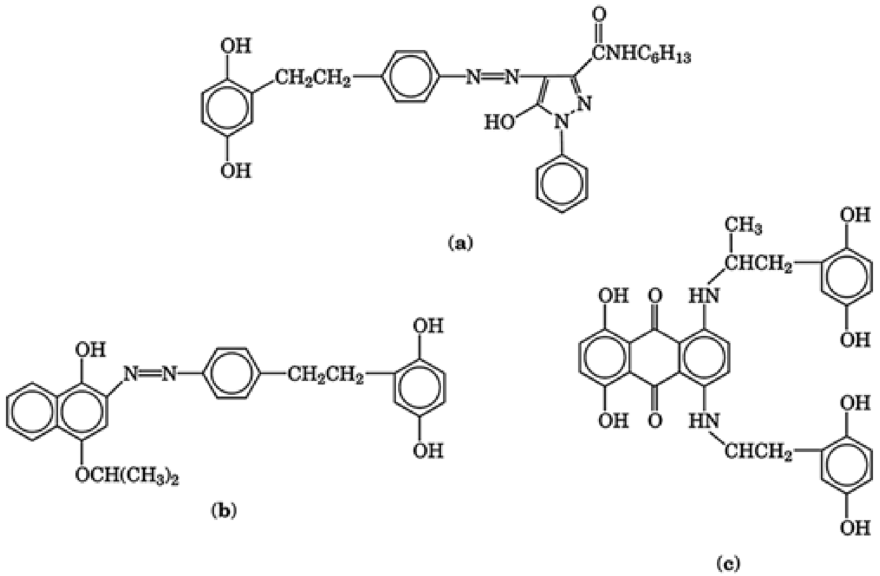


Fig. 6. Dye developers used in Polacolor (1963): (**a**) yellow [14848-0008-9]; (**b**) magenta [1880-52-5]; and (**c**) cyan [2498-16-0].

5. Instant Color Imaging Processes

5.1. Methods of Color Reproduction

The reproduction of color requires the selective recording and presentation of principal regions of the visible spectrum, which extends roughly from 400 to 700 nm. For most processes three records are used, corresponding, respectively, to the blue (400–500 nm), green (500–600 nm), and red (600–700-nm) regions.

In subtractive color photography, the three images are formed within a multilayer film comprising separate silver halide emulsion layers, respectively sensitive to blue, green, and red light. Early experimental color negatives for instant photography used subtractive negative layers in a screenlike configuration (29); the three color elements were arrayed side-by-side in an arrangement that had been used with moderate success in earlier work. These structures were abandoned in favor of multiple continuous layers (30).

Processing of a subtractive color film produces positive images in terms of complementary dyes: the blue record is transformed to an image in yellow, or minus blue, dye; the green record to an image in magenta, or minus green, dye; and the red record to an image in cyan, or minus red, dye. When white light passes through the superposed set of yellow, magenta, and cyan images, the dye images absorb blue, green, and red components of the white light so that the transmitted light provides an image in terms of the blue, green, and red original colors. Subtractive color systems include all of the instant print and large format transparency materials.

In additive color photography, the three color records are separated laterally by an array or screen of blue, green, and red filter elements superposed over a single panchromatic silver halide emulsion. Processing produces a positive transparency comprising black-and-white records in silver of the respective blue, green, and red components of the original scene. When these silver images are projected in registration with the superposed color screen, the images add to reproduce the full color image. Additive color photography is used only for transparencies, because the minimum density is too high for reflection prints. Polachrome 35-mm slide films, discussed in Section 6.3, use additive color.

5.2. Subtractive Dye Imaging Systems

There are numerous methods for producing instant dye images from the records formed in a set of blue-, green-, and red-sensitive emulsions that constitute a multilayer color film (4,6,30). Although image dyes may be formed *in situ* by chromogenic color development, as in noninstant color films, in most instant color processes preformed dyes are transferred from the negative to an image-receiving layer. The dyes or dye precursors may be initially diffusible in alkali, in which case they will be immobilized imagewise, or they may be initially immobile in alkali and released imagewise to transfer. Positive-working processes produce dye transfer density inversely related to the developed silver density; conversely, negative-working processes produce dye transfer density in direct proportion to the developed silver.

The use of a negative-working emulsion, in which the exposed grains develop to form a negative silver image, in a positive-working dye transfer process results in the formation of a positive dye transfer image. With negative-working dye processes, positive images may be obtained by using direct reversal, or direct positive, emulsions, which develop unexposed rather than exposed grains to form positive silver images. As an alternative to using direct positive emulsions, unoxidized developer remaining after development of a negative-working emulsion may reduce prefogged silver in an adjacent layer; the resulting oxidized developer may then couple to release dyes that form positive dye transfer images (31,32)

5.2.1. Dye Developer Processes

The first instant color film, Polacolor, introduced the dye developer (33), a bifunctional molecule comprising both a preformed dye and a silver halide developer. The multilayer Polacolor negative (30) comprises a set of three negative-working emulsions, blue-, green-, and red-sensitive, respectively, each overlying a layer containing a dye developer complementary in color to the emulsion's spectral sensitivity. During processing, development of exposed grains in each of the emulsion layers results in oxidation and immobilization of a corresponding portion of the contiguous dye developer. Dye developer that is not immobilized migrates through the layers of the negative to the image-receiving layer to form the positive image.

In addition to having suitable diffusion properties, dye developers must be stable and inert within the negative before processing. After completion of the process, the dye developer deposited in the image-receiving layer must have suitable spectral absorption characteristics and stability to light.

The requirements of a developer moiety for incorporation into a dye developer are well fulfilled by hydroquinones. Under neutral or acidic conditions hydroquinones are very weak reducing agents and the weakly acidic phenolic groups confer little solubility. In alkali, however, hydroquinones are readily soluble, powerful developing agents. Dye developers containing hydroquinone moieties have solubility and redox characteristics in alkali related to those of the parent compounds.

Among the first dye developers were simple azohydroquinones, having hydroquinone and a coupler attached directly through an azo group to form the chromophore, and hydroquinone-substituted anthraquinones. These compounds were very active developing agents and they diffused readily to form excellent positive images. However, because the hydroquinone was an integral part of the chromophore, the colors shifted with pH changes and with oxidation state of the hydroquinone. To circumvent such unwanted color shifting, alkylene links that interrupt conjugation were added as insulation between the chromophore and developer moieties (34).

5.2.1.1. Insulated Dye Developers. In the course of developing the Polacolor and SX-70 processes, many insulated dye developers were synthesized and investigated. An extensive review of this work is available (35). The insulating linkage, chromophore, and developer moiety can each be varied. Substituents on the developer modify development and solubility characteristics; substituents on the chromophore modify the spectral characteristics in terms of both color and light stability. The attachment of two dyes to a single developer by amide linkage has also been described (36).

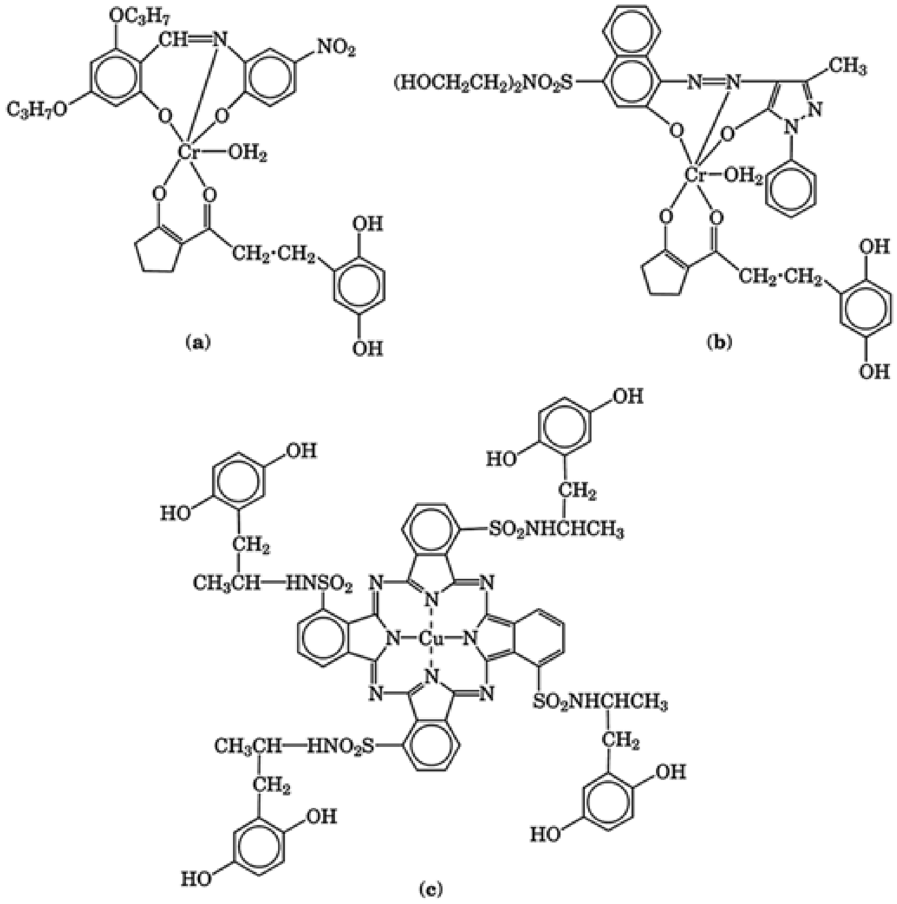


Fig. 7. Metallized dye developers used in SX-70 film (1972) and Polacolor 2 film (1975): (**a**) yellow [31303-42-1]; (**b**) magenta [59518-89-7]; and (**c**) cyan [28472-22-2].

Pyrazolone dyes are particularly versatile yellow chromophores; the yellow dye developer used in Polacolor, the first instant color film, was a pyrazolone dye. The structures of the three Polacolor dyes are shown in Figure 6. The study of azo dyes derived from 4-substituted-1-naphthols led to the chromophore used in the Polacolor magenta dye developer. The Polacolor cyan dye developer contained a 1,4,5,8-tetra-substituted anthraquinone as chromophore (37).

Figure 7 shows the structures of the metallized dye developers used in the first SX-70 film (1972) and in Polacolor 2 (1975). The images formed by these dye developers are characterized by very high light stability (38). The metallized cyan dye developer is based on a copper phthalocyanine pigment (39). Incorporation of developer groups converts the pigment into an alkali-soluble dye developer. A study of the chromium complexes of azo and azomethine dyes led to the design of the magenta and yellow metallized dye developers (40). The latter was derived from the 1:1 chromium complex of an *o,o*′-dihydroxyazomethine dye.

Later versions of both integral and peel-apart color films utilize a stable nonmetallized magenta dye developer [78052-95-6] (**1**) containing a xanthene dye moiety (41,42). This dye developer has much less unwanted blue absorption than previous magenta dye developers and is thus capable of providing more accurate color rendition (43).

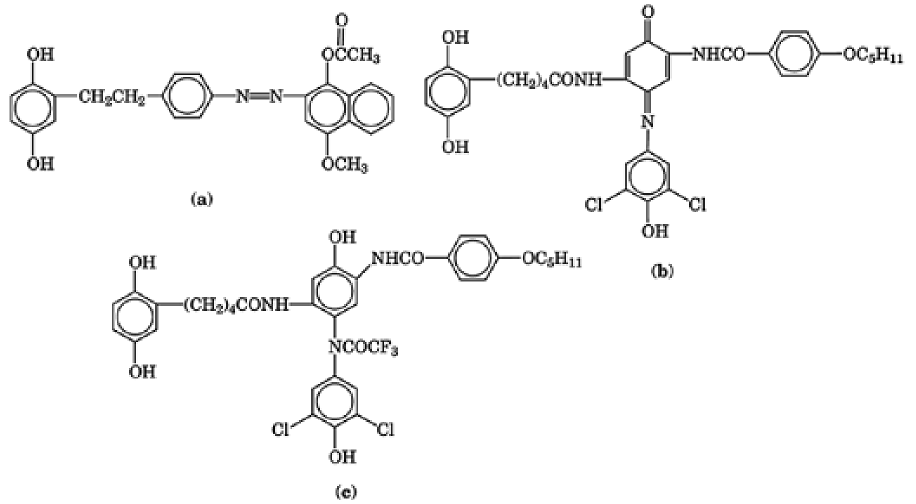
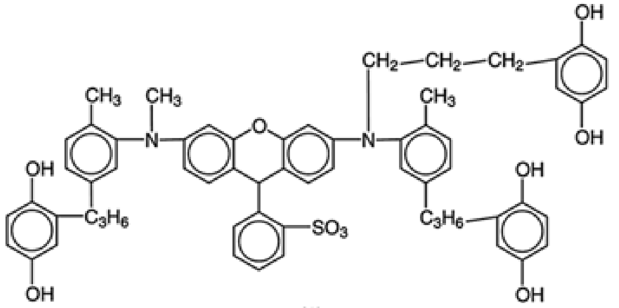


Fig. 8. Color-shifting dye developers: (**a**) yellow dye developer [16044-30-7] that becomes magenta upon hydrolysis; (**b**) cyan dye [50695-79-0] that becomes colorless upon protonation; and (**c**) leuco form of a dye developer [50481-86-2] that becomes yellow upon hydrolysis and oxidation.



(1)

5.2.1.2. Color-Shifted Dye Developers. Although as of 2001 none of the commercialized films incorporate color-shifted dyes, such compounds have been investigated extensively. These materials offer the option of incorporating the dye developer and the silver halide in the same layer without losing speed through the unwanted absorption of light by the dye developer. Prototypes are shown in Figure 8. The magenta azo dye developer shown in Figure 8**a** has been color-shifted by acylation (44). In the form shown, its color is a weak yellow. Indophenol dye developers color-shifted by protonation have been described (45). The cyan indophenol dye developer, (Fig. 8**b**), shows little color when the chromophore is in the protonated form. In alkali, the dye is ionized to the colored indophenoxide form, and in this state it may be stabilized by association with a quaternary mordant in the receiving layer.

Another approach involves the formation of dye images from colorless oxichromic developers, leuco azomethines stabilized against premature oxidation by acylation and linked to developer moieties (46), as shown in Figure 8**c**. The transferred images are oxidized in the colored form either by aerial oxidation or by oxidants present in the receiving layer.

