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Chemistry and Processes of Color Photography

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I. Introduction

Innumerous people around the world have taken at some point in their lives pictures with a photographic camera, then submitted the film for commercial processing, and received at the end either a package of color prints or a series of transparencies. Yet even as scientists, few of us may have a detailed knowledge of the chemical reactions which occur in this entire procedure. Deamination, sulfonation, coupling, and redox reactions among others may be occurring during the process of forming an image dye.

Several processes have evolved over the years for reproducing an image for color prints. They can be grouped into those methods requiring a two-step procedure and those necessitating one step. In the two-step method, the so-called negative to positive system, an individual “burns” a positive image of an object into a negative film using a camera. The negative film is sent to a processing laboratory where the film is imaged on a positive paper. In the one-step method, the positive image of the object is “burned” directly into the positive paper, producing a color print. Instant color photography and the dye-bleached process are both examples of one-step methods. The dye couple process exemplifies the two-step method.

The chemical transformations which occur during processing and the composition of these films and papers are both complex and fascinating. It is our intent to describe in this review the various photographic processes with special emphasis on the chemical reaction mechanisms involved in color reproduction. Parts of this review are based on a topic paper, submitted in fulfillment of a requirement for a course in Industrial Organic Chemistry, presented by one of the authors at the University of Wisconsin—Milwaukee in 1989.

In order to better understand the intricacies of the various processes, a historical background will be chronicled. The beginning of the understanding of light and its application to color reproductions will be discussed. The evolution of these ideas into premodern color photography and their link with present day technology will follow.

The theories of color reproduction are briefly covered in order to understand the fundamental principles of color photography. The two theories, additive and subtractive, are discussed in some detail. An understanding of these basic theories will enable us to interpret the modern processes of today.

II. Scope and Limitations

This review is organized according to processes of color reproduction. The emphasis will be on the three most widely used processes, i.e., on the “dye-coupled”, “dye-transferred”, and “dye-bleached” processes. One process not currently utilized extensively will be investigated as a process of the future, the so-called electronic photography.

Throughout the review emphasis will be placed on the reaction mechanisms which are involved in the chemical transformation producing a colored photograph. It will not deal with the imaging equipment such as cameras and their components nor on the automated equipment used to process the films and papers. The exception will be electronic photography where the focus will be on electronic components rather than chemical reactions.

The chemistry and processes of color photography is an immensely broad topic with an overwhelming number of references. Nevertheless, most information on color photography is concentrated in relatively few dominant companies and is often proprietary. Publications have been limited to theoretical and historical information. Details of the actual compounds involved in these processes are often buried in the patent literature but several reviews have been published[1−7] that cite additional references and actual examples of compounds employed. To manage this enormous topic the literature has been selec-

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Ronald Theys received his B.S. degree in 1980 from Marquette University. After graduation, he worked as a photographic formulations chemist at Photo Chemical Developments, Inc., North Chicago, IL, until 1989. While there, he held the positions of quality control chemist, chief chemist, and vice president. In 1989, he joined Professor M. Mahmun Hossain's research group at the University of Wisconsin—Milwaukee and received his Ph.D. in 1994. His doctoral research was concerned with use of organoiron complexes in organic synthesis. In 1994, he joined Aldrich Chemical Company as a publications specialist and is now the product line manager for general organics.

George Sosnovsky has been professor of chemistry at the University of Wisconsin—Milwaukee since 1967. At present, he is Professor Emeritus and Adjunct Professor in the Department of Chemistry. He received his Ph.D. from the University of Innsbruck in 1948. After graduation, his experience included research at CSIRO and ICI, Australia, 1949–1956; Postdoctoral Research Associate, University of Chicago, 1956–1959; Senior Scientist, IIT Research Institute, Chicago, 1959–1963; Associate Professor, IIT, Chicago, 1963–1966; and Special Senior Research Fellow of Public Health Service at the University College, London, and the University Tubingen, 1967–1968. He was the co-founding editor of *Synthesis, International Journal of Methods in Synthetic Organic Chemistry*, and served as editor from1969 to 1985. He was regional director for the National Foundation for Cancer Research, 1980–1985. He has authored about 170 publications and a book *Free Radical Reactions in Preparative Organic Chemistry* (Macmillan, 1964). During those years his interests spanned over a wide range of topics, such as research and development of fungicides, herbicides and insecticides; amidine derivatives as antiradiation agents; diazo dyes leading to a commercial copying process; free radical chemistry, in particular, metal ion-catalyzed redox reactions involving antioxidants and reactions with peroxides; discovery of the peroxy ester reaction; photochemical synthesis; oxidative phosphorylation reactions; synthesis of spin-labeled phosphorus compounds of biological interest, including anticancer agents; transphosphorylation reactions using imidazole and related compounds as transfer agents; organosulfur and organselenium compounds; and synthetic methodology. In more recent years, his research interest focused on medicinal chemistry, specially, on structure–activity relationship of anticancer drugs involving design and biological evaluations of new anticancer drugs. Related to this theme also were pursuits in the synthesis of contrast-enhancing agents for diagnostic NMR-imaging (MRI), radiation sensitizers, and syntheses of aminoxyl-labeled probes for studies of intracellular environments, such as hypoxic cells by EPR and MRI.

tively searched manually and by computer through September 1994.

III. History

The origin of color photography can be traced to as far back as human's inquisitive nature into the understanding of vision and the nature of light. In 1611 Antonius de Dominis postulated[8] that light was composed of three colors. However it was not until 1666 that Sir Isaac Newton proved[9] that light is actually a spectrum of colors. Newton's famous dispersion of light through a prism experiment was the beginning of the understanding of color. Newton's experiment opened up a range of applications. In attempting to reproduce color engravings, Jacob Christoph Le Blon in 1722 printed[8] using colored inks based on Newton's color scheme. Le Blon was able to produce all the colors of the spectrum by using red, yellow, and blue colored inks. Carl Wilhelm Scheele in 1777 utilized[8] Newton's prism to expose silver halide separately with various colors of light. Scheele discovered that different amounts of silver metal were produced depending on the color of the light. Thomas Young in 1802 proposed[8] that every color could be produced by three primary colors and related this fact to vision. Young postulated that the eye blended the three colors using sensors to give the perception of multiple shades of color. In 1861, James Clerk Maxwell used[10,11] Young's theory to produce the first color image using the three colors projected in register, i.e., exact superimposition. Maxwell's experiment substantiated Young's theory of color vision, and gave birth to the additive theory of color photography. According to the additive theory, colors are made up of two or more primary colors: red, green, and blue.

In 1862 nearly one year after Maxwell's experiment, Louis Ducos du Hauron described[12] an additive theory of color photography in a letter to the French Academie de Medicin et Sciences. Later, du Hauron outlined[13] the subtractive theory for preparation of a color photograph. According to the subtractive theory color can be achieved by either absorption or subtraction of the primary colors from white light. Du Hauron proposed a "tripack" emulsion to utilize the subtractive theory. The emulsion consisted of three layers of silver halide separately containing the three subtractive primary colors, i.e., cyan (light greenish-blue), magenta (light bluish-red), and yellow. Du Hauron's theories have probably contributed the most to advance the concept of modern color photographic processes.[12,14]

In 1873 Hermann Vogel advanced du Hauron's concepts even further when he discovered[8] a way to spectrally sensitize a silver bromide emulsion by the use of dyes. This discovery expanded the sensitivity of emulsions from the blue region to green and paved the way for others to expand sensitivity through to red. In 1912 Rudolph Fischer employed spectrally sensitized emulsions, and the concept of the subtractive process, to propose[15] a new method of color reproduction, i.e., a dye-coupled method based on the formation of a colored image by the interaction of an oxidized reducing agent with certain coupling chemicals. The first commercially successful product to utilize Fischer's method was introduced[14] by Eastman

Kodak in 1935. This Kodachrome process involving a dye-coupled method, was marketed as a 35mm reversal film for still photographs. One year later Agfa introduced[16,17] Agfacolor, a product which incorporated the coupling chemicals in the film's emulsion. Kodak followed suit[12] with Ektachrome film in 1940.

During this same period in time, Bela Gaspar advanced[18] a process in which preformed dyes were partially bleached out of the emulsion and thus the remaining dyes formed the colored image. Gasparcolor, was introduced[14] in Germany in 1933, and it was based on a method called silver dye-bleach. The prints using this process were superior in color to those obtained by other processes of that period. This process was a predecessor to the more modern version called Cibachrome manufactured by Ciba-Geigy.

In 1963 another major step in the history of color photography was taken when Edwin Land of Polaroid introduced[19] the Polacolor film as the first instant color film. In this process diffusion transfer was utilized to produce color pictures. Different versions have since been developed involving the concepts of either silver or dye transfer.

The most recent advancement in color photography was introduced by Sony Corporation in 1981.[20] In this process a magnetic video disk was used, thus eliminating the need for silver halides. The birth of electronic photography has changed the classical concept of color photography.[12] This process and other modern color photographic processes will be discussed later in greater detail.

IV. Additive and Subtractive Processes

Additive and subtractive processes relate the properties of light to color. The additive process is exemplified by color television where a mosaic of black and white images are employed with red, green, and blue filters in front of them. The subtractive process is utilized in most color photographic processes. Both concepts are nevertheless interconnected.

The additive process is based on the production of color by the combination of either two or more primary colors. Thus red, green, and blue colors variously combined produce all colors of the visible spectrum. By combining all three of the colors white is produced (Figure 1).

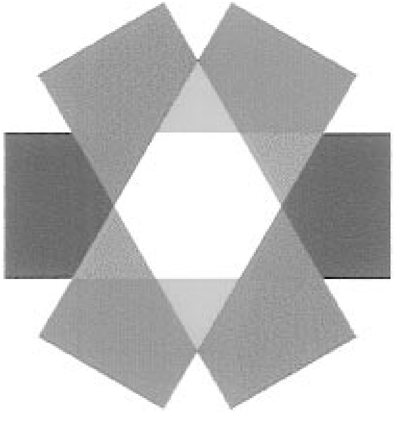


Figure 1. Additive color mix.

However, the additive process cannot be used in dye superimposed systems. One layer of an additive primary colored dye removes two-thirds of white light. For example, a layer of a red dye would remove blue and green wavelengths from white light. A superimposed layer of a blue dye would remove red and green wavelengths, resulting in no transmission of light, that is, only black would result.

The subtractive process is based on the production of color by either the subtraction or absorption of the three primary colors. The three primary subtractive colors are yellow, magenta, and cyan. Subtractive colors are the complement of additive colors. Yellow color absorbs blue light, magenta absorbs green light, and cyan absorbs red light. By subtracting one of the three primary additive colors from white light, the other two remain to produce a specific color. One example would be the subtraction of blue light from white light. Green plus red combine to give the color yellow.

A combination of all of the subtractive primaries would absorb all wavelengths of the white light. In the absence of light, black would be observed (Figure 2). Like the majority of photographic film processes, the concept of subtractive color is utilized in the dye-coupled process.

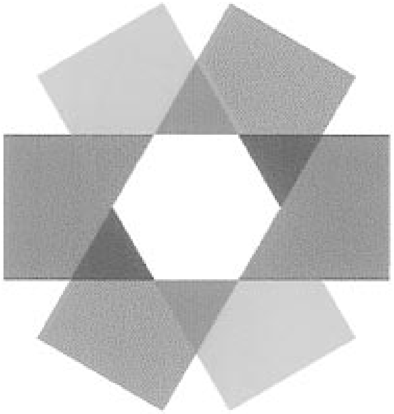


Figure 2. Subtractive color mix.

V. Dye-Coupled Process

A. Mechanism

The mechanism of image dye formation requires a colored object, light, an imaging device such as a camera, film, and processing solutions. Light is reflected off the object and focused by means of a lens on the film. A color photographic film consists of many layers. Some of these layers are often composed of so-called "emulsions," which are actually dispersions of solid silver halides in gelatin. Nevertheless, in the present review the traditional term "emulsions" will be retained. Silver halide grains serve as the recording media of the imaged object. Since the silver halide emulsion layers contain three different sensitizing dyes, each sensitive to a certain wavelength of light, only light within that wavelength range will be absorbed by silver halide in that layer. The other wavelengths of light will pass through to the layers below. Hence, the silver halides in each layer are exposed to light and become the latent image sites.

Scheme 1

$$G_{(AgBr)} + h\nu \longrightarrow G^{+} + e^{-}$$

$$AgBr + e^{-} + G^{+} \longrightarrow Ag^{\circ} + Br^{\bullet} + G$$

$G_{(AgBr)}$ = Sensitizing dye G adsorbed on AgBr crystal.