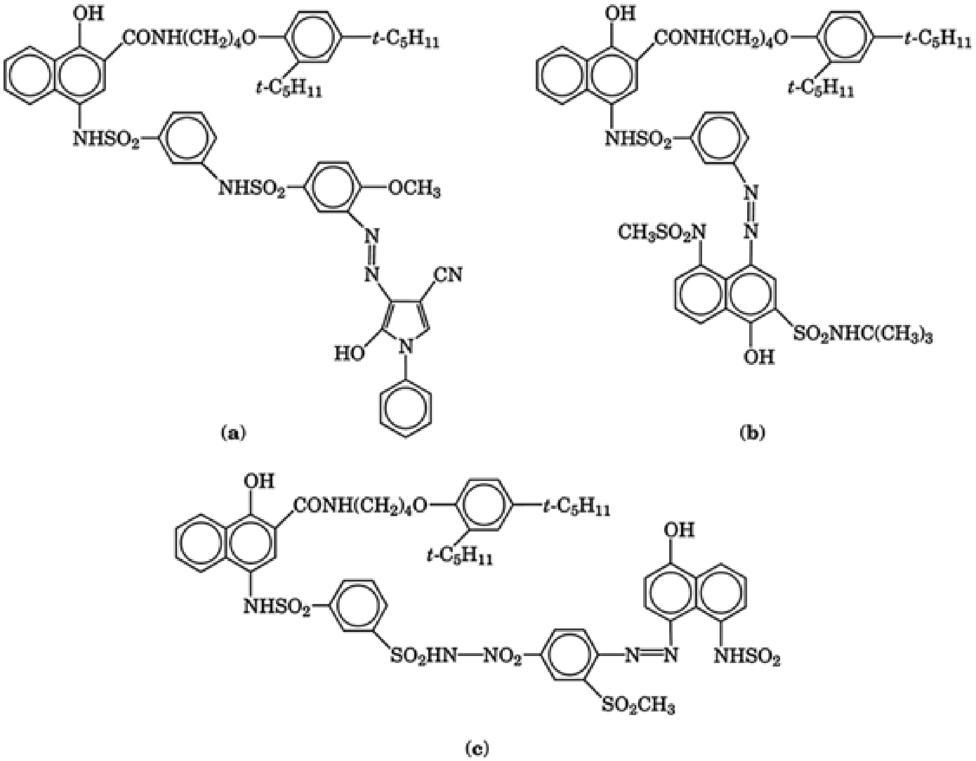


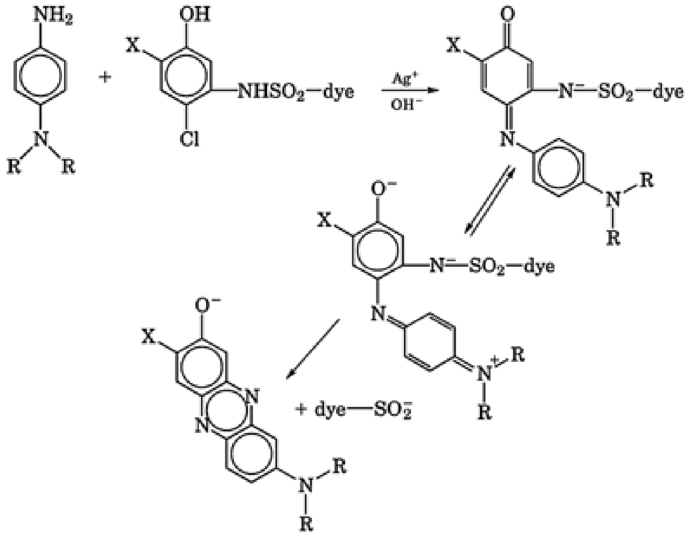
Fig. 9. *p*-Sulfonamidonaphthol dye releasers used in Kodak integral instant films: (**a**) yellow; (**b**) magenta [67041-93-4]; and (**c**) cyan [42905-20-4].

5.2.1.3. Additional Chromophores. Other types of dyes that have been studied as chromophores in dye developers include rhodamine, azamethine, indophenol, and naphthazarin dyes. Cyanine dyes, although not generally stable enough for use as image dyes, have also been incorporated in dye developers (47).

5.2.2. Dye-Release Processes

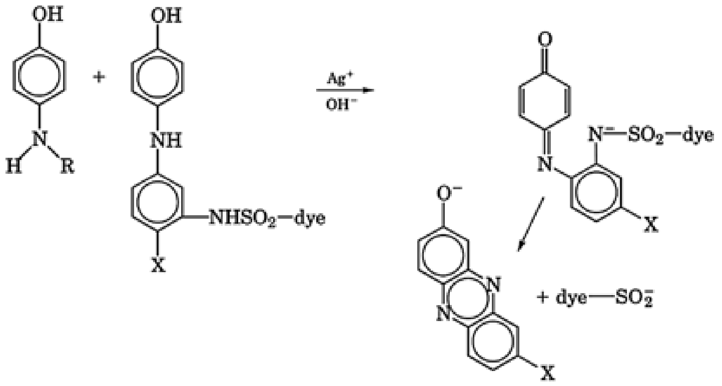
5.2.2.1. Release by Oxidation. Dyes or dye precursors may be released from alkali-immobile compounds through interaction with the mobile oxidized form of a developing agent. Mobility of the oxidized developing agent is important because both the silver halide and the dye or dye precursor are initially immobile in alkali and thus cannot interact directly. The mobile oxidized developing agent may participate directly in dye release or it may act as an electron-transfer agent between silver halide and a dye releaser that is initially a reducing agent. With alkali-mobile image-forming species, such as the alkali-mobile dye developers, the use of electron transfer by auxiliary developers is optional, whereas with alkali-immobile species the use of an electron-transfer agent may be essential to the process.

The image-related transfer of a diffusible dye formed as a product of the oxidation of a dye containing a developing agent moiety was described in 1966 (48). The process depends on the preferential transfer of an oxidation product having greater mobility than the unoxidized species. The use of images in terms of oxidized developer to release dyes initially immobilized through a sulfonamide linkage has been described (49). In one approach, color coupling leads to ring closure and concomitant release of an alkali-soluble dye (eq. **4**). Here, R = H or alkyl and X = an immobilizing group.



(4)

A second approach utilizes the oxidation of a low mobility 4-hydroxydiphenylamine to which an image dye is linked through a sulfonamide group. Oxidation and hydrolysis result in ring closure and release of the alkali-soluble dye (eq. **5**). Here R = alkyl and X = an immobilizing group.



(5)

These release processes are negative working, with dye released where silver development takes place. A positive image may be obtained from such a negative-working process by using a direct positive emulsion such that the unexposed grains, rather than the exposed ones, undergo development. Alternatively, both the immobile dye releaser and silver-precipitating nuclei are included in a layer adjacent to the emulsion layer, and the processing reagent includes a silver halide solvent. In unexposed regions, soluble silver complex diffuses into the layer containing the nuclei and the immobile dye releaser. Development of silver is catalyzed by the nuclei, and the resulting oxidized developing agent cross-oxidizes the dye releaser, as in equation **5**. The oxidized dye releaser undergoes ring closure, and the mobile dye is released for transfer to a receiving layer. The transferred image in this case is positive.

Immobile *p*-sulfonamidonaphthol dye-release compounds (Figure 9) were used in the discontinued Kodak instant color films (50).The compounds undergo imagewise oxidation to quinonimides through interaction with

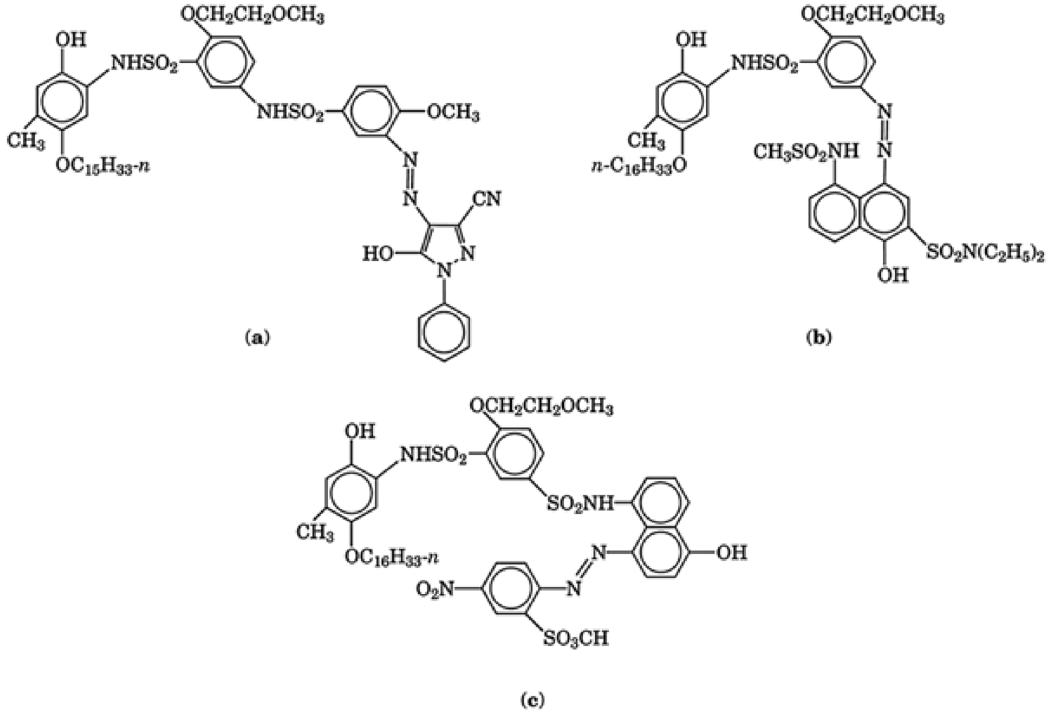
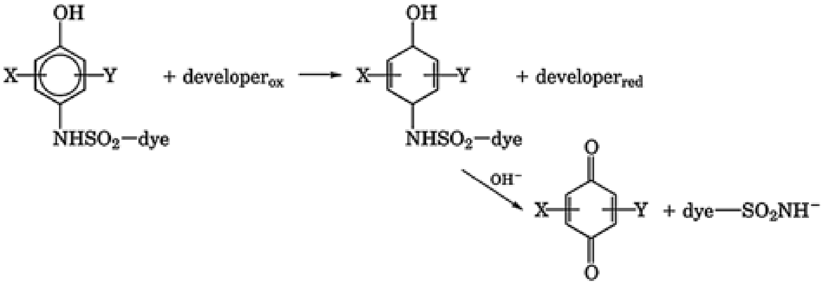


Fig. 10. *o*-Sulfonamidonaphthol dye releasers used in early Fuji instant films: (**a**) yellow [06249-54-6]; (**b**) magenta [73869-83-7]; (**c**) cyan.

an oxidized developing agent, followed by alkaline hydrolysis of the quinonimides to release soluble, diffusible image-forming dyes and immobile quinones (eq. **6**). Here X and Y are immobilizing groups.



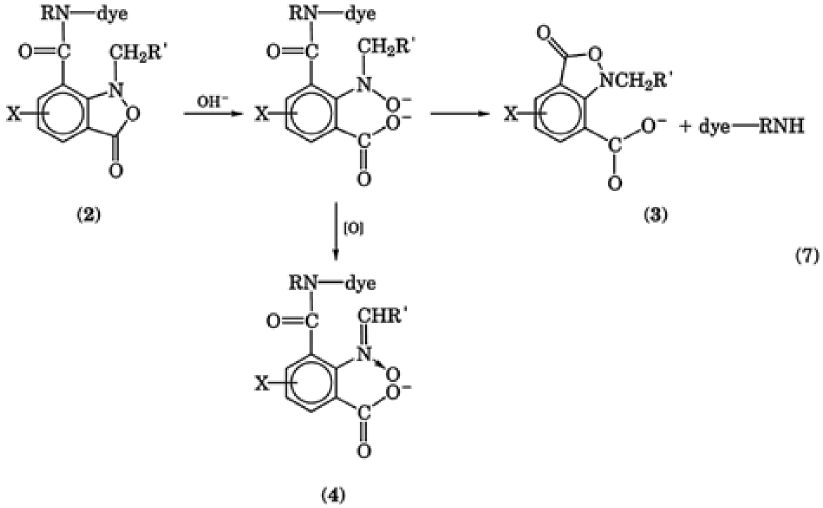
(6)

Fuji instant color films are based on a similar dye-release mechanism using the *o*-sulfonamidophenol dye-release compounds shown in Figure 10 (51). Similarly, immobile *p*-sulfonamidoanilines, where Y is H and the phenol group is replaced by an NHR moiety, may be used as dye releasers.

o-Sulfonamidophenol dye-release compounds are also used by Fuji in the photothermographic printing process introduced in 1987 as Fujix Pictrography (52). In this material, the chosen developer moiety of the dye releaser is a weak reducing agent at room temperature, and processing is effected at 90°C.

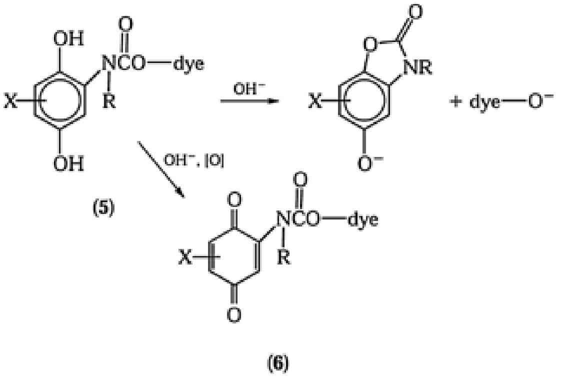
Further examples of image-derived labilization and release by hydrolysis include redox dye releasers that contain ballasted hydroquinones using sulfonyl, oxy, or thio linkages. Imagewise oxidation to form quinones, followed by alkaline hydrolysis, releases mobile image dyes (53). Corresponding hydroquinone derivatives without such ballast are dye developers that transfer in nondeveloping regions to form positive images (54).

A dye-release system that yields positive images may also be based on immobile benzisoxazolone dye releasers, such as compound (**2**), where X is an immobilizing group and R and R′ = alkyl. For these compounds, oxidation prevents cleavage. In alkali the heterocyclic ring opens, forming a hydroxylamine, and in unexposed areas, where silver halide is not developing, the hydroxylamine cyclizes to form a second benzoxazolone (**3**), eliminating the dye moiety. In exposed areas, silver halide is reduced by a mobile developing agent, which in turn transfers electrons to oxidize the hydroxylamine to the nonreleasing species (**4**) (see eq. **7**).