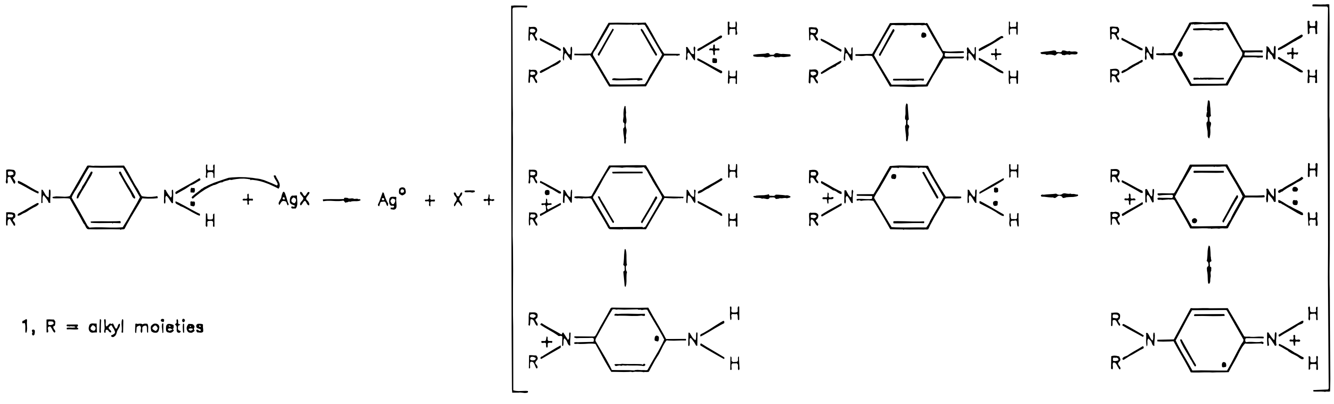
The electron transfer model,[21] fashioned after the Gurney-Mott mechanism,[22] has been used to explain how a latent image site is formed (Scheme 1). Thus, initially a photon of light dislodges an electron from the spectral sensitizing dye (G) which is adsorbed on the silver halide crystal. The spectral sensitizing dye extends the sensitivity of silver halide to light beyond its intrinsic wavelength sensitivity of 540 nm. The electron travels through the crystal until it combines with a silver ion at the surface of the crystal to form a metallic silver atom Ag^0.[23,24] A bromine atom ($Br^\bullet$) and the spectral sensitizing dye (G) are concomitantly generated. To direct the electron flow to a specific site on the grain, manufacturers dope the emulsions with compounds such as silver or gold sulfides to serve as electron traps.[25] Absorption by more photons by the same crystal results in electron migration to the atom of silver at the surface. In this way an invisible speck of a few silver atoms adheres to the surface of the silver halide crystal. This speck, composed of more than three atoms of silver,[26,27] is a latent image site and serves as a conductor through which electrons are transferred from the developing agent to the entire silver halide crystal. Imaged silver halide grains thereby become black metallic silver which has the microscopic appearance of black filaments.[28]

Latent image sites are reduced by color developing agents which are *p*-phenylenediamine derivatives **1** (Scheme 2).[14] The reaction of the oxidized color developing agents with color couplers in the emulsion produces a colored dye. Silver ion reduction is always the rate-determining step in the mechanistic pathway of the dye-coupled process.[6] A highly reactive, unstable semiquinone **2** is generated as a positively charged free radical whose lifetime is prolonged by resonance stabilization (Scheme 2).[29] The semiquinone intermediate is then further oxidized to a quinonediimine ion **4** (Scheme 3).

Two competing reactions can generate **4** since one additional molecule of latent image silver halide can react heterogeneously with the semiquinone **2** to produce **4**, presumably after a proton abstraction to form a neutral radical **3** (Scheme 3).[30] Alternatively, a homogeneous dismutation can occur with two molecules of semiquinone **2** regenerating the *p*-phenylenediamine **1** and the quinonediimine **4**.[31−36] The initial deprotonation would be expected in an alkaline bath such as the color developing solution (Scheme 3). In this scheme the sodium hydroxide could be replaced with an alkaline buffer.

The fully oxidized form of the *p*-phenylenediamime, namely the quinonediimine **4**, is the reactive species which unites with the coupling agent in the emulsion to produce a colored dye.[32,33] Couplers are usually present in the emulsion layers of the film but may, alternatively, be present in the processing solutions. Their structures vary according to the color of the desired dye. In general, couplers can be symbolized by ZCHXY (**5**), where Y and Z represent either parts of a chain or ring structure, and X represents either a hydrogen or a leaving group.[14] At a high pH of the developing bath, the coupler is deprotonated to an

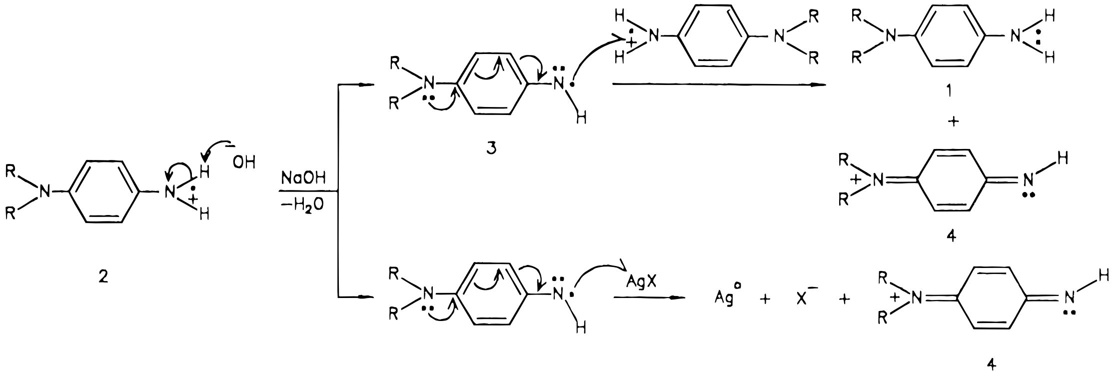
Scheme 2



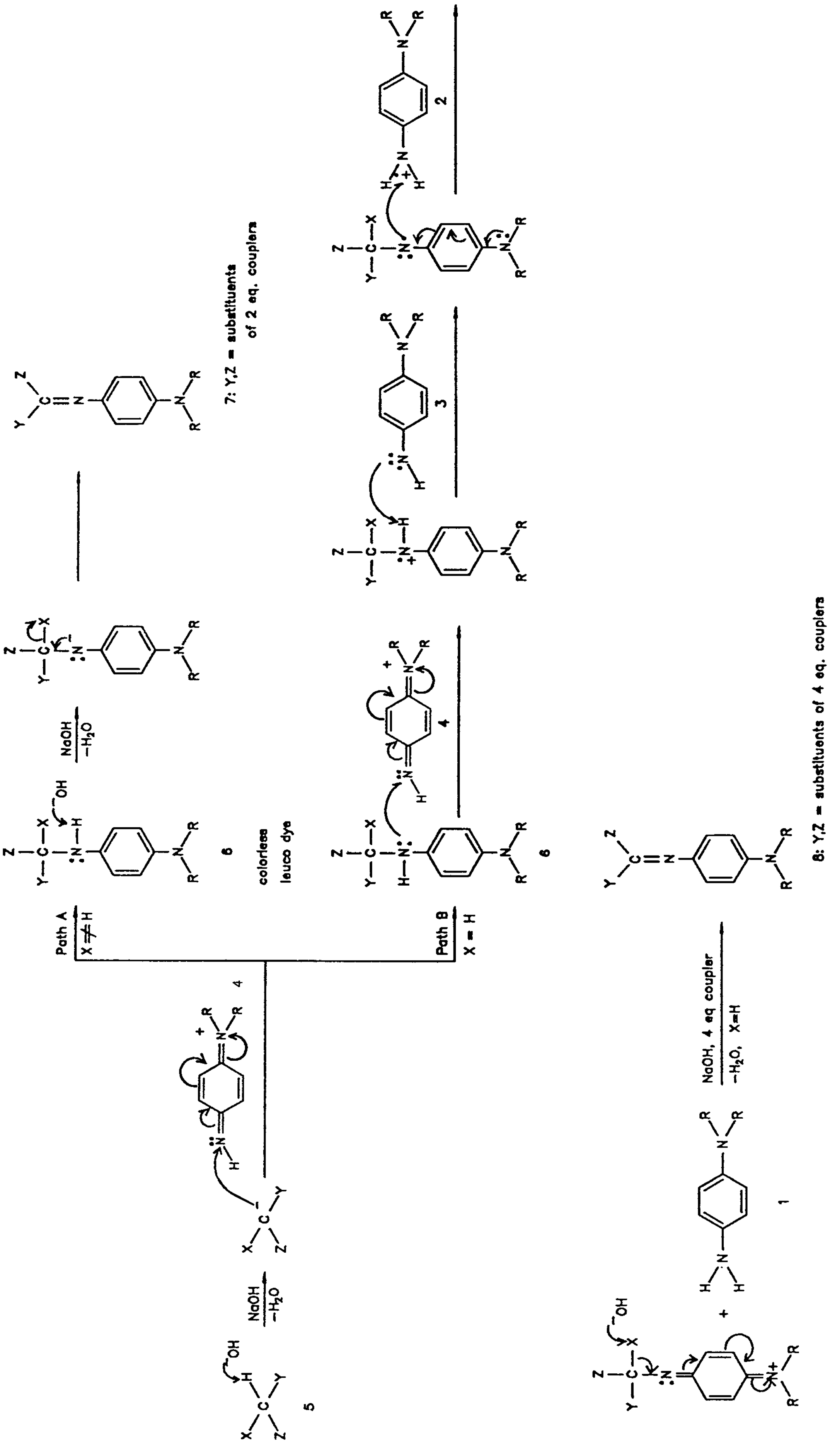
1, R = alkyl moieties

2

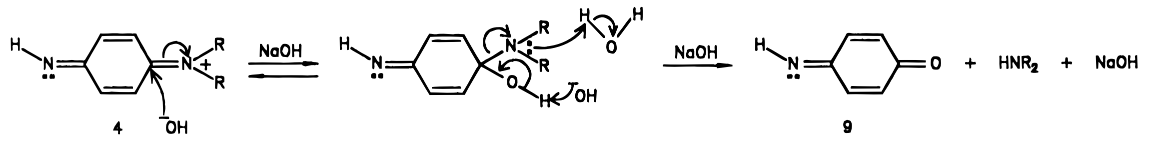
Scheme 3



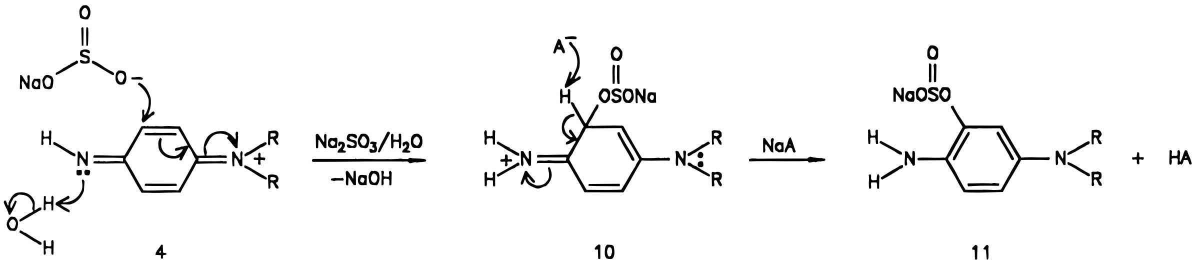
Scheme 4


5
NaOH
−H₂O
4
Path A
X ≠ H
Path B
X = H
6
colorless leuco dye
NaOH
−H₂O
7: Y,Z = substituents of 2 eq. couplers
6
4
3
2
NaOH, 4 eq coupler
−H₂O, X=H
1
8: Y,Z = substituents of 4 eq. couplers

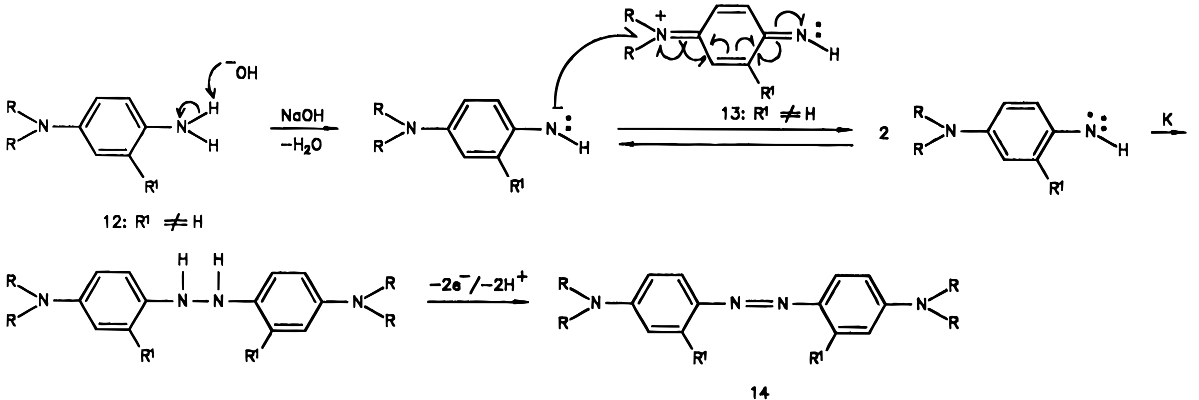
Scheme 5



Scheme 6



Scheme 7



K = rate determining step

anion. The anionic coupler adds to quinonediimine **4** to form a colorless leuco dye **6** (Scheme 4). In this scheme the sodium hydroxide could be replaced with an alkaline buffer. In the case that the substituent X is eliminated as an anion (Scheme 4, path A), the coupler is then classified as a two equivalent coupler, i.e., only two molecules of silver halide are required to produce one molecule of the dye **7**. However, if X is eliminated as a proton (Scheme 4, path B), then the coupler is termed a four equivalent coupler since four molecules of silver halide are required. In such case an extra molecule of the quinonediimine **4** is essential to oxidize the intermediate leuco dye to the desired colored dye **8**.

However, several competing side reactions can occur with the highly reactive quinonediimine **4** during the dye formation. Thus, deamination, sulfonation, and self-condensation reactions can compete with the coupling reaction because of the presence of nucleophilic species other than the anionic coupler.

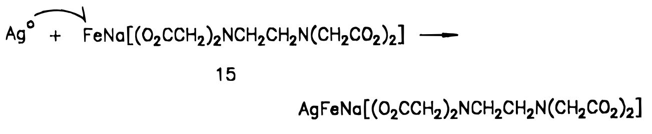
Deamination of quinonediimine **4** to quinonemonoimine **9** results from the attack by the hydroxide ion on **4** (Scheme 5).[6,37] As a consequence, an undesirable dye may be produced from reaction of the anionic coupler with **9**.[14]

Furthermore, the presence of sulfite salts as preservatives in the developing solution also compete with the coupling reaction by sulfonating the quinonediimine to give **11** (Scheme 6). A protonated species **10** was suggested[38] as an intermediate and the reaction was found to be sensitive to various buffer anions (A^-). Common buffering agents, such as sodium carbonate, potassium carbonate, potassium phosphate, and sodium metaborate are usually present.