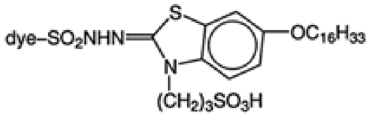
(7)

Another positive-working release utilizing cyclization, illustrated by equation 8, starts with an immobile hydroquinone dye releaser (**5**), where R = alkyl and X is an immobilizing group. Cyclization and dye release take place in alkali in areas where silver halide is not undergoing development. In areas where silver halide is being developed, the oxidized form of the mobile developing agent oxidizes the hydroquinone to its quinone (**6**), which does not release the dye (55).

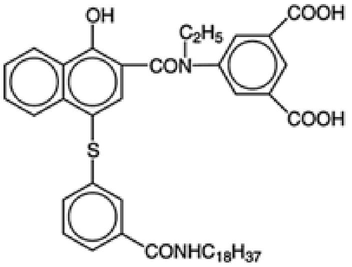


(8)

Redox dye-release systems based on immobile sulfonylhydrazones, as in compound (**7**), were disclosed in 1971. These compounds are oxidized by oxidized *p*-phenylene developing agents, yielding azosulfones that undergo alkaline cleavage to release soluble moieties (56). To minimize stain, the developing agent may itself be rendered immobile and used in conjunction with a mobile electron-transfer agent (57).



(7)



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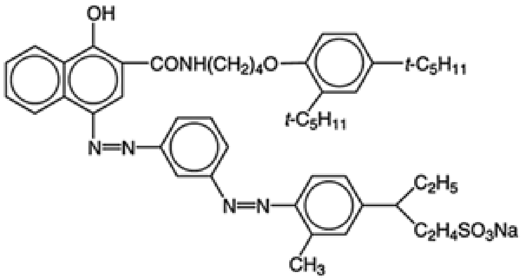


(9)

5.2.2.2. Displacement by Coupling. The coupling reactions of color developing agents have been used as release mechanisms for initially immobile image dyes or dye precursors (58). The dye-releasing coupler may have substituents in the coupling position that are displaced in the course of the coupling reaction with an oxidized color developer. In one process, the eliminated substituent is the immobilizing group, so that the dye formed by coupling is rendered mobile. Compound (**8**) [5135-15-9] is an example of a coupler that splits off an immobilizing group in this manner. In a related process the coupler itself is the immobile moiety, as in (**9**) [4137-16-0], and the substituent that is split off is a mobile dye.

5.2.2.3. Dye Release by Reduction. The early Agfa-Gevaert instant reprographic processes Agfachrome-Speed and Copycolor CCN introduced a method of releasing positive dye images by the reduction of the alkali-immobile dye-releasing quinone compounds shown in Figure 11 (59). These compounds were incorporated within the light-sensitive emulsion layers along with a ballasted electron-donor compound. During processing there was competition between the oxidized developer and the reducible dye releaser for reaction with the electron donor. In exposed areas, silver halide developed, and the oxidized developer that formed was reduced by the electron donor. In unexposed areas, the electron donor reacted instead with the dye releaser, reducing its quinone moiety. The reduced dye releaser in turn underwent a quinone methide elimination in alkali, releasing a mobile dye, as shown in equation **9**. The system produces positive color images with negative-working emulsions. R, R′, R″, and R‴ are all alkyls.

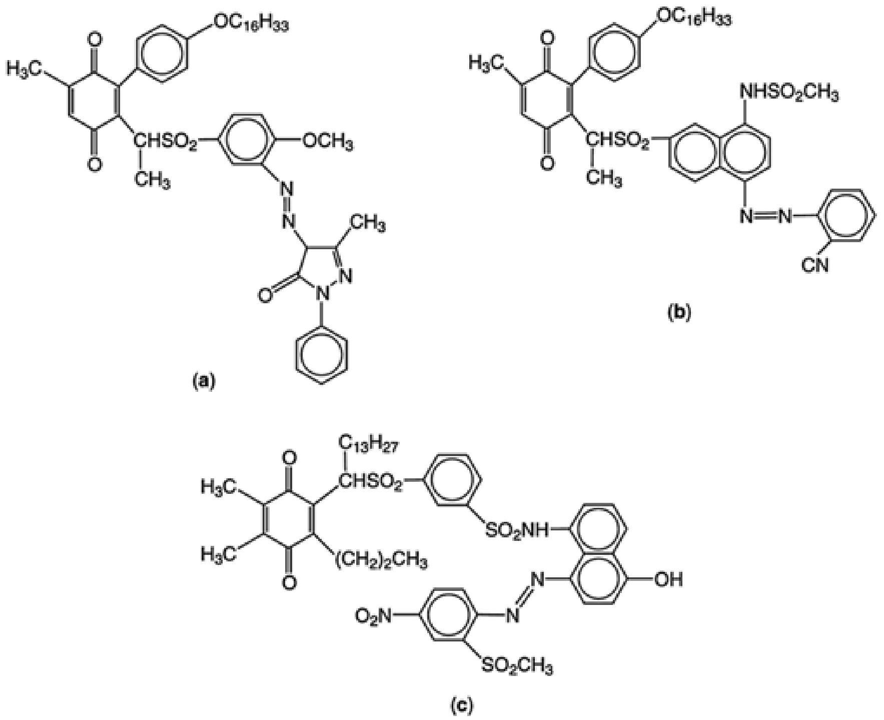
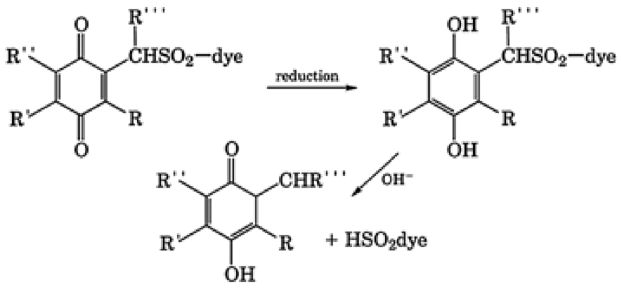
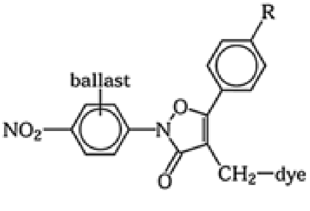


Fig. 11. Dye releasers used in Agfachrome-Speed and Copycolor films: (**a**) yellow [85432-41-3]; (**b**) magenta [80406-97-9]; (**c**) cyan.



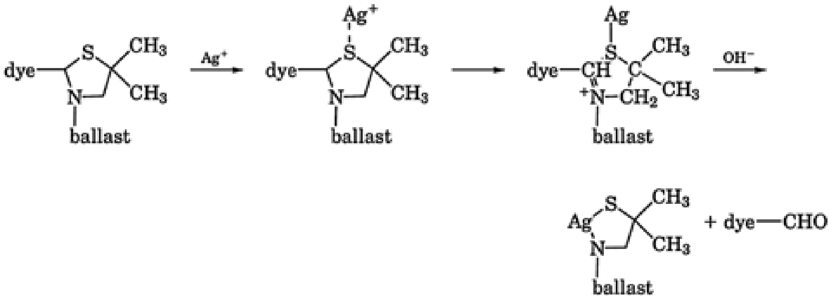
(9)

5.2.2.4. Dye Release by Ring Opening, Single Electron Transfer. A positive-working system based on ring opening by the cleavage of a single N–O bond in a 2-nitroaryl-4-isoxazolin-3-one compound such as compound (**10**) has been described (60). In exposed areas, silver halide reduction is accompanied by oxidation of an electron-transfer agent, which cross-oxidizes an electron donor. In unexposed areas, the electron donor initiates the ring opening and consequent dye release (61). The *ring opening by single electron transfer* (ROSET) system was first used in Fuji Colorcopy DC photothermographic color print material provided for use in the Fuji Colorcopier DC3000 (62). The ROSET chemistry is used in Pictrostat 100, 300, and 50 systems.



(10)

5.2.2.5. Dye Release by Silver-Assisted Cleavage. A soluble silver complex formed imagewise in the undeveloped areas of the silver halide layer may be used to effect a cleavage reaction that releases a dye or a dye precursor. Polaroid Spectra film introduced silver-assisted thiazolidine cleavage to produce the yellow dye image (63), a system subsequently used in Polaroid 600 Plus, later designated Polaroid 600 Platinum, and in Polacolor Pro 100 films. The process yields positive dye transfer images directly with negative-working emulsions (64). An example is the silver-assisted cleavage of a dye-substituted thiazolidine compound, as shown in equation **10**. The dye is initially linked to a ballasted thiazolidine, which reacts with silver to form a silver iminium complex. The alkaline hydrolysis of that complex yields an alkali-mobile dye. Concomitantly, the silver ion is immobilized by reaction with the ballasted aminoethane thiol formed by cleavage of the thiazolidine ring.



(10)

Discrimination between exposed and unexposed areas in this process requires the selection of thiazolidine compounds that do not readily undergo alkaline hydrolysis in the absence of silver ions. In a study of model compounds, the rates of hydrolysis of model *N*-methyl thiazolidine and *N*-octadecyl thiazolidine compounds were compared (65). An alkaline hydrolysis half-life of 33 min was reported for the *N*-methyl compound, and a half-life of 5525 min (3.8 days) was reported for the corresponding *N*-octadecyl compound. Other factors affecting the kinetics include the particular silver ligand chosen and its concentration (66).

5.2.3. Dye Formation Processes

5.2.3.1. Color Development. Experimental chromogenic negatives included a structure comprising interdigitated multilayer color-forming elements (30). With the advent of dye developers, chromogenic three-color work was discontinued. However, a monochrome “blue slide” film, PolaBlue, was introduced in 1987. Color development of the exposed film forms a nondiffusing dye image within the emulsion layer (67). In 1988, a chromogenic photothermographic process based on immobile couplers and a color developer precursor was described (68).

In another process, instead of color coupling to form the image dyes, coupling was used to immobilize preformed dyes in exposed areas (69). Unreacted coupling dye transferred to form a positive dye image. Each of the coupling dyes incorporated the same coupler moiety, so that all would react at the same rate with the oxidized developing agent.

Coupler-developers comprising a color coupler and a color developer linked together by an insulating group have been described (70). In areas where silver halide undergoes development with such a compound, the coupler-developer is oxidized and immobilized by intermolecular coupling. In undeveloped areas, the coupler-developer transfers to a receiving layer, where oxidation leads to intermolecular coupling to form a positive dye image.

5.2.3.2. Other Colorless Dye Precursors. Color images may be produced from initially colorless image-forming compounds other than the traditional chromogenic couplers. The use of colorless compounds avoids loss of light by unwanted absorption during exposure, and the colored form is generated during processing. A leuco indophenol may be used both to develop a silver image in the negative and to form an inverse, positive dye image in the receiving layer (71). Colorless triazolium bases have also been proposed as image dye precursors (72). In unexposed regions, where silver halide is not undergoing development, unused developing agent reduces such a base to its colored form, rendering it immobile. In developing regions, the base may migrate to a receiving layer and there undergo reduction to form a negative dye transfer image.

5.2.4. Stabilization of Dye Images

Regardless of the method of formation of the component images dye, a major consideration is the stability of the final color image in the receiving layer. Unlike the dye images produced by bath processes, the instant image is formed in a single processing step and is not washed or treated afterward. Therefore the instant process must incorporate both image-forming reactions and reactions that provide a safe environment for the finished image. In the integral films, not only the positive color image layer, but also the negative layers that remain concealed within the film unit, must be rendered inert.

The subtractive instant color films provide for image stabilization by the inclusion of polymeric acid layers that operate in conjunction with timing layers to provide a carefully timed reduction in pH following image formation. Reducing the pH terminates development reactions and stops the migration of dyes and other alkali-mobile species, thus stabilizing both the dye image and its environment.

Stabilization by timed pH reduction was first provided in the original Polacolor film and continued in later Polacolor films. As shown in Figure 12, the Polacolor positive sheet includes a timing layer and a polymeric acid layer (73). In integral films, the timing layer and the acid polymer layer may alternatively be placed beneath the emulsion layers (74). The permeability of the timing layer determines the length of time before alkali reaches the polymeric acid layer and begins to undergo neutralization. The consumption of alkali rapidly reduces the pH of the image-receiving layer to a level conducive to print stability.

To provide for suitable timing of the pH reduction over the wide range of temperatures that may be encountered, the instant films may use polymeric timing layers in which permeability to alkali varies inversely with temperature. In the integral films, where all components are retained within the film unit after processing and the moisture content remains high for several days, care must be taken to avoid materials that could migrate or initiate unwanted reactions even at reduced pH.

Another concern is the stability of the image dyes to prolonged exposure to light. Many dyes that would otherwise be suitable as image dyes undergo severe degradation upon such exposure and are particularly sensitive to ultraviolet (uv) irradiation. Important considerations include the dye structures and the structure of the mordant in the image-receiving layer, as well as the chemical environment following the termination of processing.

The metallized dyes introduced in the SX-70 and Polacolor 2 films and included in later films have outstanding stability to light and are also highly stable in dark storage (75). The light stability of certain nonmetallized dyes may be increased by posttransfer metallization. For integral films, further protection against uv attack may be afforded by the incorporation of uv absorbers in the transparent polyester cover sheet. This sheet also provides protection against physical damage and attack by external chemicals. Similarly, Polacolor images show enhanced stability when laminated in plastic covers that provide uv filtration and

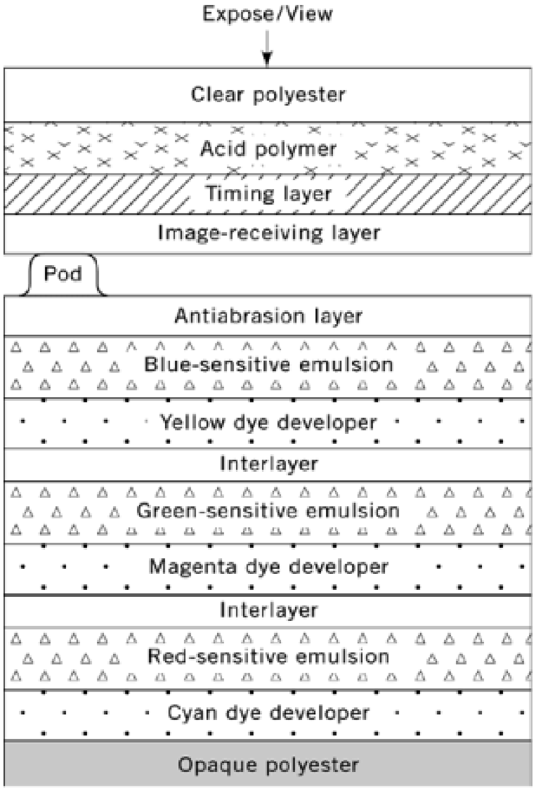


Fig. 12. Schematic cross section of Polacolor positive and negative sheets (not to scale). During processing pressure rollers rupture a pod attached to one of the sheets, thereby releasing a viscous reagent. The viscous reagent temporarily laminates the two sheets and initiates processing. As the exposed silver develops *in situ*, the associated dye developers undergo oxidation and immobilization. In unexposed regions the dye developers diffuse from their respective layers to the image-receiving layer, where they form the positive color image. After the required processing time, the two sheets are stripped apart. The reagent adheres to the negative, which is discarded, and the finished color print is ready for viewing, The timing layer and the acid polymer layer, which underlie the image-receiving layer, provide a timed pH reduction that stabilizes the color print.

exclude air and moisture from the image environment. Spray coating of large format Polacolor images, such as used in the early Polacolor museum replicas, with a solution of a uv absorber in a poly(methyl methacrylate) carrier, also afforded protection against prolonged light exposure.