In the case when the concentration of a *p*-phenylenediamine derivative **12** is very high, a condensation reaction of the *p*-phenylenediamine with the corresponding quinonediimine derivative **13** can occur to form an azo dye **14**. A mechanism for this side reaction was suggested[39] on the basis of a kinetic investigation. The rate of dimerization is retarded by bulky R^1 substituents in **12** (Scheme 7).

After the reaction of the coupler and quinonediimine to form the requisite dye, the remaining unexposed silver halide and the residual silver metal must be removed to preserve the image. To accomplish this removal, the film is passed into a bleaching and then into a fixing solution.[14,40−42] The silver metal is oxidized to ionic silver by a bleaching agent, such as a ferric EDTA complex **15**, which is reduced to a ferrous EDTA complex **16** (Scheme 8). A fixing agent, such as sodium thiosulfate, complexes with the unexposed silver halide to form a soluble complex **17** (Scheme 9). This process allows the

Scheme 8



$$Ag^0 + \underset{15}{FeNa[(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2]} \longrightarrow \underset{16}{AgFeNa[(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2]}$$

Scheme 9

$$AgX + nNa_2S_2O_3 \longrightarrow \underset{17}{Na_{2n-1}Ag(S_2O_3)_n} + NaX$$

silver–thiosulfate complex **17** to diffuse out of the emulsion layers and into the fixing solution.

A final stabilizing bath completes the sequence of solutions used to process the film. The function of this bath and its composition will be discussed in greater detail in the next section as well as the composition and purpose of other processing solutions.

B. Processing Solutions

1. Developers

Developing solutions are composed of many different compounds each designed for a specific purpose. The reduction by the developer of the latent image silver halide to metallic silver generates the quinonediimine **4** which is needed for dye formation. Developers generally are composed of water, chelates, “restrainers”, i.e., compounds which significantly diminish indiscriminate reduction of the silver halide, preservatives, buffers, developing agents, solvents, and other additives.

Chelating agents are added to prevent hard water buildup since[14,40] impurities in the tap water which is used to dilute concentrated developers, and in the manufacture of developers will buildup on processor rollers resulting in scratches to the emulsion. In addition, these impurities can accelerate decompositions of the developing agent. Particularly destructive metal impurities include copper and iron. With certain types of sequestering agents such as EDTA, the effect of chelation may actually accelerate the oxidation of either the developing agent or the preservative,[43] and for this reason phosphonic acids are preferred as sequestrating agents.[44]

Preservatives[6,14] are also added to the color developer formulation to protect the developing agent from aerial oxidation during storage and use according to Scheme 10. The protection is accomplished by the use of two agents, i.e., sulfites (Scheme 11) and hydroxylamines (Scheme 12). Agents such as, oxytetronic acid,[45,46] oxytetronimide,[45,46] ascorbic acid,[45] hydrazines,[47,48] and sodium formaldehyde sulfoxalate[48] have also been suggested; however, in practice sulfites and hydroxylamines prevail. The amount of sulfite must be kept to a minimum since it can inactivate the developer by reacting with the oxidation product of the developing agent (Scheme 6), the very species responsible for dye formation, and for this reason hydroxylamines,[47–50] in particular, the sulfates and hydrochlorides are utilized. Hydroxylamine reacts with oxygen to form nitrogen and water (Scheme 12). The amount of hydroxylamine must also be kept low since it can act as a solvent for silver halides, removing some of the silver halide before it can be utilized in the formation of a dye.

Scheme 11

$$Na_2SO_3 + {}^1/_2\, O_2 \longrightarrow Na_2SO_4$$

Scheme 12

$$2\, NH_2OH + {}^1/_2\, O_2 \longrightarrow N_2 + 3\, H_2O$$

The most important component of the developer formulation is the developing agent. The preferred agents in use today are the *p*-phenylenediamine derivatives. Some typical examples are shown in Table 1.[4,14,40,51] To reiterate the function of the developing agent, it reduces the exposed silver halide grains to metallic silver and thus facilitates the formation of the oxidized species of the developing agent. This species reacts with a color coupler in the emulsion to form a dye. The mechanism governing this reaction was discussed in subpart A.

Another component of a color developing solution is the buffering agent.[14] This chemical helps to maintain a steady pH during the lifetime of the developer. Since the overall reaction of the silver reduction and dye formation yields hydrogen bromide, it becomes necessary to temper the effects of a steady decrease in pH. A poorly buffered solution can cause an imbalance in the color contrast of the picture.[52,53] Typical buffering agents include carbonates, phosphates, and borates. The carbonates have the disadvantage of generating carbon dioxide in the emulsion layers on transfer of the film from the developer solution to the acidic bleach–fixing solution. Sudden formation of carbon dioxide gas in the emulsion layers disrupts the uniformity of silver and dye by bubbling through the layers.

Restrainers and antifoggants are added to developing solutions to inhibit indiscriminate reduction of silver halide.[14,40] In the absence of these compounds the unexposed silver halide grains are considerably reduced. In the presence of restrainers or antifoggants, development rates of nonlatent image silver halide are retarded relative to the latent image of

Scheme 10

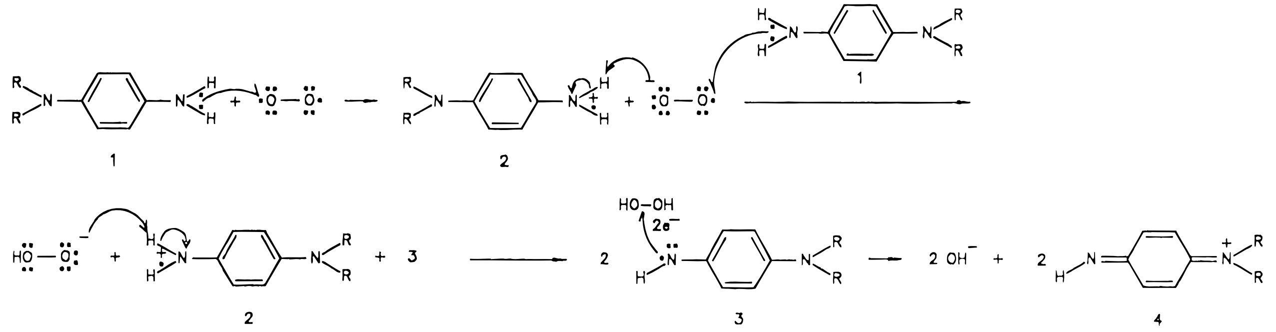
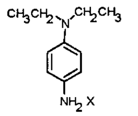
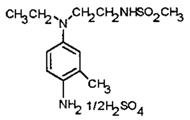
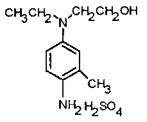
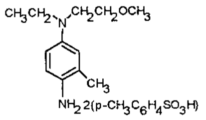
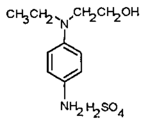
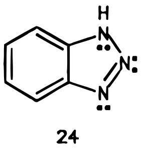


Table 1. Color Developing Agents

Structure	Chemical Name	Trade Name	Reference
 **18a** X=HCl **18b** $X=SO_2\ 1/2H_2O$ **18c** $X=1/2H_2SO_4$	*N*,*N*-diethyl-*p*-phenylenediamine		
	18a monohydrochloride	CD1	14,40,51
	18b sulfur dioxide complex	Activol	14,40,51
	18c sulfate	Activol No.7	14,51
 **19**	*N*,*N*-diethyl-3-methyl-*p*-phenylenediamine monohydrochloride	CD2, Activol No.2	4,14,40,51
 **20**	*N*-ethyl-*N*-(β-methylsulfonamidoethyl)-3-methyl-*p*-phenylenediamine sesquisulfate monohydrate	CD3, Activol No.3	4,14,40,51
 **21**	*N*-ethyl-*N*-(β-hydroxyethyl)-3-methyl-*p*-phenylenediamine sulfate	CD4	4,14,40,51
 **22**	4-Amino-*N*-ethyl-*N*-(2-methoxyethyl)-*m*-toluidine-di-*p*-toluenesulfonate	CD6	14,51
 **23**	*N*-ethyl-*N*-(β-hydroxyethyl)-*p*-phenylenediamine sulfate	Activol No.8	14,40,51

silver halide.[54] Combinations of an inorganic restrainer and an organic antifoggant are often employed. Soluble bromides and iodides are used as restrainers. Since antifogging agents are more active than restrainers, lower concentrations of antifoggants such as benzotriazole (**24**), 6-nitobenzimidazole (**25**), 3,5-dinitrobenzoic acid (**26**), and 1-phenyl-5-mercaptotetrazole (**27**) are typically used.



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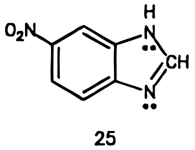

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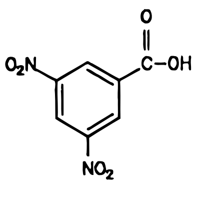

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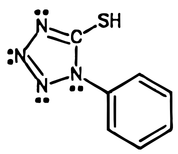

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In addition, other components may be incorporated into the developer formulations including "balancing agents", development accelerators, optical brighteners, and coupling agents although the latter two are most often incorporated into the emulsion. Balancing agents[55−57] are noncoupling reducing agents which help to balance the intensity of one dye with the other two. Development accelerators are employed to speed up the development process by allowing faster penetration of the developing solution into the emulsion layers. Typical accelerants include straight-chained and heterocyclic amines,[58−61] alkanol amines,[58,59] and polyethylene glycols.[62] They are believed[40] to function either by reduction of surface tension or by reduction of charge repulsions. Optical brighteners[63] serve to whiten the background of print papers. Coupling agents[14] may be added to the developing solution; however, in this case it becomes necessary to use three different developers to process one film. The following compounds are typical examples of commercial couplers. Thus, the cyan coupler *N*-(*o*-acetamidophenethyl)-1-hydroxy-2-naphthamide (Kodak coupling agent, C-16), the magenta coupler 1-(2,4,6-trichlorophenyl)-3-*p*-nitroanilino-5-pyrazolone (Kodak coupling agent, M-38), and the yellow coupler α-benzoyl-*o*-methoxyacetanilide (Kodak coupling agent, Y-54).[14] An example of a rapid developing solution is shown in the following formulation.[63]

Typical Formulation for Developer

diethylenetriaminepentaacetic acid	1.0 g
diethylene glycol	10.0 mL
sodium sulfite	2.0 g
potassium bromide	0.5 g
hydroxylamine sulfate	3.0 g
4-amino-3-methyl-*N*-ethyl-*N*-[bis(methyl sulfonamido)ethyl]-*p*-phenylenediamine sulfate	5.0 g
sodium carbonate (monohydrate)	30.0 g
fluorescent whitening agent (4,4-diaminostilbene type)	1.0 g
deionized water to make 1 L	pH 10.1

The film may then be passed sequentially through a bleaching bath and a fixing bath. The purpose and composition of the bleaching and fixing solutions will be elaborated in the next section.

2. Bleach and Fixing Formulations

The purpose of a bleaching solution is to convert the residual imaged silver to ionic silver; the fixing solution, to remove the formed silver halide and the remaining nonimage silver halide, from the emulsion layers.

The major component of a bleaching solution is an oxidizing agent. Bleaching agents oxidize metallic silver to ionic silver. They are typically composed of inorganic transition metal cations and anions of organic acids. Cobalt(III),[64,65] copper(II),[65,66] and especially ferric(III)[66−68] ethylenediaminetetraacetic acids or 1,3-propylenediaminetetraacetic acid[69] are most often used.

Fixing agents solubilize silver halide to remove the ions from the emulsion. Common silver halide solvents include ammonium thiosulfate and ammonium thiocyanate. Ammonium salts have been found to reduce processing times as compared to sodium salts.[65,70]

Accelerating agents speed up the process of bleaching and fixing. A wide range of compounds have been proposed for this purpose, such as, polyethylene oxides,[71] iodides,[72] heterocyclic mercaptan compounds,[73] organic sulfide diols,[74] and amines.[75]

With some color paper processes the fixing and bleaching formulations are combined into one solution that is referred to as a bleach-fix or sometimes blix. In addition to fixing, bleaching, and accelerating agents the blix formulation may also contain other components, such as, solvents, preservatives, buffering agents, hardening agents and reducing agents. The preferred solvent is water although alcohols[76,77] are sometimes included in small amounts.

Sodium sulfite is usually added to the blix formulation to act as a preservative for thiosulfates. Buffers are generally drawn from the borate and phosphate chemical family. The buffer reduces the effect of an increase in pH which results from either developer or stop bath carryover.

Hardening agents which are contained in the blix cross-link the gelatin to make it more resistant to mechanical abrasion. These compounds are typically aldehydes, such as formaldehyde[78,79] and glutaraldehyde[79] or in the case of a two-bath sequence (bleach−fixer), metal ions such as aluminum[80] and zironium[81] are contained in the fixer.

Reducing agents are added when either a stop bath or water bath is eliminated between the developer and blix.[82,83] These compounds prevent excessive fog formation by lowering the oxidation rate of unused developing agent which is carried over from the developer into the blix. Oxidized developing agents would otherwise react with couplers in nonimage areas to produce fog.

In order to preserve the stability of a blix it is essential to maintain a near neutral pH. Values of pH below 5.5 generally are a sign of a quick deterioration attributable to the attack of the oxidizing agent on thiosulfate. Blix solutions with pH values higher than 8.0 result in stable albeit ineffective bleaching properties. Therefore, a pH of 6.5−7.0 is used to provide adequate bleaching power while maintaining a good stability. An example of a simple blix composition is as follows:[84]

Typical Formulation for Bleach−Fix

ferric chloride, 6 mol of water	24.0 g
ethylenediaminetetraacetic acid, tetrasodium salt	40.0 g
sodium thiosulfate, 5 mol of water	150.0 g
sodium sulfite, desiccated	15.0 g
water to make 1 L	pH 7.0

3. Stabilizer Formulations

A stabilizer formulation is usually employed as the final bath before the print is dried, i.e., after the blix a water wash is followed by one or several stabilizing solutions. Stabilizer solutions allow adjustment of the emulsion pH to between 4 and 6,[42] increase the long-term stability of the dyes, and function simply as washes. Antioxidants and reducing agents have been used in stabilizer formulations. An antioxidant, such as, sulfite,[85,86] either alone or in combination with a reducing agent such as hydroquinone,[86] has proven to be effective. Other stabilizers have been formulated to contain aldehydes, such as, formaldehyde[87,88] and acetaldehyde[88] in combination with surfactants. The significance of aldehydes in the stabilizer will be discussed in the image stability section. There it will be shown how aldehydes preserve certain magenta dyes.