5.2.4.1. Stability of Instant Dye Images. As with all dye color images, changes with age with age depend on the conditions to which the images are subjected. Detailed recommendations on the display, storage, and preservation of instant photographs have been published (76). Testing of instant color images in dark storage and under both accelerated and normal light exposure conditions has enabled evaluation and estimates of longevity among instant color prints.

Polacolor 2 images, which utilized the metallized dyes described earlier, and Polacolor ER prints, in which the magenta dye is a nonmetallized xanthene dye, both have shown significantly higher light stability than the original Polacolor images (77). At elevated temperatures in dark storage and with prolonged exposure to daylight, some yellowish stain was reported for both early integral and early peel-apart films (78). Standardized testing established in 1991 provides protocols for stability evaluation of both instant and noninstant products (79).

6. Instant Color Film for use in Instant Cameras

6.1. Polacolor

The first instant color film, Polacolor, was introduced by Polaroid Corporation in 1963, utilized dye developers for image formation (see earlier section on Dye Developer Processes). To use negatives having multiple continuous layers, hold-release mechanisms were developed to keep each dye developer in close association with the emulsion designated to control it until development had progressed substantially (30,80).

6.1.1. Polacolor Negative Structure

In addition to the design and selection of dye developers characterized by a high development rate relative to the diffusion rate, useful measures included the introduction of small quantities of highly mobile auxiliary developers and the intercalation of temporary barrier layers between the three monochrome systems of the negative. Figure 12 shows the layered structure of the original Polacolor negative.

6.1.2. Auxiliary Developers

The use of auxiliary developers as electron-transfer agents, although not necessary for alkali-mobile dye developers, is usually advantageous (33). The auxiliary developer is smaller and more mobile than the dye developers and can more rapidly reach the exposed silver halide grains to initiate development. The oxidation product of the auxiliary developer in turn oxidizes and immobilizes the associated dye developers. Some auxiliary developing agents that have been used in this way are Phenidone, Metol, and substituted hydroquinones, such as 4′-methylphenylhydroquinone [10551-32-3], $C_{13}H_{12}O_2$ (81), either alone or with Phenidone (82) (eq. **12**).

6.1.3. Barrier Layers

Depending on composition, barrier layers can function simply as spatial separators or they can provide specified time delays by swelling at controlled rates or undergoing reactions such as hydrolysis or dissolution. Temporary barriers assist in preventing interimage crosstalk. For example, a temporary barrier prevents cyan dye developer migrating toward the image-receiving layer from competing with the overlying magenta dye developer in reducing the green-sensitive emulsion in exposed areas.

Preproduction dye developer negatives used a combination of cellulose acetate and cellulose acetate hydrogen phthalate as barrier layers. The images produced from these negatives were outstanding in color isolation, color saturation, and overall color balance. However, solvent coating was required with this composition, and it was not used in production. The original Polacolor negative had water-coated interlayers of gelatin (83). Later Polacolor negatives, starting with Polacolor 2, and the integral film negatives use as interlayers combinations of a polymer latex with a water-soluble polymer. A key development was the synthesis of latices that would function as temporary barriers, reducing interimage problems. The water-soluble polymer functions as a permeator, so that the barrier properties are tunable (84). Additional interlayers may contain filter dyes, pigments, or reactive components.

6.1.4. Polacolor Receiving Sheet

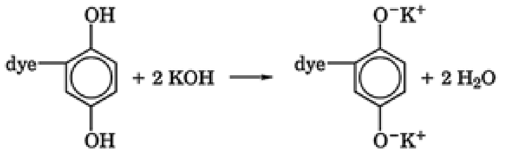
The original Polacolor receiving sheet comprised three active layers (Figs. 12 and 13). The outermost layer is an image-receiving layer comprising poly(vinyl alcohol) and the mordant poly(4-vinylpyridine), which immobilizes image dyes. (85). Next was a polymeric timing layer, and then an immobile polymeric acid layer. In subsequent Polacolor receiving sheets, the permeability of the timing layer to alkali was made greater at at lower temperatures than at elevated temperatures, thereby providing appropriate timing of pH reduction over a range of temperatures before the alkalinity of the system is reduced (86). The removal of alkali from the image-receiving layer prevents salt formation on the print surface after the negative and positive sheets are stripped apart. The reduction of pH in the image layer proceeds to completion after the sheets are separated.

6.1.5. Image Formation and Stabilization

The sequence of reactions responsible for image formation and stabilization begins as the exposed negative sheet and the image-receiving sheet pass together through a pair of rollers, rupturing the reagent pod attached to one sheet and releasing a viscous reagent. The reagent temporarily laminates the two sheets together. Alkali in the reagent permeates the layers of the negative, ionizing and solubilizing each of the dye developers and an auxiliary developer contained in layers of the negative.

As the reagent reaches them the emulsions undergo development in exposed regions and the associated dye developers become oxidized and immobilized. In unexposed areas, dye developer molecules migrate to the image-receiving layer and are mordanted and immobilized there forming the positive dye image. The auxiliary developer assists in color isolation by serving as an electron-transfer agent between the less mobile dye developers and the exposed silver halide. As the auxiliary developer is oxidized by the development of silver, it yields an oxidation product that in turn oxidizes dye developer molecules. Further control of the development process is effected by alkali-releasable antifoggants, such as phenylmercaptotetrazole, contained in the dye developer layers.

As the reagent reaches them the emulsions undergo development in exposed regions and the associated dye developers become oxidized and immobilized. In unexposed areas dye developer molecules migrate to the image-receiving layer and are mordanted and immobilized there, forming the positive dye image. The auxiliary developer assists in color isolation by serving as an electron-transfer agent between the less mobile dye developers and the exposed silver halide. As the auxiliary developer is oxidized by the development of silver, it yields an oxidation product that in turn oxidizes dye developer molecules. Further control of the development process is effected by alkali-releasable antifoggants, such as phenylmercaptotetrazole, contained in the dye developer layers.



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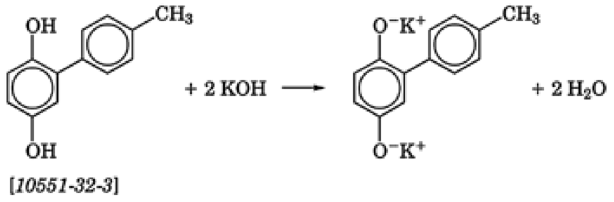

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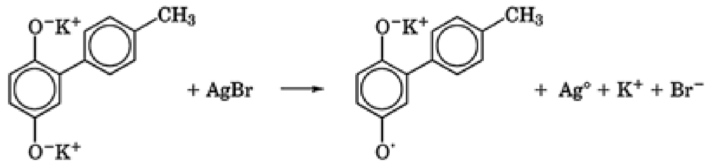

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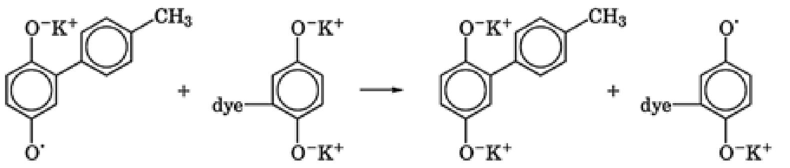


(14)

The polymeric acid layer in the receiving sheet terminates the process. Acting as an ion exchanger, the acid polymer forms an immobile polymeric salt with the alkali cation and returns water in place of alkali. Capture of alkali by the polymer molecules prevents deposition of salts on the print surface. The dye developers thus become immobile and inactive as the pH of the system is reduced.

Polacolor processing takes ~ 60 s. Within this period the image-forming and image-stabilizing reactions proceed almost simultaneously. When image formation is terminated by stripping apart the negative and positive sheets, the print is ready for viewing; its surface is almost dry, and the pH of the image layer is rapidly approaching neutrality. The surface dries quickly to a hard gloss, and the finished print is durable and stable.

6.1.6. Polacolor 2; Polacolor ER

Polacolor was replaced in 1975 by Polacolor 2, a film with improved light stability, provided by the metallized dye developers shown in Figure 7. An extended range version, Polacolor ER, introduced in 1980, used the cyan and yellow metallized dye developers together with a magenta dye developer [78052-95-6] (**1**) containing a xanthene. This dye was chosen because it reduced unwanted blue absorption, thereby providing improved color fidelity. Polacolor ER films are balanced for daylight exposure and rated at ISO 80.

6.1.7. Polacolor Pro; Professional Polacolor Films

Hybrid Polacolor negatives, starting with Polacolor Pro (1996), use dye developers for cyan and magenta in combination with silver-assisted cleavage to generate the yellow image (87). Hybrid negatives had been introduced in 1986 in the integral film Spectra. (Polaroid integral films are discussed further in Section 6.2.) These films also utilize a *completion developer*, such as 2,5-di-*tert*-butyl hydroquinone, which reduces nonimage silver and lessens reciprocity failure. The use of a completion developer also contributes to increased color fidelity and whiter whites.

In the hybrid negatives, interlayers not only act as barriers but may also contain filter dyes, pigments, or reactive components. A feature introduced by the Type 600 integral film and included in the hybrid Polacolor negatives is the incorporation of pigmented spacer layers behind the blue- and red-sensitive layers. These layers contribute to the efficiency of the negatives. A new interlayer in the hybrid negatives contains a colorless hydroquinone-based developer for the blue-sensitive emulsion (88). Another interlayer provides a silver scavenger that prevents release of yellow dye by silver ions originating in the underlying green- and red-sensitive layers.

Figure 13 is a schematic section of the Polacolor Pro hybrid negative. The negative comprises three layered color sections: the blue-sensitive emulsion, its colorless developer, the yellow dye releaser, and a yellow dye filter layer; the green-sensitive emulsion and the magenta dye developer; the red-sensitive emulsion and the cyan dye developer. Spacers and additional interlayers separate these three sections. During exposure the yellow filter layer and each of the dye developers function as antihalation dyes for the respective emulsion layers above them. The yellow filter dye protects the green- and red-sensitive layers below from exposure to blue light, and the magenta dye developer protects the red-sensitive emulsion below from exposure to green light.

Polacolor Pro daylight films are rated at ISO 100, and a tungsten version is rated at ISO 64. Formats include both pack films and sheet films. Film types include Polacolor 579, Polacolor 679, and Studio Polaroid.

6.2. Polaroid Integral Films

The first integral film, SX-70, and the SX-70 single lens reflex camera, described by Figure 14, were introduced in 1972. These products heralded totally new concepts in instant photography (89). With this system, in-camera initiation of processing became fully automatic. The negative and the receiving sheet are sealed into a single unit, which also contains the pod. Immediately after exposure, the film unit passes between processing rollers and is ejected from the camera. During spreading, the reagent, which contains a white pigment, forms a new

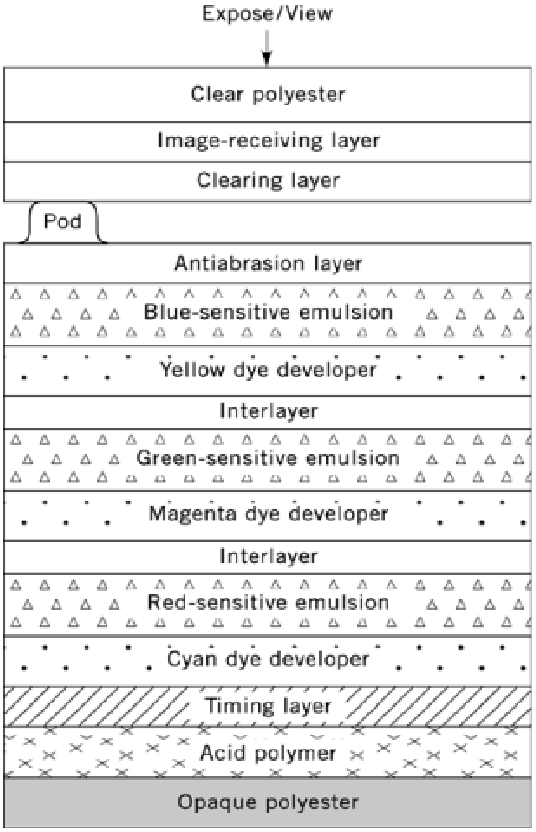


Fig. 13. Schematic cross section of Polacolor Pro, a hybrid peel-apart film. The yellow image is formed by dye release based on silver-assisted cleavage of a yellow dye releaser. The magenta and cyan image components utilize dye developers as in the earlier Polacolor films.

layer between the negative and the image-receiving layer. There are no air spaces in the multilayer structure after processing. Processing continues within the film unit under ambient conditions, and the emerging image becomes visible as the processing reaches completion. The image is seen by reflected light against the new pigmented layer within the unit.

Polaroid followed the original SX-70 film with Time-Zero SX-70 film (1979), and the high speed 600 film (1981) used in cameras designed to accept only the high speed films.

6.2.1. SX-70 Film Structure

The integral film format required some components quite different from those used in the peel-apart system. Figure 15 is a schematic cross section of the SX-70 film unit. The two sheets comprising the film unit were analogous to Polacolor negative and positive sheets. The two outermost layers, both polyester, provided structural symmetry that ensured flatness of the film unit under all atmospheric conditions. The upper polyester sheet was transparent and the lower one opaque black. Light passing through the upper sheet exposed the layers of the negative, and the picture was viewed through the same sheet. A durable, low index of refraction, quarter-wave antireflection coating on the outer surface of the transparent polyester minimized flare during exposure, increased the efficiency of light transmission during both the exposure of the negative and the viewing of the final image and facilitated seeing the image through the polyester with minimum surface luster (90).