C. Composition of Color Sensitive Materials

Three types of materials are commonly employed depending on the end use of the reproduction. Whether it should be a film negative, a film positive, or a positive print on paper, they all have certain similarities in the composition of their emulsions. All of these emulsions contain silver halide grains, an emulsion matrix, color couplers, and other necessary components. The various chemicals and their structures will be explored in addition to the structures of each type of material.

1. Emulsion Chemicals

a. Silver Halide and Its Matrix. Common silver halides which are used in the emulsion include silver chloride, silver bromide, silver chlorobromide, silver chloroiodide, silver bromoiodide, and silver chlorobromoiodide. The function of these silver halides is to act as a light-sensitive material in mediating the formation of the image of the object. The silver halides are essential in the formation of oxidized color developers which combine with the color coupler to form an image dye. The choice of which silver halide to use depends on the desired properties of the film, such as speed, contrast, graininess, and resolution which may be manipulated by the choice of either one or a combination of silver halides. The speed of an emulsion is a measure of the sensitivity to the intensity of light which is needed to expose an object. The greater the speed the less light is required to expose the material. Larger silver halide crystals are generally more light sensitive than smaller particles.

However, this same consideration for speed is also related to graininess. Graininess is defined as the visual sensation of nonhomogeneity of an image.[89] The smaller the surface area of the silver chloride crystal the finer the grain will be. The use of finer grains results in higher resolution. Resolution or resolving power is defined as the maximum number of lines per unit length which are distinguishable by the eye in an image.[89] The appearance of a picture with many smaller, finer grains looks sharper than one with fewer larger grains. By choosing silver halide crystals as uniform in size as possible, an emulsion of high contrast can be produced. A low contrast emulsion can be achieved by choosing many different crystal types and sizes. The size of a silver halide crystal is generally, from an average size of 0.03 to 2 μm.[90] The shape may be either spherical, cubic, octahedral, or tabular, i.e., a thin, flat grain with large surface area.

Most color negative and reversal film emulsions contain either silver bromide or silver bromoiodide.[91] Silver chloride emulsions have largely replaced silver chlorobromide emulsions in color papers which are processed, for example, by the simple, environmentally benign RA-4 process.

A substance is required to bind the silver halide to the material support and to keep it dispersed. Gelatin is most often used as the silver halide emulsifier.[92] Besides the already stated functions, gelatin is also permeable, and hence it allows the processing solutions to penetrate and undergo reactions. Silver halide grains are physically adsorbed to gelatin, probably through the basic amino groups in the gelatin molecule.[40]

Gelatin also acts as a chemical sensitizer after exposure of the silver halide. Because of recurring sulfur linkages in the gelatin molecule and/or sulfur-containing trace impurities, gelatin functions as a chemical sensitizer.[93−95] Related to the theory of latent image formation is the nature of silver halide sensitization. In order to form a latent image, a reactive bromine atom is produced on the surface of the crystal after photolysis. The sulfur groups in gelatin prevent recombination of the bromine atom with the latent image silver speck by reacting with the bromine.[96]

Gelatin also functions as a matrix for other additives such as coupling agents, spectral sensitizers, dye stabilizers, antifoggants, and many other chemicals. However, gelatin is not the only hydrophilic colloid that can be used in photography.[14] Substitutes that have been evaluated to replace gelatin have not been found to be as useful as gelatin. They include proteins, such as gelatin derivatives, graft copolymers prepared from gelatin and other high molecular weight polymers, albumin, casein, carbohydrate derivatives (such as cellulose derivatives including hydroxyethyl cellulose, carboxymethyl cellulose, and cellulose sulfate), sodium alginate, starch derivatives, and various kinds of synthetic hydrophilic high polymers including homo- and copolymers, such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-*N*-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, and polyvinylpyrazole.[97]

b. Coupling Agents. **i. Function of Coupler.** Coupling agents are critical to the process of color image formation. Together with the oxidized developing agent the image dye is produced. By forming yellow, magenta, and cyan dyes these colored dyes absorb blue, green, and red light, respectively. Consequently, they either reflect or transmit the other two primary colors of light. For example, a cyan image dye is expected to absorb radiation in the red region of the visible spectrum and to transmit radiation in the green and blue regions.[98] A colored picture is the result. The dye-forming couplers are incorporated into separate light-sensitive layers. The layering sequence depends on how the object is to be reproduced. In the case of a color negative process, the yellow dye-forming coupler is nearest to the top of the film followed by the magenta dye-forming coupler layer. The bottom layer of the film is the cyan dye-forming coupler layer. The yellow layer is on top to permit the use of a filter layer below it. The filter layer removes undesirable blue light to prevent exposure to the underlying green- and red-sensitive layers, which have native sensitivity to blue light. Often more than one layer for each color record is included, differing in its sensitivity to light, for example the so-called fast and slow layers. Other interlayers may be present which separate the coupler layers.

ii. Types of Couplers. Different types of couplers can be used to form the yellow, magenta and cyan dyes. Often the chemical reaction may require either 2 or 4 equiv of the coupler to form a dye. The type of a particular dye will determine whether it is a 2 or 4 equiv coupler. Which type of coupler is best suited for formation of the individual subtractive dyes will be discussed in the next section.

1. Yellow-Forming Couplers. α-Pivaloylacetanilide (**28**)[99−105] and α-benzoylacetanilide (**29**)[106−110] type couplers (Figure 3) are the most important class of yellow-forming couplers, the former reacting to produce dyes which reportedly[98] have improved light stability as well as narrower bandwidths. Pivaloylacetanilide couplers usually are observed to have higher pK_a values than benzoylacetanilide couplers, but the latter result in dye products with higher color density.[98] The reactivity of a coupler with quinonediimine is related to the pK_a of the coupler and the nucleophilicity of the resulting coupler anion. A higher pK_a causes a decrease in the concentration of the active anion but studies have shown that the resulting anion is more nucleophilic.[111]

The R^1 substituent in Figure 3 represents either a reactivity altering group or a group which causes a shift in the hue of the resulting dye. A so-called “ballast” is attached to the aromatic ring to anchor the coupler in the appropriate layer and to prevent its dye from wandering into adjacent layers. The ballasting substituents consist of either a long ali-

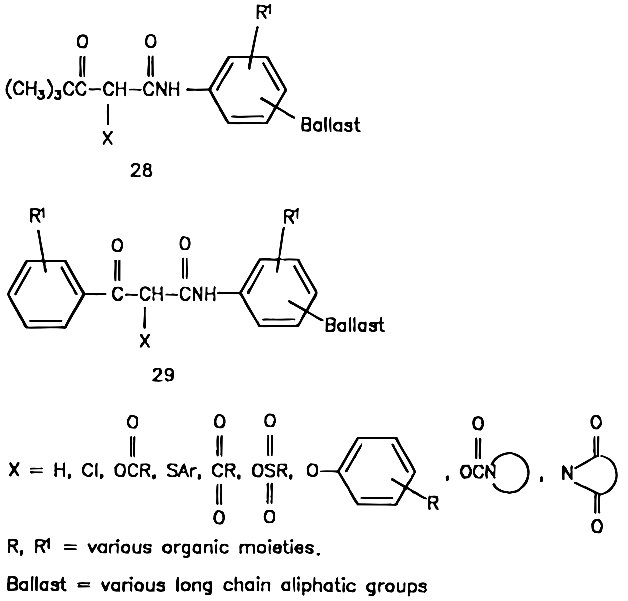


Figure 3. Yellow-forming couplers.

phatic chain or a combination of an aliphatic and aromatic group.

The chemical reaction mechanism of these two main types of yellow-forming couplers with the quinonediimine **4** is illustrated in Scheme 13. The mechanism for generation of **4** was described in Schemes 2 and 3. The hydroxide ion abstracts a proton from the coupler and the ionized coupler then reacts nucleophilically with **4** resulting in the formation of the intermediate leuco dye **30**. At this point the mechanism for conversion of **30** to the yellow dye depends on the group which must be removed. Thus, for two equivalent couplers, which have groups that are readily eliminated, the leuco dye is initially ionized and then undergoes elimination of the X^- group to form **32**. In the case of X = H, the leuco dye **30** must be oxidized in order to form the yellow dye **32**. Oxidation of the leuco dye by another molecule of quinonediimine **4** and subsequent deprotonation of intermediate **31** results in the yellow dye **32**.[6]

Although these two types of yellow dye forming couplers are the most important, others, such as indazolones[112] and benzisoxazolones,[113] have been reported.

2. Magenta-Forming Couplers. Magenta couplers form magenta dyes which are designed to absorb green light in the 500−600 nanometer wavelength range. 5-Pyrazolinone-,[114−119] indazolone-,[120] pyrazolobenzimidazole-,[121,122] and pyrazolotriazole-[123−128] type couplers may be used for the formation of magenta color images.[63] Although, to date, the 5-pyrazolinone-type couplers (Figure 4) have been used extensively, the more recently introduced pyrazolotriazoles are reported to have certain advantages. The 3-arylamino- and 3-acylamino-substituted compounds (**33** and **34**, respectively) are the most widely used of the pyrazolinone class (Figure 4). Ballasting groups are normally attached through the 3-position.

The applications of magenta-forming pyrazolotriazole couplers **35** (Figure 5) have improved thermal stability and lower, unwanted, absorptions when compared to the pyrazolinone couplers.

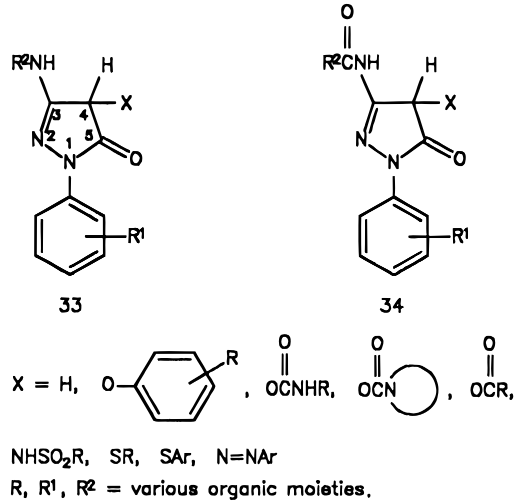


Figure 4. Magenta-forming couplers.

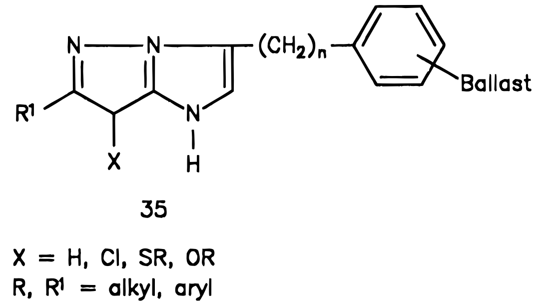


Figure 5. Magenta-forming pyrazolotriazole couplers.

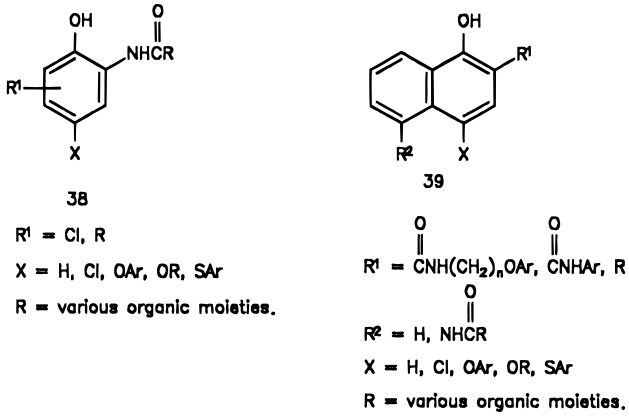
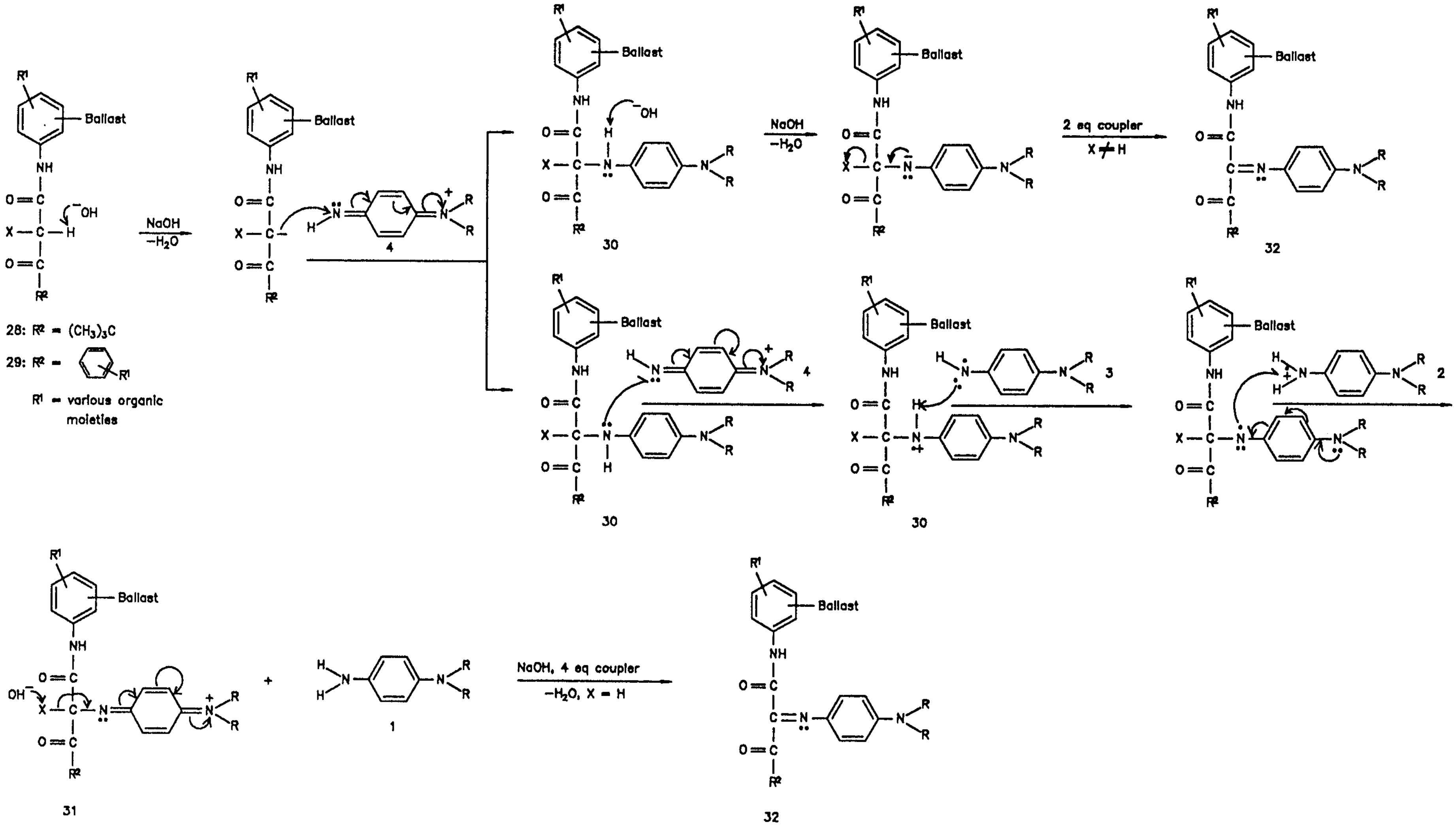


Figure 6. Cyan-forming phenol- and naphthol-type couplers.

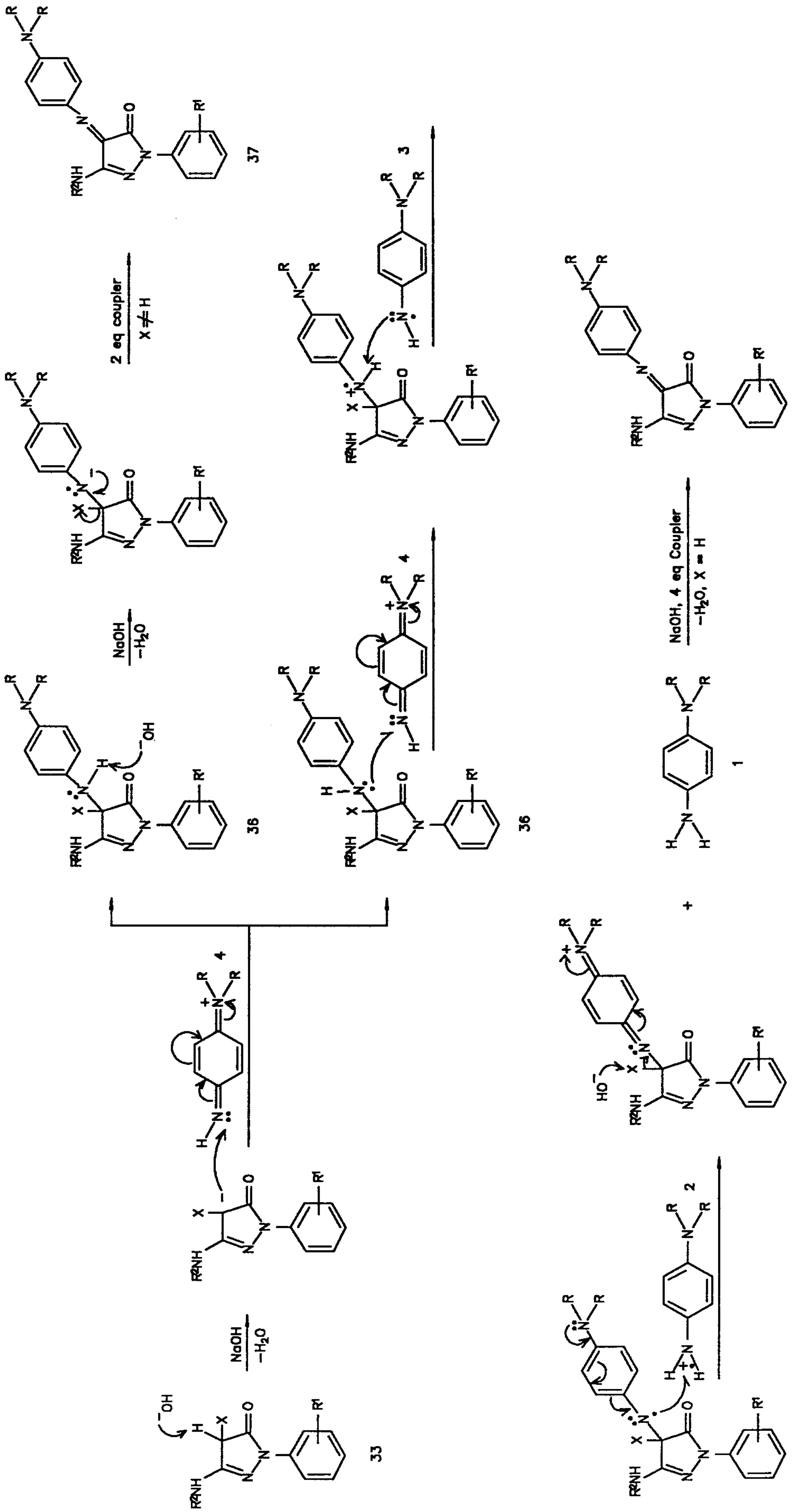
A proposed mechanism for producing a magenta dye is illustrated in Scheme 14 using the 3-(arylamino)-2-pyrazolin-5-one (**33**) as a representative example. Ionization of **33** under alkaline conditions allows addition of the formed anion to the previously generated quinonediimine **4**, yielding the leuco dye intermediate **36**. After ionization of the leuco dye, elimination can occur if the original coupler was a two equivalent species, otherwise an oxidation step is required to produce the desired magenta dye **37**.

3. Cyan-Forming Couplers. Cyan couplers form cyan dyes which absorb red light in the 600−700 nanometer wavelength range. Practically all cyan couplers are either substituted phenol-[7,129−136] or naphthol-[7,137−143] type couplers (**38** and **39**, Figure 6). Ballasting groups are usually attached through the 3-position on the amide functionality. In recent years 2-aryl-5-(arylamido)phenols (**38**, R^1 = 5-arylamido)

Scheme 13


R1
Ballast
NH
OH
X
H
R2
NaOH
−H2O
28: R2 = (CH3)3C
29: R2 =
R1 = various organic moieties
4
30
NaOH
−H2O
2 eq coupler
X ≠ H
32
3
2
31
+
1
NaOH, 4 eq coupler
−H2O, X = H
32

Scheme 14


33
NaOH
$-H_2O$
4
35
36
NaOH
$-H_2O$
2 eq coupler
X ≠ H
3
37
2
1
NaOH, 4 eq Coupler
$-H_2O$, X = H
37
R²NH
R¹
X
R
N
O
OH
HO
H

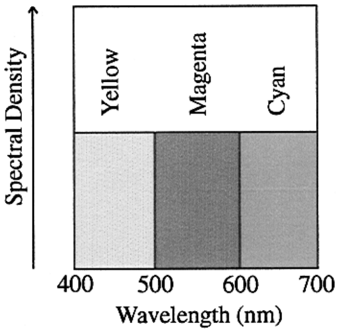


Figure 7. Ideal absorption density characteristics of color negatives.

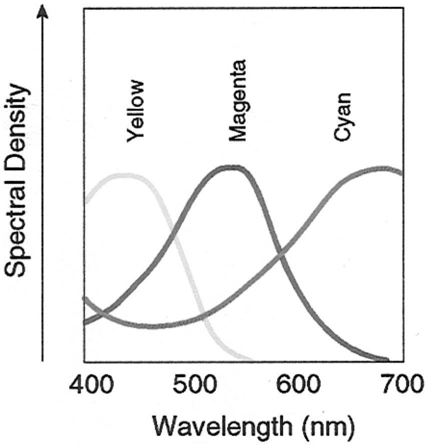


Figure 8. Actual absorption density characteristics of color negatives.

have been frequently cited[129,144,145] as a class of cyan couplers, having superior dye hue and dye stability.

Phenol and naphthol couplers are weak acids which ionize in alkaline solution. Thus, the reactions with the color-developing agent occurs at the 4-position. A proposed reaction mechanism is illustrated in Scheme 15 using a reaction of a phenol-type cyan-forming coupler **38** with **4** to generate a cyan-colored dye **40**.

iii. Deficiencies and Improvements. *1. Light Absorption Properties*. Color dyes derived from color couplers ideally absorb only the wavelength ranges mentioned previously, i.e., specifically, 400−500 nm for a yellow dye, 500−600 nm for a magenta dye, and 600−700 nm for a cyan dye. However, dyes produced by the interaction of couplers and oxidized developing agents are not ideal. The cyan dye supposedly absorbs only red, the magenta only green, and the yellow only blue. Although yellow dyes typically have some unwanted green absorption, they are generally more spectrally sufficient than either magenta or cyan dyes. This insufficiency by magenta and cyan dyes leads to color degradation problems with blue and green reproduction and brightness problems with yellow and red shades, when prints are made from the negatives.[146] Ideal absorption characteristics for the three subtractive primary colors are shown in Figure 7, and the actual absorption pattern of typical dyes are presented in Figure 8.[147] A large amount of overlap into other absorption areas is apparent. An example is shown in Figure 9 where a substantial amount of blue light is absorbed by a magenta dye. Spectral density is often used as a measure of the amount of optical absorption by the three image dyes when the measurements are obtained with a monochromatic radiation source tuned to the maximum spectral absorption of the dyes.[148] In practice, the measurements are taken of a narrow band of wavelengths as indicated in Figures 7−9.[149]

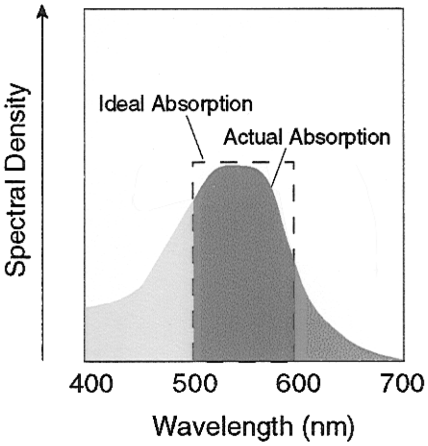


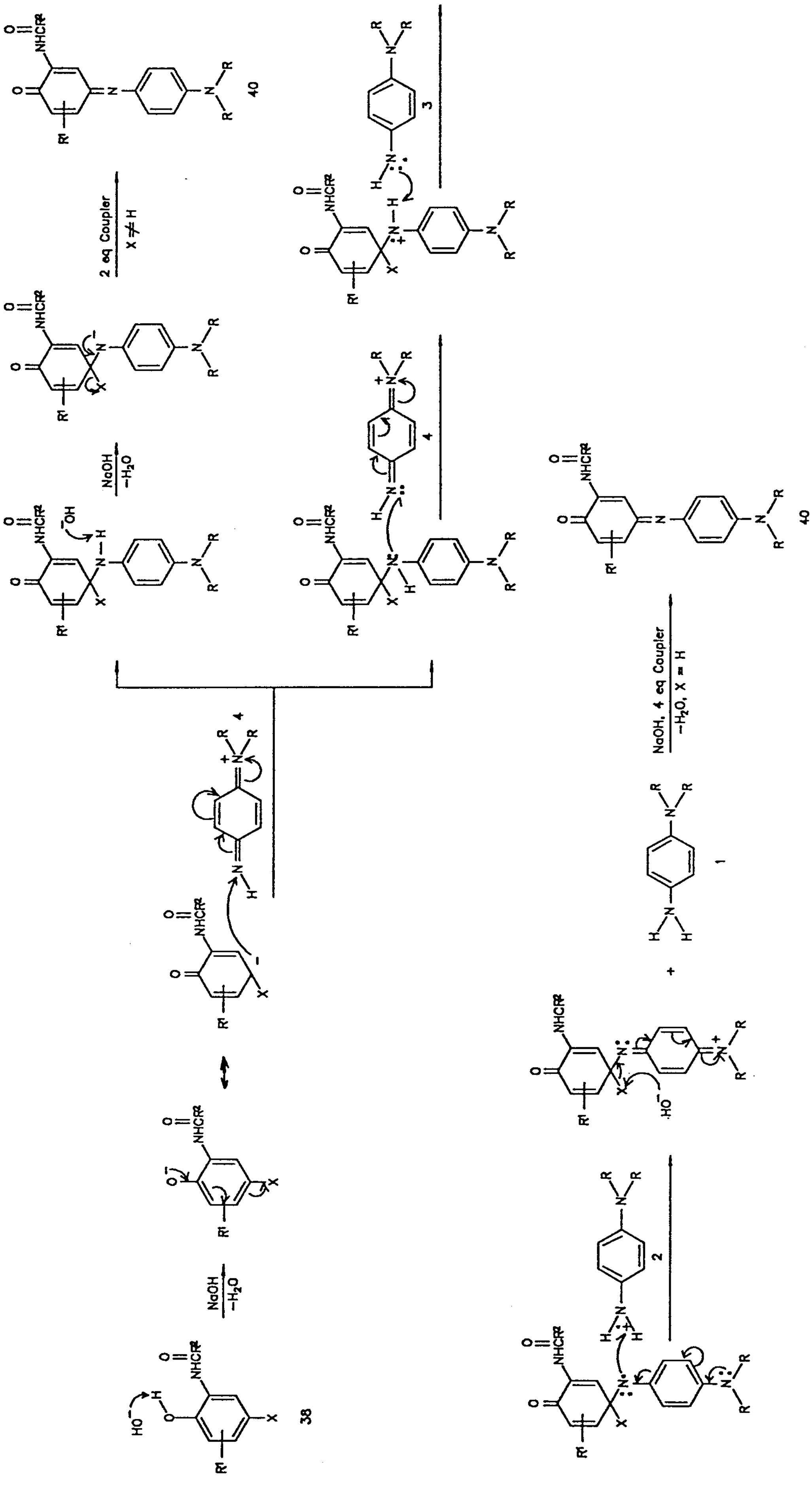
Figure 9. Absorption characteristics of a color negative for a magenta dye.