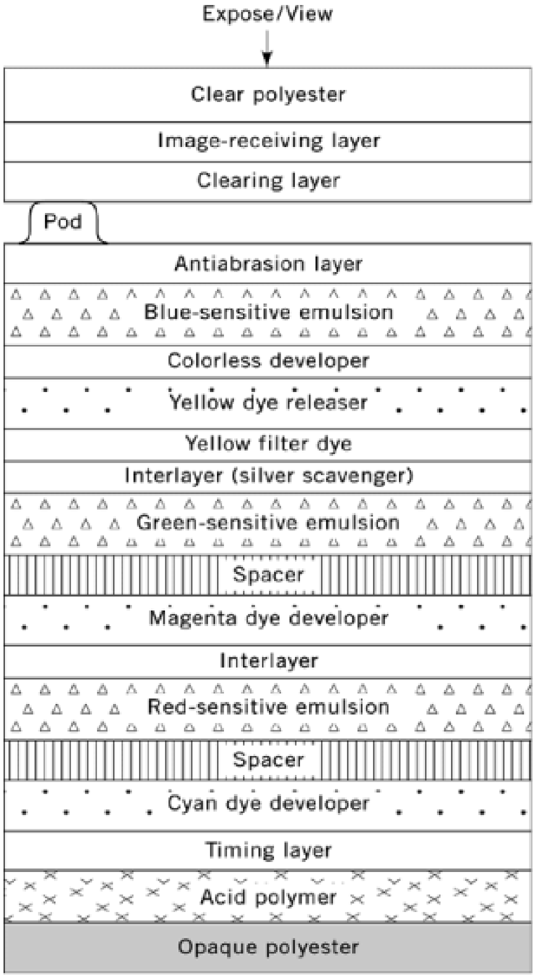


Fig. 14. Schematic cross section of the original SX-70 camera in viewing mode. Rays of light pass through the camera lens to the permanent mirror (**a**), which reflects them downward to a decentered Fresnel mirror (**b**) that lies just over the image plane. The Fresnel reflects the light rays upward to mirror (**a**), which directs them through the small aperture (**c**) to a decentered aspheric mirror (**d**). This mirror reflects the rays through the decentered lens (e) to the eye. The folded light path facilitated the camera's compact design. In the taking mode the hinged unit swings up against mirror (**a**) and another mirror on the back of the Fresnel reflects the light rays downward to expose the uppermost film unit. In the original SX-70 camera, the surface of the Fresnel was roughened to form a focus screen. This system worked well at high light levels but was less accurate at low light levels. Later versions incorporated a small circular split-image rangefinder that comprised a pair of decentered Fresnel sections; decentering is the optical equivalent of tilting, and matching the two images provided accurate focus control. Still later models incorporated a fully automatic sonar rangefinder.

Color balance of an integral film exposed through the transparent polyester sheet may be adjusted by incorporating color-correcting filters in a layer of the positive sheet; these dyes are subsequently bleached to colorless form during processing (91).

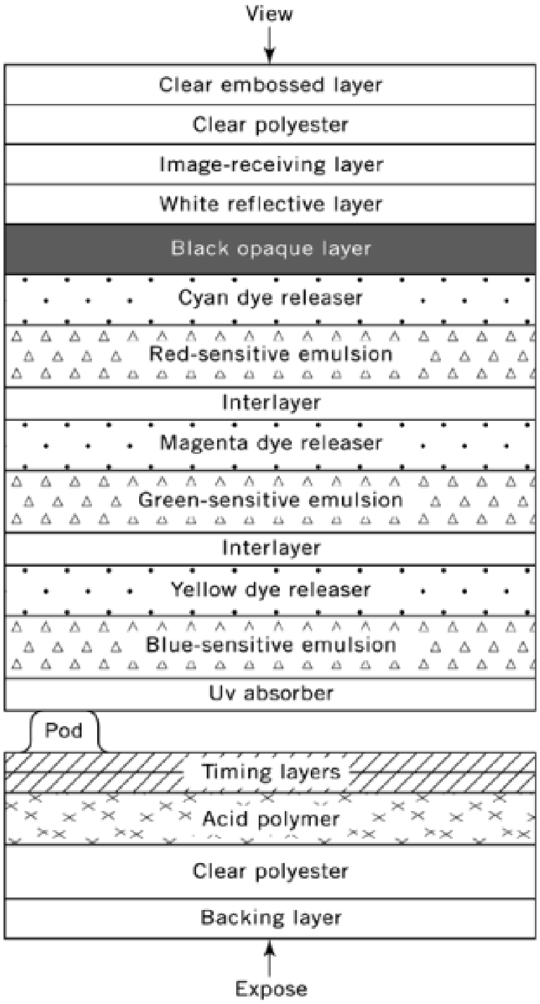


Fig. 15. Schematic cross section of an SX-70 integral film unit. The film is exposed through the clear upper sheet. As the reagent is spread from the pod, it forms a white pigmented layer. The image formed in the image-receiving layer is viewed against the reflective pigment layer.

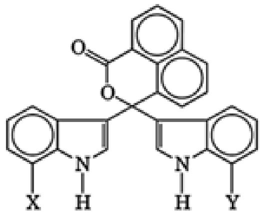
6.2.2. SX-70 Image Formation

A small pod concealed within the wide border of the SX-70 film unit contained the viscous reagent. As an exposed film unit was ejected through the processing rollers and out of the camera, the pod burst and the viscous reagent spread between the top negative layer and the image-receiving layer, forming a new layer comprising water, alkali, white pigment, polymer, and other processing addenda. As in Polacolor processing, alkali rapidly permeated the layers of the negative. In exposed areas, silver halide was reduced and the associated dye developer was oxidized and immobilized. In unexposed areas, the dye developers, ionized and solubilized by the alkali, migrated through overlying layers of the negative to reach the image-receiving layer above the new stratum of pigment-containing reagent. The transferred image is visible through the transparent polyester sheet.

6.2.3. Opacification

An important aspect of the SX-70 system is that the developing film unit is ejected while still sensitive to light. Hence, both surfaces of the negative must be protected from ambient light during development. Two potential sources of fog must be prevented when the film emerges from the camera. The first, lateral light piping within the transparent polyester sheet, is prevented by incorporating a very low concentration of a light-absorbing pigment, such as carbon black, in the sheet. A pigment concentration that increases transmission density normal to the surface by only 0.02 provides efficient absorption of light that otherwise could travel laterally by internal reflection within the sheet (92). Additional protection against further exposure is provided by the combined effects of opacifying dyes and light-reflecting titanium dioxide pigment included in the viscous reagent layer (93).

The opacifying dyes used in the SX-70 and subsequent Polaroid integral films represent a new class of phthalein dyes (94) designed to have unusually high pK_a values. The solution of an indicator such as those represented by compound (**11**) is highly colored when the dye is at or above its pK_a values and becomes progressively less colored as the pH is reduced. The very high pK_a values of these opacifying indicators are induced by hydrogen-bonding substituents located in juxtaposition to the hydrogen that is removed by ionization (95). The pK_a values for a series of naphthalein opacifying indicators are shown below compound **11**.



(11)

X	Y	pK_a	CAS Registry Number
H	H	11.1, 13.8	[68975-54-2]
COOH	COOH	13.2, > 15	[68975-55-3]
COOH	$NHSO_2C_{16}H_{33}$	12.9, > 15	[37921-74-7]

The reduction of pH within the film unit is effected by a polymeric acid layer, as in the Polacolor process. The contiguous timing layer controls the onset of neutralization. In the original SX-70 film unit these layers were on the inner surface of the transparent polyester sheet (Fig. 14) (16). In Time-Zero SX-70 and later Polaroid integral films these layers are on the inner surface of the opaque negative support, as shown in Figure 16 (96).

6.2.4. Time-Zero/SX-70 Film

The Time-Zero/SX-70 film (1979) radically reduced the time required for completion of the development process and also changed the appearance of the emerging print. In the original SX-70 film, the picture area initially showed the pale green color of the opacifying dyes. This color gradually faded over a few minutes' time as the pH dropped. With a Time-Zero/SX-70 print the image becomes visible against a white background only a few seconds after the film unit has been ejected, and the picture appears complete within about a minute.

The faster appearance of the image and the change in background color reflect changes in film structure and composition. When the reagent is spread, it contacts a new *clearing layer* on the receiving layer surface. The

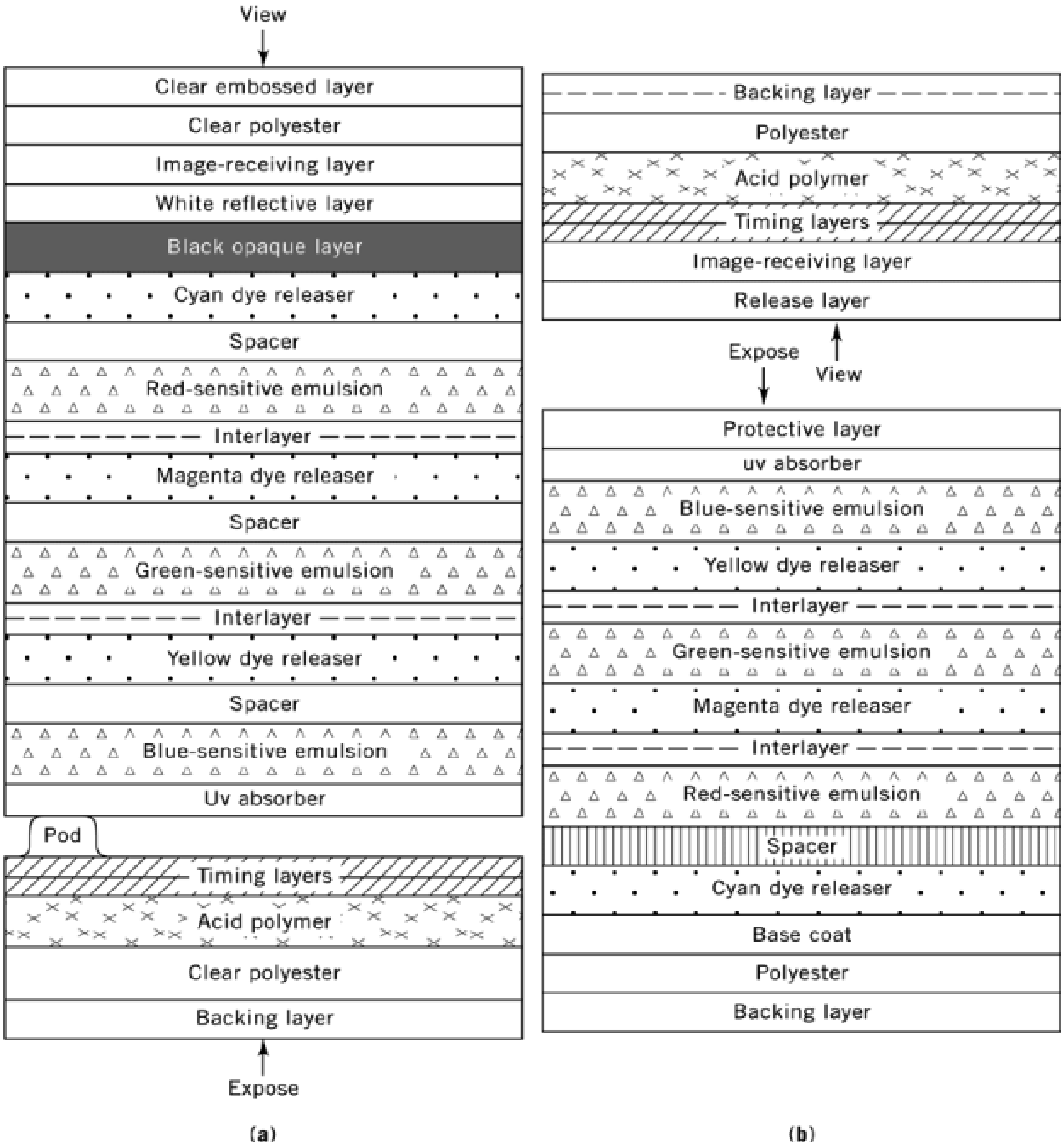


Fig. 16. Schematic cross section of Time-Zero/SX-70 integral film. In this film, the polymeric acid layer and the timing layer are located beneath the negative layers, rather than in the positive sheet. Time-Zero and all later Polaroid integral films have an antireflection layer coated on the outer surface of the clear polyester layer through which the image is viewed.

clearing agent immediately decolorizes the opacifying dyes at the interface of the reagent layer and the receiver layer without affecting the opacifying dyes within the pigmented reagent layer. This decolorization provides a white background for the emerging image while the opacifying dyes within the reagent layer continue to protect the developing negative (97).

An effective clearing layer comprises a low molecular-weight poly(ethylene oxide) hydrogen bonded to a diacetoneacrylamide-*co*-methacrylic acid copolymer. The alkali of the reagent breaks the complex, releasing the ethylene oxide polymer and decolorizing the nearest opacifying dyes. The Time-Zero reagent incorporates as a thickener poly(diacetoneacrylamide oxime). This polymer is stable at very high pH but precipitates below pH 12.5. Its use at concentrations $<1\%$ provides the requisite reagent viscosity and permits rapid dye transfer (98). A further aid to rapid transfer is the use of negative layers appreciably thinner than those of the original SX-70 negative.

The Time-Zero film process has an efficient receiving layer consisting of a graft copolymer of 4-vinylpyridine and a vinylbenzyltrimethylammonium salt grafted to hydroxyethylcellulose (99). The fidelity of color rendition was improved in the Time-Zero film by the use of the xanthene magenta dye developer (**1**), which has reduced blue absorption.

Cameras using SX-70 films include both folding single-lens reflex models that can focus as close as 26.4 cm (10.4 in.), designated as SX-70 cameras, and nonfolding models having separate camera and viewing optics. Pictures may be taken as frequently as every 1.5 s. The SX-70 picture unit is 8.9×10.8 cm, with a square image area $\sim 8 \times 8$ cm. The SX-70 film pack contains 10 of these picture units, a flat 6-V battery about the size of a film unit, and an opaque cover sheet that is automatically ejected when the pack is inserted into the camera. SX-70 films are balanced for daylight exposure and are rated at ISO 150. The temperature range for development is $\sim$7–35°C. The range may be extended to 38°C with a slight exposure compensation.