In the case when ideal spectral absorption by image dyes cannot be achieved, a color correction method called color masking[150−154] is employed to “cover up” these deficencies when making color reproductions from color negatives. The use of colored couplers in color negative films in combination with colorless couplers has solved many of the problems related to nonideal absorption. Colored couplers remain in the nonimage areas of emulsions to compensate for the undesired absorptions. In the image areas the colored coupler reacts with the oxidized developer and the colored moiety, usually attached in the “coupling-off” position, i.e., at the carbon atom where elimination occurs and the carbon where oxidized developer attaches, is released and washed out of the film. Since magenta and cyan dyes are spectrally the most nonideal (Figure 8), their layers contain colored couplers. Yellow-colored magenta couplers[155] are used to produce an equal density in both the image and nonimage areas of the green-sensitive layer. In this way blue light is absorbed equally in the entire layer.

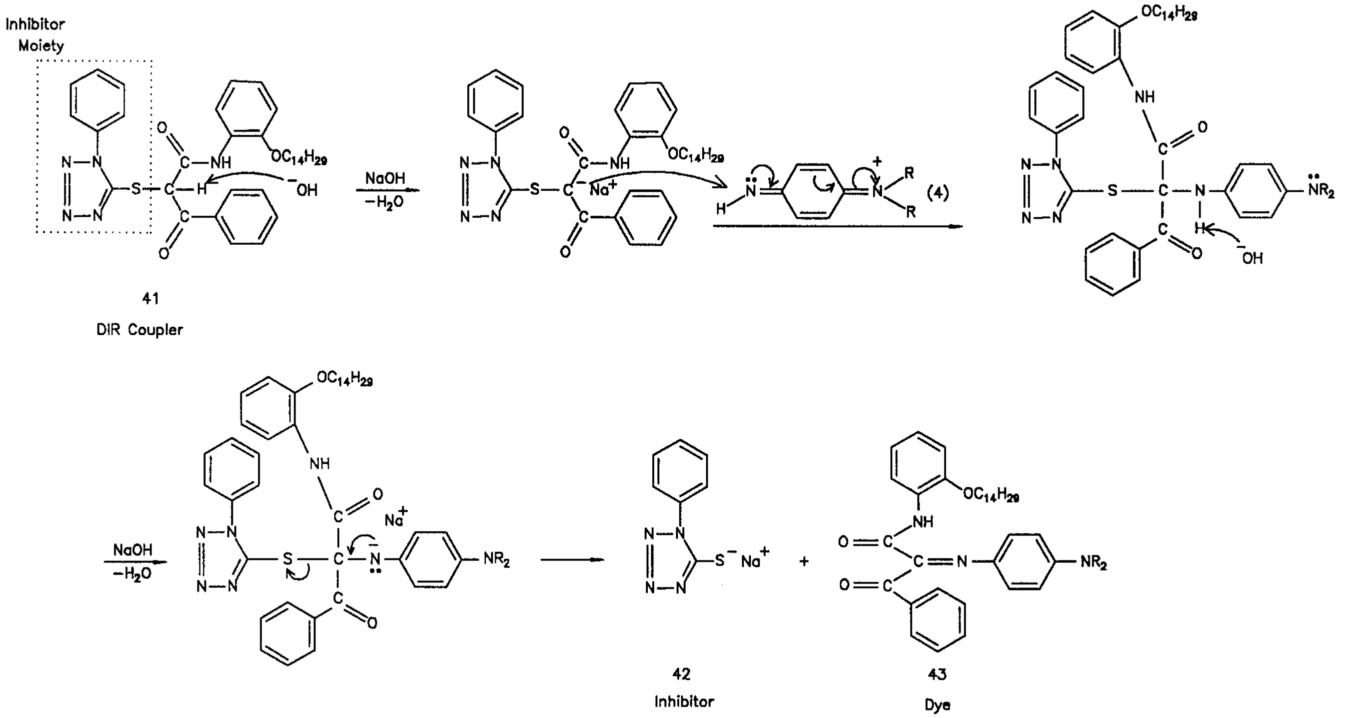
The same is true for unwanted green and blue absorption in the red-sensitive layer. As illustrated in Figure 8 cyan-producing couplers absorb large amounts of green and small amounts of blue light. For this reason red-colored cyan couplers are used. The combination of the colored-masking agents in the green- and red-sensitive layers gives negative films a red-orange cast. Colored couplers have one disadvantage. They act as filters for light which would normally be absorbed by silver halide and, thus, a loss in photographic sensitivity results. For this reason a magenta-colored yellow-masking coupler is not used in color negative films.

An approach to color correction which has been claimed[98] to eleviate the sensitivity loss associated with colored couplers is the use of couplers capable of releasing fluorescent dyes after color development. The fluorescent dye emits light which optically compensates for unwanted absorption of the coupler formed dye. The fluorescent dye must be optically colorless when attached to the coupler but when

Scheme 15


NaOH
−H₂O
2 eq Coupler
X ≠ H
NaOH
−H₂O
NaOH, 4 eq Coupler
−H₂O, X = H
NHCR²
R¹
X
38
40
1
2
3
4

Scheme 16



released it should be capable of fluorescing in a manner sufficient to provide optical compensation relative to the unwanted absorption of the coupler-formed dye.

Another approach to the problem of light absorption during exposure by the colored-masking couplers is to incorporate masking couplers which have absorptions in innocuous regions of the spectrum during exposure but which are converted during the solution processing to dyes absorbing in regions which require masking.[156]

2. Development Inhibitor Releasing (DIR) Couplers. Improvements in unwanted image dye absorptions and in image quality have also been achieved by employing couplers substituted with a releaseable moiety which affects the silver development. A moiety which is called a development inhibitor may be released from a coupler during dye formation. Development inhibitors and development antifoggants are synonymous terms, the latter was discussed previously (section V.B). The reactions of couplers called DIR, or development inhibitor releasing, couplers[157−159] with the oxidized developing agent produce the colored dyes. While this reaction is occurring, a development inhibitor is released, usually from the “coupled-off” position. This inhibitor influences the course of the subsequent development and, when properly manipulated, can lead to significant improvements[89,158−160] in sharpness and graininess of the image as well as improvements in correction of unwanted color absorption.

Sharpness and graininess of the image are improved as a result of the interaction between the released inhibitor fragment and the silver halide grains. Sharpness is defined[149] as the transition between two density levels, i.e., the edge. Sharpness loss is a result of light scattering and diffusion processes. These effects, that result in image spread, are reduced by releasing the inhibitor fragments near the latent image. The result is to enhance the density at the edge relative to the macro density, and thus, the sharpness.[4] Graininess was defined previously (section V.C) as the visual sensation of nonhomogeneity of an image. Graininess is proportional to the dye density divided by the square root of the number of silver halide grains. The use of DIR couplers allows more silver halide grains to be incorporated in the emulsion without a resulting increase in dye density after development.[4] The released inhibitor fragment from the DIR coupler allows the latent image silver halide grains to develop only partially. As a result, the dye density is maintained while the number of silver halide grains is increased, i.e., the graininess is improved.

By using a DIR coupler the unwanted green absorption of a cyan dye can be compensated by a proportional reduction in the amount of magenta dye, i.e., a green light absorber, which is formed in an adjacent layer. Compensation is achieved as a result of an interlayer migation by the released development inhibitor from the cyan layer to the silver halide in the magenta layer where the inhibitor interacts with the exposed silver halide grains to either slow down or stop the development process. Hence, a reduction in the amount of magenta dye proportional to the amount of cyan dye formed is achieved. In practice, both DIR and conventional couplers are usually added to emulsion layers.

A proposed mechanism for simultaneous dye formation and inhibitor release, from a DIR coupler, is illustrated in Scheme 16 by a yellow-forming color coupler **41**. Elimination of the mercaptotetrazole anion **42** as the inhibitor also generates the desired color dye **43**. Much more complex DIR couplers have been patented[161] recently, but these contain similar components to compound **41**.

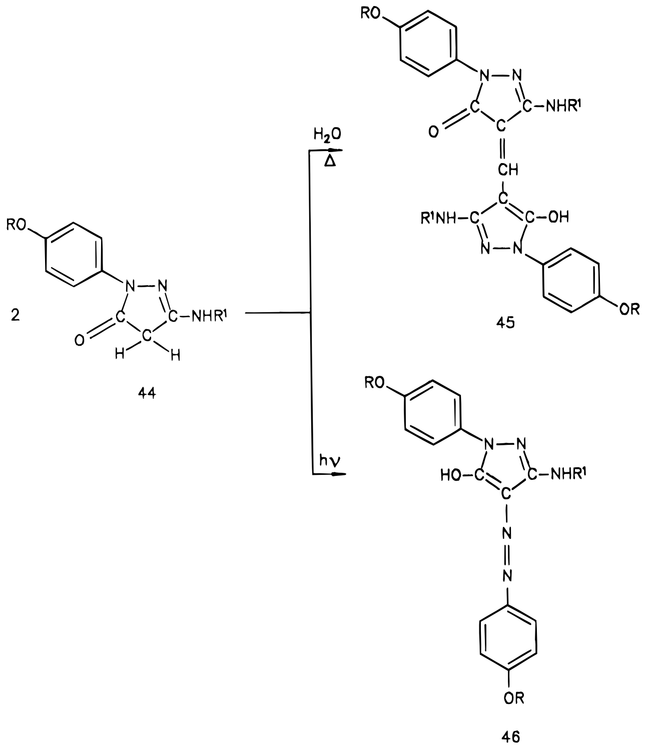
Other variations of a DIR coupler include delayed-release, self-destruct, and universal DIR couplers. A delayed-release DIR coupler[162,163] releases an inhibitor precursor which generates an active inhibitor after a time delay. Delaying formation of the inhibitor reduces unwanted intralayer effects. In the case of self-destruct DIR couplers,[164,165] inhibitors are released which have a finite lifetime and thus, prevent a detrimental buildup of inhibitor in the developer solution as more film is processed. A universal DIR coupler,[166−169] which may be used in any coupler-containing layer of the emulsion, reacts with oxidized developer to release an inhibitor but the dye that is formed is either colorless, fragments into colorless components, or it is washed out from the layers.

3. Image Stability. Choosing the optimal type of coupler depends not only on the absorption of the forming dye but also on the stability of that dye and of its corresponding coupler. Dye fading is a serious concern of all manufacturers of sensitized materials. No silver-based color photographic product has permanent stability under all conditions of use. All dyes will change by color fading in time, only the rate of fading distinguishes the more stable dyes from those less stable.[170] Determining such changes is a difficult task since it would be necessary to wait a number of years to evaluate the results. Consequently, in order to reduce these prolonged time periods, manufacturers have developed accelerated laboratory test methods which enable them to determine the most stable dyes for their products. The following conditions were identified as effecting the stability of dyes. Stability can be broken down into dark and light fading. Dark fading is affected by temperature, humidity, and atmospheric conditions. Light fading is affected by photochemical conditions. In general, the higher the temperature and humidity the greater the “dye fade”. Atmospheric constituents which most often cause colorants to fade are sulfur oxides, nitrogen oxides, and ozone.[171] Atmospheric oxygen also can be[172] a significant contributor to the fading of certain types of yellow and magenta dyes. In contrast, it was found[172] that oxygen actually inhibited the fading of cyan dye. Thus, to control the oxygen penetration of the gelatin and the paper support, in order to stabilize the cyan dye, while preventing the oxygen from fading the magenta and yellow dyes, antioxidants were incorporated[172] in the photographic material.

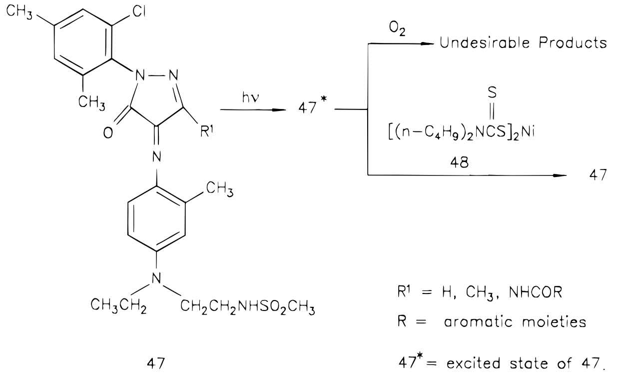
Dark and light stability of 5-pyrazolone magenta-forming couplers **44** and their dyes were extensively investigated,[170] and it was found[170] that the yellowing in prints was caused by reactions of the residual coupler to give as the principal product the coupler **45** in the dark, and azo dye **46** in the light (Scheme 17). Substitution at the two ortho positions on the phenyl ring (ortho substitution not shown in Scheme 17) resulted in more stable couplers by drastically reducing the undesirable reaction rate and forming reaction products which absorbed in the ultraviolet.