6.2.5. Type 600 Film

The first high speed integral film, Type 600 (1981), was rated at ISO 640, approximately two stops faster than the earlier SX-70 films. Features included high speed emulsions and reflective pigmented spacer layers underlying the blue- and red-sensitive emulsion layers. The dye developers were the same as those used in Time-Zero/SX-70 film. As in Time-Zero film, the polymeric acid layer and the timing layer were located over the opaque polyester layer, below the negative layers, and the structure included an additional clearing layer between the reagent layer and the image-receiving layer. Although the Type 600 film was similar in format to the SX-70 film, the higher speed film could not be used in the SX-70 cameras. New cameras, including a single lens reflex model, were provided for use with the Type 600 film.

6.2.6. Spectra Film

Spectra film was introduced in 1986 as a part of a new camera-film system featuring a rectangular picture format, 7.3×9.2 cm. The Spectra system introduced the first hybrid film structure (87), as shown schematically in Figure 17. Spectra film utilized silver-assisted thiazolidine cleavage for formation of the yellow dye image and dye developer image formation of the magenta and cyan images, as described in the earlier section on Polacolor Pro film.

Among later integral films that follow the same hybrid scheme are Spectra Platinum (also known as Image Extreme), 600 Plus Film (1988), Spectra HighDefinition film (1991), 600 Plus HighDefinition (1993), and 600 Platinum. Variations include a number of specialty films, some incorporating preexposed patterns, and 600 Write On, a matte version of Platinum film that enables writing on the processed print surface. All are rated at ISO 640.

Integral films for specialized applications are obtained by preexposing the film to unique patterns. Polaroid provides to quantity users integral films that are customized with preprinted borders or messages within the image area. Polaroid Copy&Fax Film incorporates a preexposed halftone screen that improves the quality of images produced by photocopying or fax transmission of continuous tone photographs. With Polaroid GridFilm, a preexposed grid pattern provides each print with a built-in scale for measurement of image features.

6.2.7. Type 500 Films; Pocket Films

Type 500 film (formerly known as Captiva, Vision, and 95) utilizes the Spectra film structure and chemistry in a smaller format, providing prints with image area 7.3×5.4 cm. This film was introduced with the Captiva

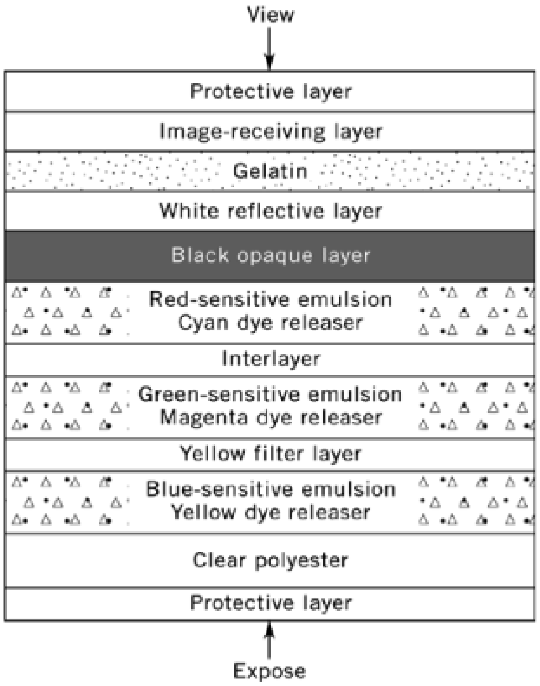


Fig. 17. Schematic cross section of Spectra integral film. The 600 Platinum film has a similar structure. In these films, the yellow image is formed by silver-assisted cleavage of a yellow dye releaser. A colorless developer reduces exposed silver halide in the blue-sensitive emulsion; in unexposed areas dissolved silver diffuses to the dye releaser layer and triggers the release of the yellow image dye.

camera, now discontinued. The Captiva camera was unique in that the developing integral film units passed between pressure rollers and around the end of the camera to a storage compartment in the back of the camera where each could be viewed as the image appeared. The same film is used in the JoyCam and in the one-time-use PopShots camera (100).

Pocket films, used in pocket-sized I-Zone cameras (101), produce integral images 3.6 × 2.4 cm. Film speed is ISO 640 and average processing time is 3 min. Pocket Sticker Film has an adhesive layer so that the prints may be affixed to a variety of surfaces. The I-Zone Convertible Pocket Camera features changeable colored faceplates, and the I-Zone Digital and Instant Combo Camera enables the user to select between digital and instant film pictures. An accessory to the I-Zone camera is the Polaroid Webster, a handheld mini-scanner, sized to scan I-Zone pictures and other small, flat objects. The scanner will store up to 20 images and upload them to a PC.

6.3. Polaroid Additive Color Films

An additive color system was first utilized by Polaroid in the Polavision Super-8 instant motion picture system, introduced in 1977 (102), and later in Polachrome 35-mm slide films. The Polaroid additive color screens comprise interdigitated stripes that range in frequency from 590 triplets/cm for Polavision to 394 triplets/cm for Polachrome. These stripes are fine enough to be essentially invisible when projected (103).

To create the stripes the film base is embossed to form fine lenticules on one surface, and a layer of dichromated gelatin is coated on the opposite surface. Exposure of the dichromated gelatin through the lenticules at an appropriate angle forms hardened line images in the dichromated gelatin. After washing away the unhardened gelatin, the lines that remain are dyed. These steps are repeated at different exposure angles to complete the formation of triads of red, green, and blue lines. The lenticules are then removed.

6.3.1. Polavision; Polachrome

The Polavision system, which is no longer on the market, included a movie camera and a player that processed the exposed film and projected the movie. The Polavision film was provided in a sealed cassette, and the film was exposed, processed, viewed, and rewound without leaving the cassette. Polaroid introduced Polachrome CS 35-mm slide film in 1982 (104), and a high contrast version, Polachrome HCP, in 1987. Polachrome films are provided in standard-size 35-mm cassettes.

6.3.1.1. Silver Image Formation and Stabilization. The integral additive transparency is based on the rapid, one-step formation of a stable, neutral, positive black-and-white image of high covering power behind the fine pattern of colored lines. The negative image formed concurrently is of much lower covering power and thus so inconsequential optically that it need not be removed to permit viewing the positive image (105). The negative image formed in the emulsion layer has only about one-tenth the covering power of the positive image. In Polavision, the negative image remained in place with the after processing, whereas in Polachrome the negative is stripped away, so that only the positive silver image layer and the additive screen are present in the processed slide.

To achieve good color rendition, it is necessary for the emulsion resolution to be significantly higher than that of the color screen. This requirement is fulfilled by using a fine-grained silver halide emulsion and coating the emulsion in a thin layer containing a minimal amount of silver. The high covering power positive image is a mirror-like deposit formed in a very thin image-receiving layer. Because the image is transferred to a contiguous layer, the resolution is higher than for images transferred through a layer of processing fluid.

The Polachrome film structure and the formation of a Polachrome color image are illustrated schematically in Figure 18. The color screen is separated from the image-receiving layer by an alkali-impermeable barrier layer. Over the image-receiving layer is a stripping layer, and above that are the panchromatic silver halide emulsion and an antihalation layer. Stabilizer precursors are contained in one or more of these layers (106). (The Polavision film structure was similar but did not include a stripping layer.) As indicated in Figure 18, exposure of the film produces blue, green, and red records behind the respective color stripes.

Processing of Polachrome 35-mm film, carried out in an Autoprocessor (Fig. 4), is initiated as a thin layer of reagent applied to a strip sheet contacts the film surface. Exposed silver halide grains develop *in situ*; unexposed grains dissolve, and the resulting soluble silver complex migrates to the positive image-receiving layer, developing there to form the thin, compact positive image layer. Following a short interval, the strip sheet and film are rewound. The strip sheet rewinds into the processing pack, which is subsequently discarded, and the film rewinds into its cartridge. The processed film is dry and ready to be viewed or to be cut and mounted for projection.

Both during and after the formation of the negative and positive silver images additional reactions take place. The antihalation dyes are decolorized, and stabilizer is released to diffuse to the image-receiving layer and stabilize the developed silver images. The developing agent, tetramethylreductic acid [1889-96-9] (**12**) (2,3-dihydroxy-4,4,5,5-tetramethyl-2-cyclopenten-1-one, $C_9H_{14}O_3$), undergoes oxidation and alkaline decomposition to form colorless, inert products (107). As shown in equation **15**, the chemistry of this developer's oxidation and decomposition is complex. The oxidation product, tetramethyl succinic acid (**13**) is not found under normal circumstances. Instead, the products are the α-hydroxyacid (**16**) and the α-ketoacid (**17**). When silver bromide is the oxidant, a four-electron oxidation can occur to give (**17**). In model experiments, the hydroxyacid was not converted to the keto acid. Therefore, it seemed that the two-electron intermediate triketone hydrate (**14**) in the presence of a stronger oxidant would reduce more silver, possibly involving a species such as (**15**) as a likely reactive intermediate. This mechanism was verified experimentally, using a controlled, constant

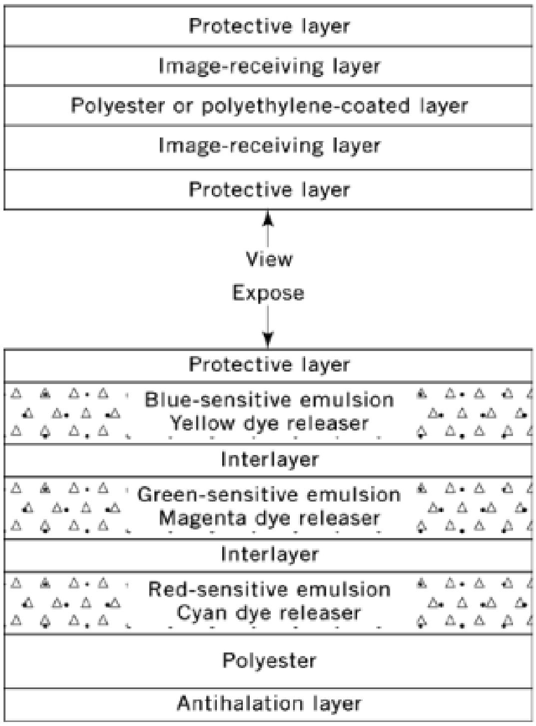
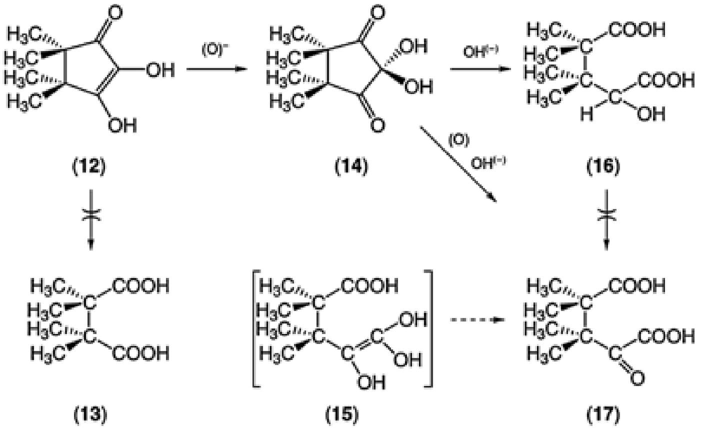


Fig. 18. Schematic representation of the Polachrome process. (**a**) The film during exposure to green light, with only the green lines transmitting light to the emulsion. In (**b**), processing has been initiated by the application of a very thin stratum of the viscous reagent represented by arrows pointing downward. The reagent reduces exposed grains *in situ*, and dissolves unexposed grains to form a soluble complex that migrates toward the receiving layer. (**c**) This part represents the completion of the process. The top layers are peeled away, leaving the integral positive image and color screen ready to view.

electrochemical potential. At potentials like that of silver chloride, four electrons were used; at lower potentials only two were used (108).



(15)

Polachrome films are exposed in standard 35-mm cameras, and the slides are mounted in standard size 5×5-cm (2×2-in.) mounts for use in conventional 35-mm projectors. Because of the density of the color base (∼0.7) the Polachrome slides are most effective when viewed either using a bright rear projection unit or in a well-darkened projection room.

6.4. Kodak Instant Films

Kodak entered the instant photography market in 1976 with the introduction of PR-10 integral color print film, rated at ISO 150, and a series of instant cameras designed for this film (9). The film system was based on a negative-working dye release process using preformed dyes (50), as described earlier under Dye Release Processes (see Fig. 9). These films and cameras were incompatible with the Polaroid instant photographic systems. Later Kodak integral films included Kodak Instant Color Film (ISO 150), Kodamatic and Kodamatic Trimprint films (ISO 320), Instagraphic print film (ISO 320), and Instagraphic color slide film (ISO 64). The films were balanced for daylight exposure. Kodak discontinued the production of instant films and cameras in 1986.These Kodak films and their chemistry are described in detail in the Kirk-Othmer 4th ed. (12)

6.5. Fuji Instant Films

The first Fuji instant system, Fotorama (1981), provided the integral color film, FI-10, rated at ISO 150 and camera were compatible with the Kodak instant system and incompatible with the Polaroid system. The film was similar in structure and processing to Kodak PR-10 film but had a different set of dye-release compounds (see Figs. 9 and 10).

A high speed integral color film, FI-800 (ISO 800), also designated as ACE film, and a new series of cameras suited to the higher speed films were introduced in 1984. The ACE products were distributed principally in Japan. Picture units are 9.7 × 10.2 cm, with image area 6.7 × 9.0 cm. FI-10 was also provided in 10 × 13-cm format for use in a special back for professional cameras.

Fuji also introduced in 1984 a peel-apart color print pack film and a series of black-and-white peel-apart pack films. These films are compatible with Polaroid cameras and camera backs that use peel-apart films. Film units measure 8.3 × 10.8 cm, with image area 7.3 × 9.5 cm.

In 1998, Fuji introduced the Instax system, which included new ISO 800 films in two formats and completely redesigned camera models (109). The films incorporated many improvements over the earlier FI-10 and ACE films, and the cameras introduced new picture formats. The Instax film units are 10.8 × 8.6 cm, with image area 9.9 × 6.2 cm. Instax Mini film units are 8.6 × 5.4 cm, with image area 6.2 × 4.6 cm.

The following sections will describe the principles involved in image formation and discuss the specific films. The Fuji films are based on a negative-working dye release process using preformed dyes. Direct positive emulsions yield positive images upon development, as described earlier under Dye Release Processes. The transfer of dyes is thus initiated by oxidized developing agent in areas where unexposed silver halide grains are undergoing development. The oxidized developing agent reacts with alkali-immobile dye-releasing compounds, which in turn release mobile image dyes that then diffuse to the image-receiving layer.

The direct positive emulsions comprise silver halide grains that form latent images internally and not on the grain surface. Reversal is effected during processing by the action of a surface developer and a nucleating, or fogging, agent present in the emulsion layer. Photoelectrons generated during exposure are trapped preferentially inside the grain, forming an internal latent image. In an exposed grain, the internal latent image is an efficient trap for conduction electrons provided by the nucleating agent. These grains have no surface latent image and do not develop in a surface developer. The unexposed grains trap conduction electrons from the nucleating agent, at least temporarily, on the grain surface, forming fog nuclei that undergo development by the surface developer.

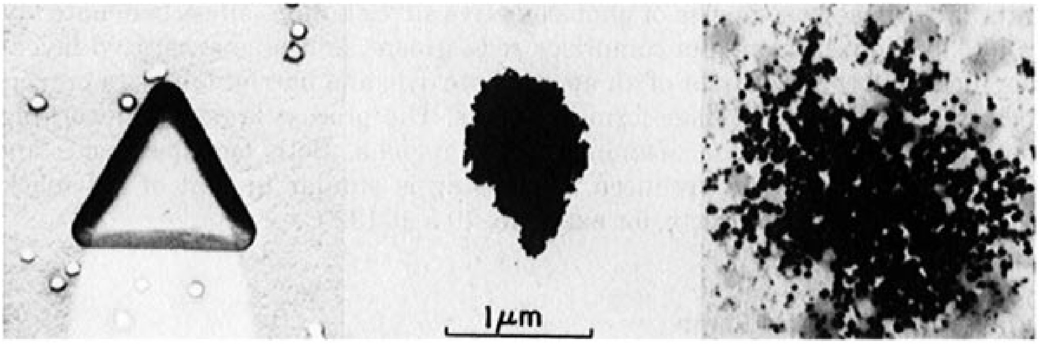


Fig. 19. Schematic cross section of Fuji FI-10 integral instant film. This film is exposed through the transparent cover sheet, and the image is viewed through the opposite surface. During processing released image-forming dyes pass through the black opaque layer and the white reflective layer to reach the image-receiving layer. During processing under ambient light the photosensitive emulsion layers are protected from further exposure by pigments within the reflective layer and the black opaque layer. The image is viewed against the reflective white pigment layer.

6.5.1. Fuji FI-10 Integral Film

The principal components of the FI-10 integral film unit are shown schematically in Figure 19. The clear polyester support, through which the final image is viewed, has on its inner surface both an image-forming section and an image-receiving section. The image-forming section includes direct positive emulsion layers, dye releaser layers, and scavenger layers; the image-receiving section includes the receiving layer and opaque layers to protect the image-forming section. The pod contains a viscous reagent and carbon black that serves as an opacifier. The transparent cover sheet through which the film is exposed has on its inner surface polymeric timing layers and a polymeric acid layer.When the exposed film unit passes between processing rollers, viscous reagent released from the pod spreads between the two sheets, initiating a series of reactions that develop the unexposed silver halide, release the dyes, and form the positive image in the image-receiving layer.

As with the Polaroid integral films, completion of processing takes place under ambient conditions outside the camera. The pigment layers of the image-receiving section protect the developing film from exposure to ambient light through the viewing surface. The carbon black layer formed as the reagent spreads prevents exposure through the opposite surface. Neutralization to terminate processing commences as the reagent permeates the polymeric timing layers and reaches the polymeric acid layer.

6.5.2. Fuji ACE (FI-800) Integral Film

The ACE film structure, earlier designated as FI-800, introduced new spacer layers that separate each of the light-sensitive emulsions from the dye releaser layer that it controls. Figure 20 is a schematic cross section. The overall thickness of the ACE negative is appreciably greater than that of the FI-10 negative, and image completion is somewhat slower. This film and the earlier FI-10 are available in Japan and in other Asian countries.

6.5.3. Fuji Peel-Apart Film FP-100

The FP-100 films, like the Fuji integral films, utilize a dye release system with direct positive emulsions. Figure 20 shows the negative structure, which includes a spacer layer between the red-sensitive layer and the cyan dye releaser layer, as in the ACE structure. Unlike the ACE negative, there are no spacers between the other emulsions and the corresponding dye releaser layers. These films are available in both 4 × 5-in. format and $3\frac{1}{4} \times 4\frac{1}{4}$-in. formats, compatible with corresponding Polaroid cameras and camera backs.

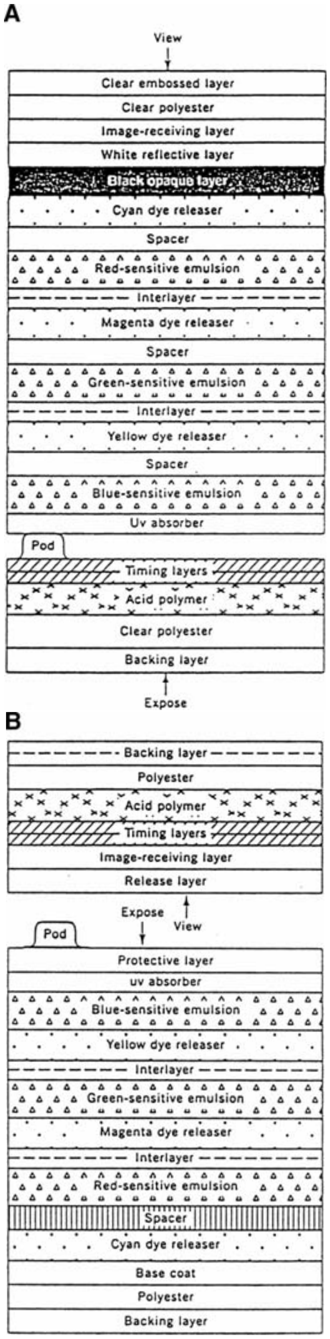


Fig. 20. Schematic cross sections of (**a**) Fuji ACE (FI-800) integral instant film and (**b**) Fuji FP-100 peel-apart instant color film. The ACE film structure includes new spacer layers between each of the photosensitive emulsion layers and the associated dye releaser layer that each controls. The higher speed of this film is attributed to new direct positive emulsions and a new dye releaser. The overall thickness of the FI-800 negative is appreciably greater than that of the earlier FI-10 negative, and image completion is somewhat slower. The FP-100 film includes a spacer layer between the red-sensitive emulsion and the cyan dye releaser layer but not between the other emulsions and their associated dye releaser layers.

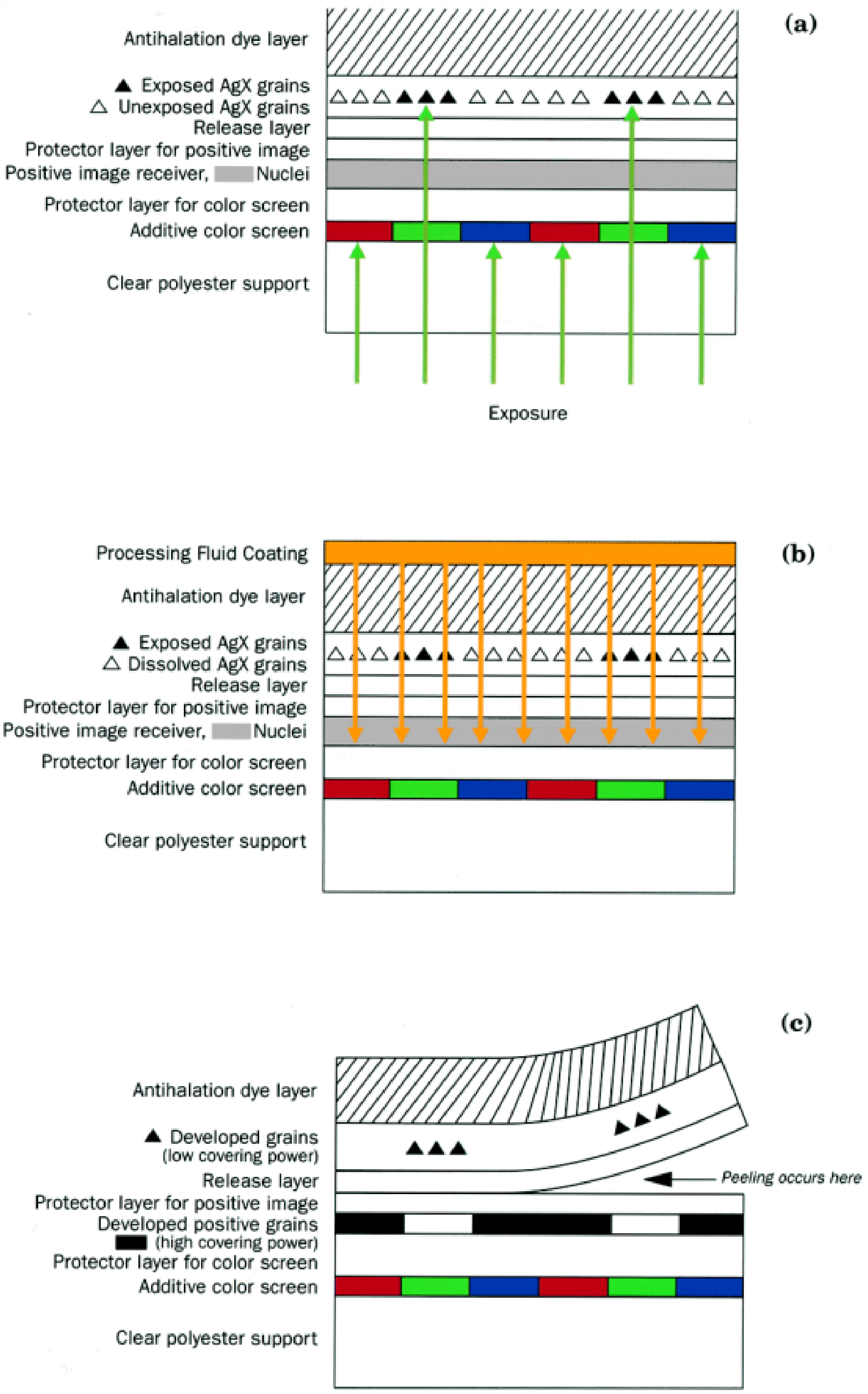


Fig. 21. Schematic cross section of Fuji Instax integral instant film during exposure (left) and after development (right). The film incorporates high-speed tabular-grain emulsions, new development accelerators, and thinner layers than in the earlier Fuji integral films. Reprinted with permission of Fuji Photo films Co., Ltd.

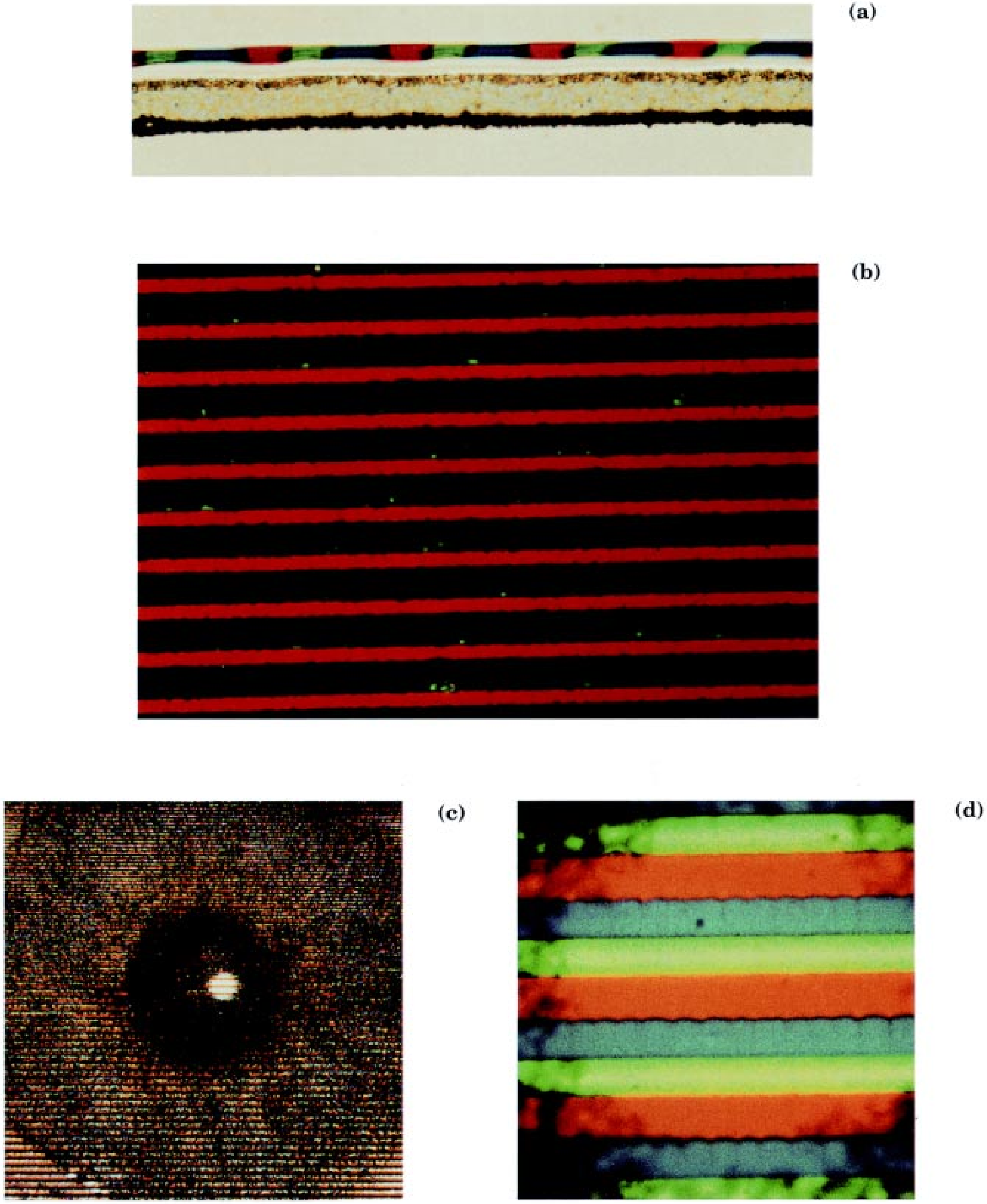


Fig. 22. Block diagram of the Fuji Pictrostat Digital 400 processing machine. The Image Input Unit incorporates scanners to accommodate reflection material, slides, and negatives, as well as interfaces for inputting digital still images and template images. The Image Processing Unit comprises a color-mapping module and an image processing module. The Image Output Unit comprises a display unit and a printer engine that exposes the film, moistens it with water, and applies heat to implement thermal development and dye transfer from donor sheet to receiver sheet. Reprinted with permission of Fuji Photo Films Co., Ltd.