Although limited largely to four equivalent pyrazolone couplers, another bothersome reaction which was found to reduce the color of the image was the interaction of the magenta dye with the residual coupler. The formation of a leuco dye resulted in a colorless product. The solution to this problem was found in the use of aldehydes either in the wash bath or stabilizer bath in order to cross-link the two couplers, since the cross-linked molecule would not react with the magenta dye.[170]

Scheme 17



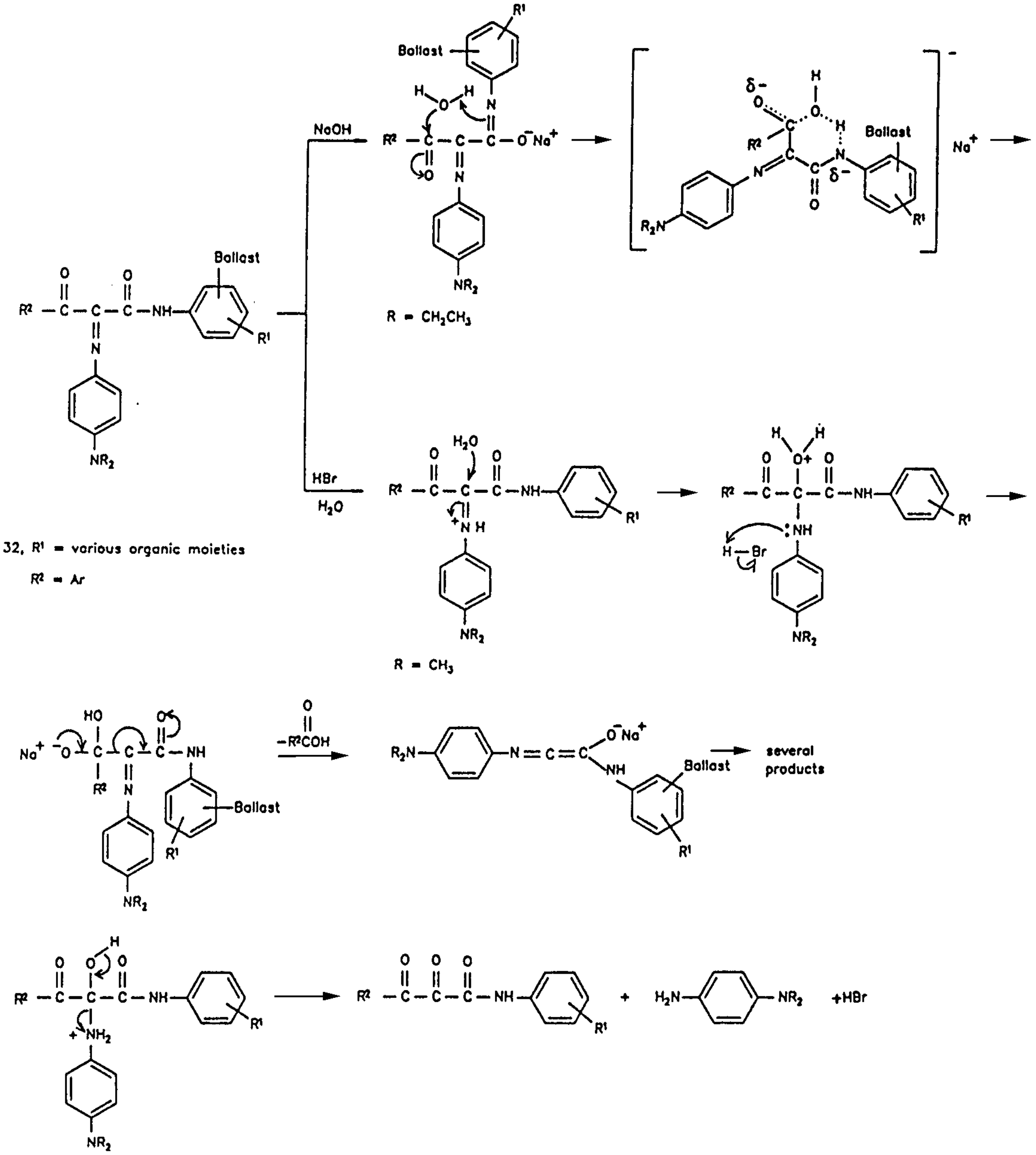
Scheme 18



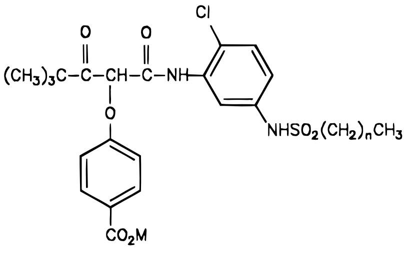
To control the photochemical degradation of magenta dyes, ultraviolet absorbers are added to layers above and below the magenta layer, and in addition, antioxidants are included.[170] The photochemical degradation involves absorption of light by a dye **47** to generate both singlet and triplet excited states **47*** (Scheme 18). Aerial oxidation of the excited molecules forms undesirable products. Stabilization of the dye involves intercepting both the actinic radiation with a UV absorber, and one or more of the reactive intermediates with a quencher, such as nickel dibutyldithiocarbamate (**48**).[170,173] A number of other stabilizers have been reported[174−177] in the recent patent literature.

Light fading associated with yellow dyes has been reduced by switching from the benzoyl group to the pivaloyl in the acetanilide-type couplers. However, yellow dye fading is often the most pH sensitive of all image degradation reactions.[170] The final pH of the print is critical since the presence of either acid or base degrades the dye.[178,179] A proposed mechanism to explain this pH sensitivity is illustrated in Scheme 19.

Scheme 19



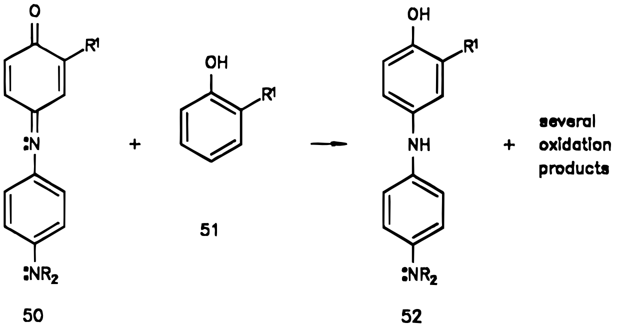
Yellow dyes can be stabilized by the use of more stable yellow couplers. Thus, the use of pivaloylacetanilides **49** with sulfonamide groups instead of the commonly used carboxylate groups has significantly extended the shelf-life stability of yellow dyes in the absence of light.[170,180] An example of the structure of one of these couplers is shown in Figure 10, whereby, the carboxylic acid group can be replaced with the $[SO_2(C_6H_4)]OCH_2C_6H_5$ moiety resulting in better properties.



49: M = H, Monovalent cation; n = 9–25

Figure 10. An example of yellow-forming couplers which are stable to pH changes.

Scheme 20



Cyan dyes, particularly the 2,5-substituted phenols, are considered to be the most light stable of the three types of colored dyes. However, for certain cyan dyes dark fading is a more serious concern than light fading since colorless leuco dyes may form. Formation of the colorless leuco dye **52** was proposed[170] to occur via Scheme 20 either by reaction of the cyan dye **50** with residual coupler **51** or with other components such as sodium thiosulfate, ferrous EDTA

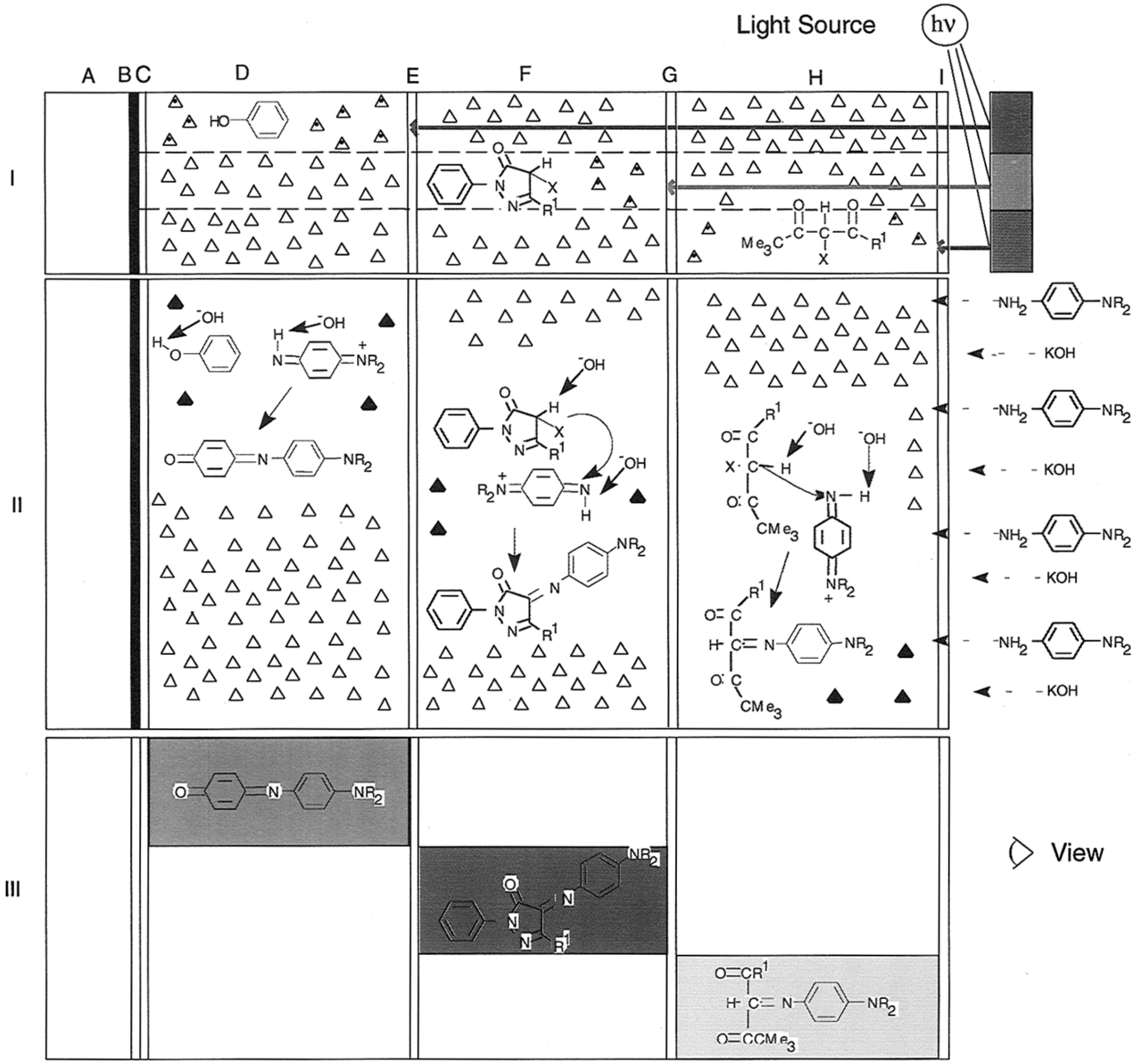


Figure 11. Processing of a color negative film by the dye-coupled process. **(I) Before Development:** Light is reflected off the colored object, silver halide (△) dispersed in the gelatin then absorbs (◬) the frequency of light characteristic of that layer. **(II) During Development:** The developer solution diffuses (←) into the emulsion layers. Reduction of the latent silver halide (◬) by *p*-phenylenediamine **1** produces silver metal (▲) and quinonediamine **4**. Ionization of the couplers allows nucleophilic addition of the anionic coupler to **4**. The various colored dyes are formed in situ. See Schemes 2−4 and 13−15 for a more detailed mechanistic description. **(III) After Silver Removal:** Removal of the residual silver metal and the silver halide (△) in the emulsion layers by the bleaching and fixing solutions leaves the colored dyes and the couplers (not shown).

and antioxidants which remain in the emulsion as a result of improper washing. Surprisingly, no further reference was found to the transformation depicted in Scheme 20. It might be of interest to further explore this type of chemistry. These side reactions can be partially avoided by using color developing agent **20** instead of **19** to form the cyan dye **50**. In addition, the use of phenol-type couplers with amide groups in the 2,5-position of the ring results in dyes which are less prone to reduction.[129,144,145]

2. Types and Composition of Film and Paper

Films can result in positive or negative images. As directly viewed materials, papers have positive images of the original scene, commonly called prints. The composition of negative and positive films is similar but the images are reversed and hence different processing chemicals are used. Examples of the structures of each of these materials will be described[181] and are typical of Fujicolor, Kodacolor, Agfacolor, and related sensitized goods.

a. Negative Film. Negative films are composed of three or more color-sensitive layers, a yellow filter layer, a protective layer, interlayers, an antihalation layer, and a clear film support. As mentioned previously (section V.C), some color negative films have so-called “fast”, “slow”, and even “mid” color-sensitive layers as alternative technologies to the composition in the example discussed here.[182]

The “subbing” layer or support layer (A) is coated with an antihalation layer (B). Over this layer is coated an optional interlayer (C). Following the