6.5.4. Fuji Instax Integral System

The introduction of Instax film in 1998 marked a complete redesign of the Fuji instant cameras and films (109). New emulsions, interlayers, dyes, dye releasers, and timing polymers are incorporated in the Instax film structure illustrated schematically in Figure 21. The use of small tabular direct positive grains permits thinner, more uniform emulsion layers. Thin interlayers, new development accelerators, and faster-acting pH reduction contribute to improved imaging properties. New features include a broadened processing temperature range, 5–40°C, improved sharpness, modulation transfer function (MTF), and color isolation; and greater light stability (110). The new film units incorporate narrower margins, with more compact reagent pods, and the reagents have more uniform spreading characteristics. The use of a single polymer, polystyrene, for the film pack and the opaque cover sheet enables efficient disposal and recycling. The Instax products are distributed in Japan, Western Europe, Canada, Mexico, Brazil, and Asia.

7. Photothermographic Imaging

7.1. Dry Silver Materials and Processes

Photothermographic materials have been developed using low sensitivity silver salts, such as silver acetylides and silver carboxylates, sometimes in combination with silver bromide. Starting in 1964, 3M produced a series of commercial dry silver products and conducted extensive research on the mechanisms involved. The dry silver products and patents, along with other 3M imaging systems, were turned over to the 3M spinoff Imation Corp. in 1996. The dry silver technology was sold to Eastman Kodak in 1999.

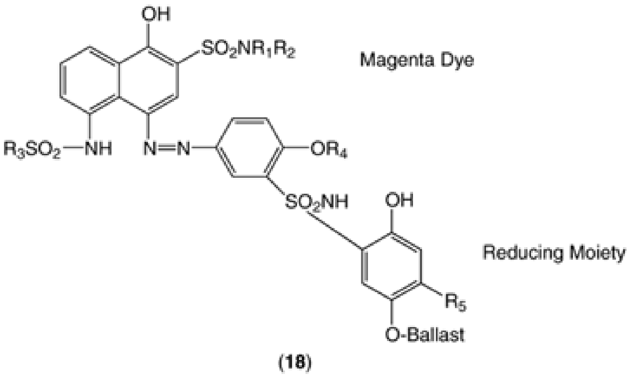
Contemporary films of this type include Kodak DryView, Fuji Dry CRI-AL film, and Konica DryPro. In these materials, infrared (ir) laser exposure creates a latent image that is developed with heat to provide high resolution images. Applications of such films include medical imaging and graphic arts. Both black-and-white and color processes have been described. Detailed reviews of photothermographic imaging materials and processes discuss the principles of such image formation (111). Although most dry silver processes utilize low speed materials, a recent patent described a camera-speed color process based on photothermographic components (112).

7.2. Fuji Photothermographic Systems

Several photothermographic systems utilizing instant color film output have been developed by Fuji in recent years. The processing takes place in dedicated equipment that uses donor and receptor sheets in roll form. All processing components are incorporated within the coatings, so that processing requires only the application of water and heat. Film speeds are generally lower than those of the films suited to instant camera use. Both analogue and digital inputs are utilized.

7.2.1. Fujix Pictrography 1000

Redox dye release chemistry by the ROSET system (see Dye Release by Ring Opening, Section 5.2) was utilized with negative-working emulsions in the Fujix Pictrography 1000 system (1987) (113). The films were sensitized for exposure to light-emitting diodes, rather than the more conventional blue, green, and red spectral regions. Exposure was by yellow (570 nm), red (660 nm), and near-infrared (nir) light-emitting diodes (LEDs). The multilayer negative comprised a yellow-sensitive emulsion layer that controlled a yellow dye releaser; a red-sensitive emulsion that controlled a magenta dye releaser; and an nir sensitive emulsion that controlled a cyan dye releaser. The peel-apart film utilized two sheets, a negative, or donor, sheet and a receptor sheet.



(**18**)

The donor sheet contained a redox dye releaser, a development accelerator, and a basic metal compound, in addition to silver halide and binder (114). The redox dye releaser was a 4-alkoxy-5-*tert*-alkyl-2-sulfonamidophenol derivative (**18**). The substituent in the 5-position, eg, a tertiary octyl group, was selected to provide the combination of stability at room temperature and reactivity at high pH and elevated temperature. The development accelerator for the high temperature processing, a silver arylacetylide, precluded the need for an auxiliary developing agent. The receiving sheet contained binder, polymeric mordant, and a chelating compound.

The exposed film was coated with a thin layer of water and brought into contact with the receptor sheet, and the assembled sheets were heated to ~90°C. The chelate compound diffused from the receiving sheet to the donor sheet and reacted with the metal compound to generate a soluble base. Under basic conditions the exposed silver halide grains and the dye releaser underhert a redox reaction. Silver halide reduction was accompanied by the release of image dyes, which diffused to the receiving layer. The two sheets were stripped apart after 20 s to reveal the color image.

7.2.2. Pictrostat 300, Pictrography 3000, Pictrography 4000, and Pictrostat Digital 400

Current versions of Fuji photothermographic systems combine laser diode exposure of silver halide emulsions with thermal development and ROSET dye release image chemistry. The Pictrostat 300 (PS300) analogue system produces color prints up to A4 size [210 × 297 mm ($8\frac{1}{4} \times 11\frac{3}{4}$ in.)] from color negatives, color positives, and three-dimensional (3D) objects.

Pictrography 4000 (PG4000), a 400 dpi digital color printer, prints up to A4 size; Pictrography 3000 (PG3000) is a 400 dpi color printer that accepts multiple paper sizes up to A3 [297 × 420 mm ($11\frac{1}{4} \times 16\frac{1}{2}$ in.)] and outputs color prints and transparencies up to A4 and A5 (148 × 210 mm, or $5\frac{7}{8} \times 8\frac{1}{4}$ in.) sizes. The Pictrostat Digital 400 (PSD400), illustrated schematically in Figure 22, is a full-color digital scanner/printer that handles a variety of input sources, including a flatbed scanner, a film scanner, and SCSI and PC card interfaces (115). The system also incorporates a digital image-processing unit (Fig. 23). The printer section of the PSD 400 is the same as that of the PG4000.

Pictro Proof is a high-speed high-quality digital color proofer introduced in 1998. It utilizes laser diode exposure and the Pictro three-color printing process, which is very similar to the PG4000 system, to facilitate computer-to-plate prepress work. Fuji also provides Pictro Match NT, a preliminary digital display system that simulates the Pictro Proof result.

8. Thermographic Imaging

Thermographic, or thermal, imaging comprises formation of images by means of the localized application of heat without the involvement of photosensitivity (116). Most contemporary thermal processes depend on solid-state thermal printheads. In a *direct thermal process*, heat effects a chemical reaction, such as that of a leuco dye with an acidic component to produce the colored form of the dye. In such systems, the color change takes place within a single sheet. In *thermal transfer processes* two sheets are involved, and each may contain reactive components. Typically, image-forming dyes or pigments transfer from one sheet or tape to the other. Dye diffusion thermal transfer (D2T2), also described as sublimation thermal transfer, has been commercialized for rapid production of continuous tone color prints. The thermal heads trigger the release of cyan, magenta, and yellow dyes from donor sheet patches to an image-receiving layer. *Inkjet printing*, based on release of inks or pigments from either thermal printheads or charge-sensitive printheads, is also used to produce high quality digital images rapidly.

Certain of the digital thermal printing systems are of interest in the context of instant photography, inasmuch as they can provide full color images, utilizing small, portable home printers that accept digital camera memory cards and do not rely on computer input. Print quality may be comparable with that of instant photographic prints on photosensitive film or paper. The Kodak Personal Picture Maker PPM 200 incorporates Lexmark inkjet technology. The Sony Snapshot Printer and the Olympus Camedia P-200 Printer use D2T2 processes. In 2001, Polaroid announced two new thermal printing processes, internally code-named Onyx and Opal. Onyx is a thermal monochrome process based on leuco dyes. Opal is a two-sheet process in which thermally activated dyes are transferred to a microporous receiving sheet (117,118). The Opal process uses a “frozen ink” comprising the dye and a thermal solvent. This frozen ink permits the use of lower processing temperature and shorter printing time than in D2T2 processes.

9. Digital/Instant Film Imaging Systems

In addition to the photothermographic and thermographic printing systems described above, there are systems that couple digital cameras or digital records with instant film printers. Fuji’s Digital In-Printer Camera uses a vacuum fluorescent printhead to expose Instax Mini film from a digital image record stored in a Smart Media card. The same print engine is used in the Fuji portable, stand-alone Digital Instax Mini Printer.

The Polaroid ColorShot Digital Photo Printer uses Polaroid Spectra film to print directly from a computer. A linear liquid crystal shutter printhead illuminated with red, green, and blue LEDs is moved over the stationary film one line at a time. The PhotoMax Digital Photo Printer is a consumer version of this printer; it also uses Polaroid Spectra film.

The Polaroid P-500 Digital Photo Printer is a compact table-top or handheld printer that is completely portable and can be used anywhere. This printer uses Polaroid Type 500 instant color film to produce high resolution color prints directly from the Compact Flash data storage cards and Smart Media memory cards used in many digital cameras. The digital data are converted by the printhead to light that exposes the film. The printer automatically reformulates the digital image up to 3 megapixels for optimum printing. The printer is powered by the battery in the Polaroid Type 500 film pack.

The Olympus Camedia C-211 digital photo printing camera integrates a digital camera with a Polaroid instant photo print engine that prints onto Polaroid Type 500 film. Polaroid’s SPd360 Studio Express system combines digital capture with film printout in a choice of six print formats, from 1 to 9 images on a single sheet. The system utilizes Polacolor Pro100 film to provide color images or Polapan Pro 100 for black-and-white images for passport and official document use.

Fig. 23. Image Processing Unit component of the Fuji Pictrostat Digital 400 machine. This unit comprises a color mapping module that provides color correction and a processing module that permits adjustments of sharpness, tone, and image composition. The processing unit interfaces with a PC and with a VGA monitor. Reprinted with permission of Fuji Photo Films Co., Ltd.

10. Applications

Instant film formats and corresponding equipment have been developed to fit a variety of specialized needs. Many laboratory instruments and diagnostic machines include built-in instant-film camera backs. Digital film recorders produce color prints, slides, or overhead transparencies from computer output and from CRT displays. Video image recorders, such as the discontinued Polaroid FreezeFrame, provide color prints and transparencies from a variety of video sources, including VCRs, laser disks, and video cameras.

An important aspect of many professional applications is the rapid on-site completion of color images. For example, in photomicrography work can continue without interruption, results can be documented quickly, and successive images of specimens that are undergoing rapid change can be immediately compared. Integral films and apparatus have been certified for use in clean room environments, where both photomicrography and photomicrography are important for documentation and diagnostic work. Instant color slides and overhead transparencies provide a way to present data and information in lectures and business meetings.

In the instant reprographic field, Copycolor materials have been used extensively for making large format seismological charts and maps for the oil industry, mapmaking, and reproduction of large graphs, charts, and engineering drawings. The films are also used for small color stats and for position proofs in layout work.

Instant photographs have been widely used for identification purposes, such as driver's licenses and other identification cards. Most passport photographs made in the United States are instant photographs, many of them in color. Special cameras for identification photography include two- and four-lens cameras to make two or four passport size photographs of the same subject, individual photographs of several different subjects, on a single sheet of instant film. Such cameras are available from Polaroid, Fuji and other manufacturers. The Polaroid ID-104 camera line is typical of such cameras. The Fuji Fotorama series, available in Japan and other Asian markets, includes two- and four-lens identification cameras.

There also are special cameras that will reproduce a passport-size photograph together with relevant text or other data on a single sheet to provide a complete identification card. The Polaroid ID-200 camera produces two such ID cards on a single sheet of 4 × 5 instant film. Several instant films provide authentication features incorporated in the film during manufacture. Polaroid Polacolor ID uv film contains an invisible security pattern preprinted into the film. This random pattern instantly appears when the ID card is scanned with uv light, making it virtually impossible to forge or alter the photograph. Polaroid Identifilm incorporates in the image sheet a preprinted, customized color or invisible ultraviolet pattern, or both, unique to the card issuer. Additional security features may be incorporated into laminating materials used to form the final ID card.

In addition to cameras designed for use in large scale production of ID photographs, there are relatively simple and inexpensive cameras designed to be used for smaller scale applications. The Polaroid BadgeCam, used in combination with custom transparent templates placed over the exposure aperture of a Captiva (Type 500) film cassette, quickly produces complete identification cards, eg, for use as visitor identification. Polaroid and Avery Dennison have introduced a kit for making identification cards using the Polaroid Pocket ID camera, pocket sticky-back film, and special badge blanks made by Avery (119).

Medical and scientific fields in which instant color films are applied include photography of the retina, using fundus cameras equipped with instant film holders (120); dental imaging with the Polaroid CU-5 close-up camera (121); chromatography; diagnostic imaging with radiopharmaceuticals; photomicrography; and Doppler blood flow studies.

Professional photographers use instant films as proof material to check composition and lighting. Large format Polacolor films are often used directly for exhibition prints. On a still larger scale, the making of full-size Polacolor replicas of works of art provides high quality images for display and for professional study and documentation.

Instant films are frequently used by photographers and artists to generate uniquely modified images (122). The *image transfer* technique begins with the transfer of a positive image from a partially developed Polacolor negative to a material other than the usual receiving sheet—eg, plain paper, fabric, or vellum (123). The transferred image may then be modified for artistic effects by reworking with watercolors or other dyes. The final transfer image is either displayed directly or reproduced for further use.

Image manipulation is a creative art form based on Time-Zero/SX-70 film images. Here the artist uses a fine stylus or a blunt object to draw on the surface of an integral film unit during its processing and for several hours afterward while the image-forming layers are still soft enough to be affected (122). The altered image may be scanned, further modified electronically, printed, or transmitted digitally.

11. Economic Aspects

In 2000, the sale of instant cameras in the United States totaled 3.9 M, up 80% from the previous year. In the same time period, digital still camera sales in the United States showed an increase of 123% from 1999, with a total of 4.1 M digital cameras sold in the year 2000 (124). Polaroid reported worldwide sales of 13.1 M instant cameras and 1.3 M digital cameras in 2000 (125).

Instant film printers incorporated into digital cameras, portable digital printers, and portable scanners for transforming instant photographs into digital records all indicate a growing trend toward integrating the two technologies.

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