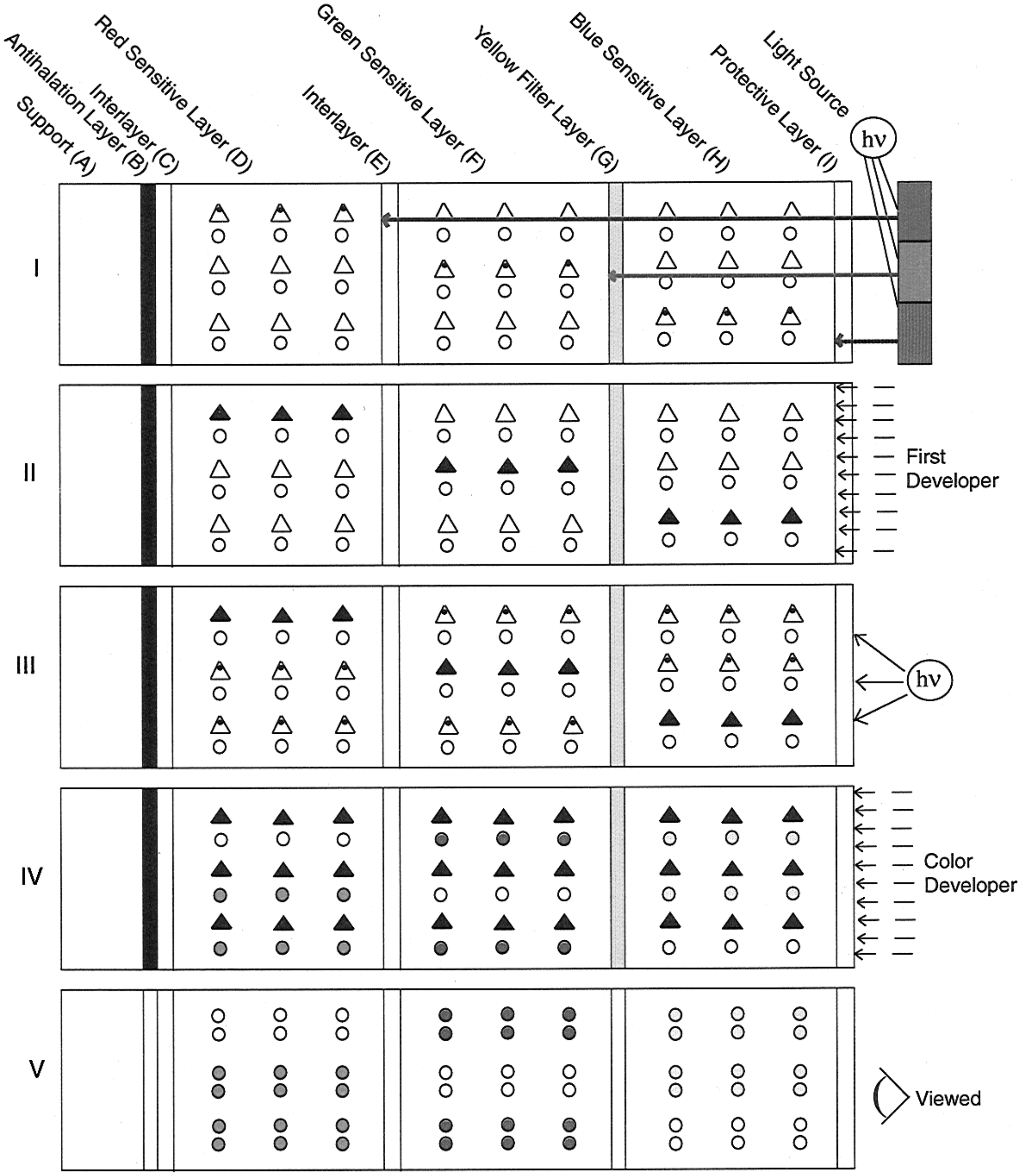


Figure 12. Processing of a color reversal film by the dye-coupled process. **(I) Before Development:** Light is reflected off the colored object. Silver halide (△) and the couplers are dispersed in the gelatin. Silver halide absorbs (◬) the frequency of light characteristic of that layer. **(II) First Development:** The first developer solution diffuses into the emulsion layers and the latent image silver halide (◬) is reduced to silver metal (▲) without dye formation. **(III) Reexposure:** The remaining silver halide is flashed with a light source, and latent image silver halide (◬) is again formed. **(IV) Color Development:** The color developer diffuses into the emulsion layers, the AgX (◬) is reduced by *p*-phenylenediamine **1** and the formed quinonediamine **4** reacts with the couplers to generate colored dyes in situ (see Schemes 2−4). **(V) After Silver Removal:** The remaining silver is removed by the bleaching and fixing solutions leaving a positive color image.

interlayer is a red sensitive layer (D), which has an interlayer (E) coated over it. The next layer to be applied is the green-sensitive layer (F). The yellow filter layer (G) is coated over the green-sensitive layer. A blue-sensitive layer (H) follows the yellow filter layer (G). Finally, a protective layer (I) is coated over the blue-sensitive layer. To illustrate this structure a cross-sectional view of Fujicolor F-II[181] can be found in Figure 11.

In this illustration three stages of processing are delineated. The first stage involves an exposure of the silver halide grains. Wherever light is reflected from a colored object, the silver halide will be exposed in the layer which is sensitive to that wavelength of light. The second stage involves the development of the latent image, forming dyes in the areas of the developed silver metal. When colored couplers are used, they will remain to compensate for nonideal dye absorption. The third stage involves the conversion of the silver metal to silver ions and removal of these ions and the remaining silver halide. In addition, the yellow dye in the yellow filter layer and the antihalation dye will be solubilized, removing the last remnants of the unprocessed film. In some films the yellow filter layer is a dispersed colloidal silver that is removed in the bleaching and fixing solutions.

b. Reversal Film. Reversal films often have exactly the same layer configuration as those used in

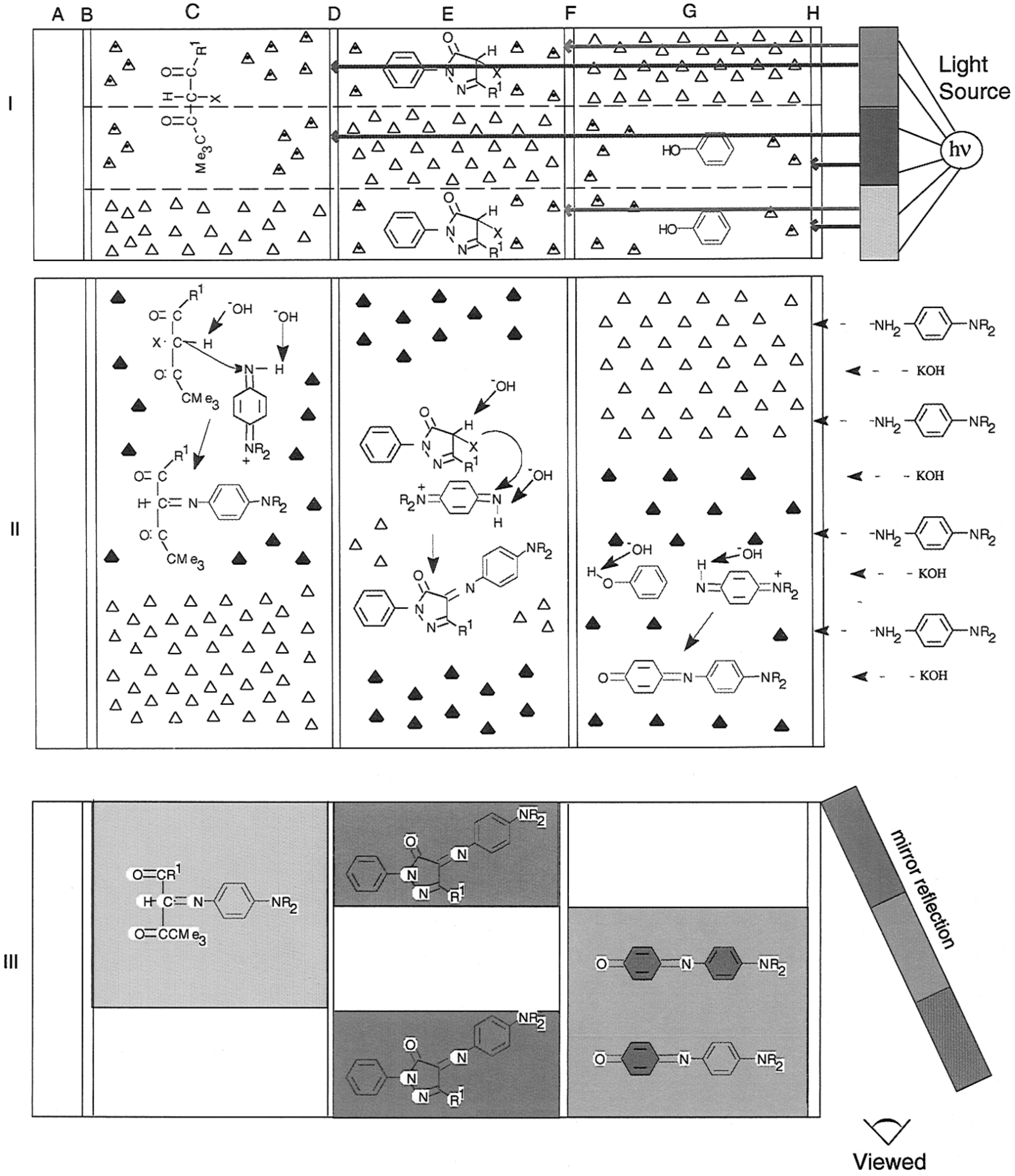


Figure 13. Processing of a color print paper by the dye-coupled process. **(I) Before Development:** Light is passed through a color negative film. Silver halide (△) dispersed in the gelatin absorbs (◬) the frequency of light sensitive to that layer. **(II) During Development:** The developer solution diffuses (←) into the emulsion layers where the *p*-phenylenediamine **1** reduces AgX (◬) to silver metal (▲), forming quinonediamine **4**. Ionization of the couplers allows nucleophilic addition of the anionic coupler to **4**. The various colored dyes are formed in situ. See Schemes 2–4 and 12–15 for a more detailed mechanistic description. **(III) After Silver Removal:** The blix solution removes the residual silver metal and the remaining silver halide from the emulsion layers leaving the colored dyes and the unreacted couplers (not shown).

negative films. The previous section on negative films also describes the layers in a reversal film. However, since the image of a reversal film is the final image, color-masking couplers which are usually added to the emulsions of color negative films for color correction, are not added to the emulsions of reversal films. Instead, couplers employed in reversal films are colorless. Additional processing solutions are required to create the positive image. In the color reversal process, an object is imaged on the reversal film, and then the film is immersed in a first developer which contains no *p*-phenylenediamine reducing agents but which contains a noncoupling reducing agent to form a silver image without dye formation. The remaining silver halide in the film is then either flashed with light or “chemically fogged”, i.e., latent image centers are created on the undeveloped grains by reducing agents such as tin salts, sodium hyposulfite, thiourea, or sodium borohydride.[14] Immersion of the reversal film in a color developing solution, such as that discussed in section V.C, allows dye formation. Thus, a dye positive image is produced. The cross section of reversal films, such as Fujichrome, Ektachrome, and Agfachrome, and the process of colored dye formation are illustrated in Figure 12.[181] Unlike these reversal films which contain incorporated couplers, with Kodachrome the couplers are diffused into the film during the process. This procedure permits a thinner film with potential sharpness benefits.

c. Positive Print Paper. A color print is made by passing light through a color negative and imaging the filtered light on the color print paper. Similar to reversal films, prints are the final image; therefore, the prints contain no colored couplers.[181] Furthermore, in print paper (Figure 13), in contrast to negative and reversal films, a yellow filter layer is not required since the sensitivity of the red- and green-sensitive layers is reduced; hence, these layers are no longer blue light sensitive. The layers of a print are also thinner than film emulsions because of a lower silver halide concentration. Additionally, to increase the sharpness and decrease fading, the red- and blue-sensitive layers are interchanged.

The composition of a typical print material is illustrated in Figure 13.[181] The paper support (A) is coated on both sides with a resin to provide wet strength and protection from gas permeation. Over the resin coat (B) is placed the blue-sensitive layer (C) followed by an interlayer (D) of gelatin. A green-sensitive emulsion (E) is coated over the interlayer (D). An interlayer (F) separates the green-sensitive layer from the red-sensitive layer (G). Finally, a protective layer (H) is coated over the red-sensitive layer. The processing of color prints is similar to that of the negative process.

VI. Instant Photography

The need for a simple, one-step color process with quick means of reproduction was fulfilled in 1963 by Edwin Land at Polaroid with the development of Polacolor.[183] The need for customary development of a negative in order to produce a positive print was eliminated in this new process. It bypassed the complex, sensitive, and time-consuming process which was, to that time, required to develop the negative film and produce a print. After Land’s process was divulged other similar processes were introduced. The following three processes which have grown in popularity will be discussed, i.e., the dye−developer, the dye-release, and the silver-transfer processes. Each of these processes occupy a specific market niche in modern color photography.

Thus, Polaroid’s Polacolor 2 and SX-70 films exemplify the dye−developer process. Kodak’s PR-10 and Fuji’s FI-10 films will be discussed in connection with the dye-release process. Although PR-10 was withdrawn from the market in 1986,[184] it will likely resurface in the future. Polaroid’s Polachrome will represent the silver-transfer process. Polacolor and PR-10 are based on the subtractive color process, whereas Polachrome is based on the additive color process. Each process will be discussed in more detail.

A. Dye−Developer Process

The dye−developer process functions by the transfer of an ionized compound called a dye−developer to a receiver, i.e., a layer which insolubilizes the dye−developer, for the formation of a colored image. A dye−developer[185] is composed of three parts, i.e., a subtractive preformed dye moiety, a reducing agent moiety, and an insulating group[186] between these two moieties. Manipulation of the mobility of the reduced form of the dye−developer and immobility of its oxidized form is a central part of this process. The location of exposed and unexposed silver halide determines the location of the oxidized and reduced forms of the dye−developer. When the dye−developer process is employed in color films, the films are composed of blue-, green-, and red-sensitive silver halide emulsion layers. Wherever silver halide is exposed, the reducing agent portion of the dye−developer indirectly reduces the latent image silver halide to silver metal. A separate, highly mobile reducing agent, called an auxiliary developer, actually reduces the silver halide and in turn oxidizes the dye−developer, thus the term indirect. As a consequence of this sequence of reactions the oxidized dye−developer is immobilized. Wherever the silver halide is unexposed the dye−developer diffuses to an internal receiver layer. The dye−developer is mordanted, i.e. insolubilized, in the receiver layer by cationic polymers. These reactions can only occur after a viscous reagent has been sandwiched between the receiver layers and the negative layers. In the SX-70 film, this alkaline reagent provides an opaque layer which acts like a paper support to allow positive print viewing. In the Polacolor 2 film, the alkaline reagent layer is discarded along with the peeled apart negative layers. Reactions which occur in the emulsion and the emulsion itself are complex. The particulars of each will be discussed in detail.

1. Emulsion

The SX-70 film[187−189] is composed of 13 layers (Figure 14), and another layer is added when the alkaline reagent is forced between the two major sections of the film. A negative section comprises the lower part of the film, and a positive section the upper part. These sections are physically one unit until they become separated by the viscous alkaline reagent after exposure. The alkaline reagent is enclosed in pods at the edge of the film. It is spread between the two sections by automatic rollers. The composition, function, and reactions of this reagent will be discussed in the next segment.

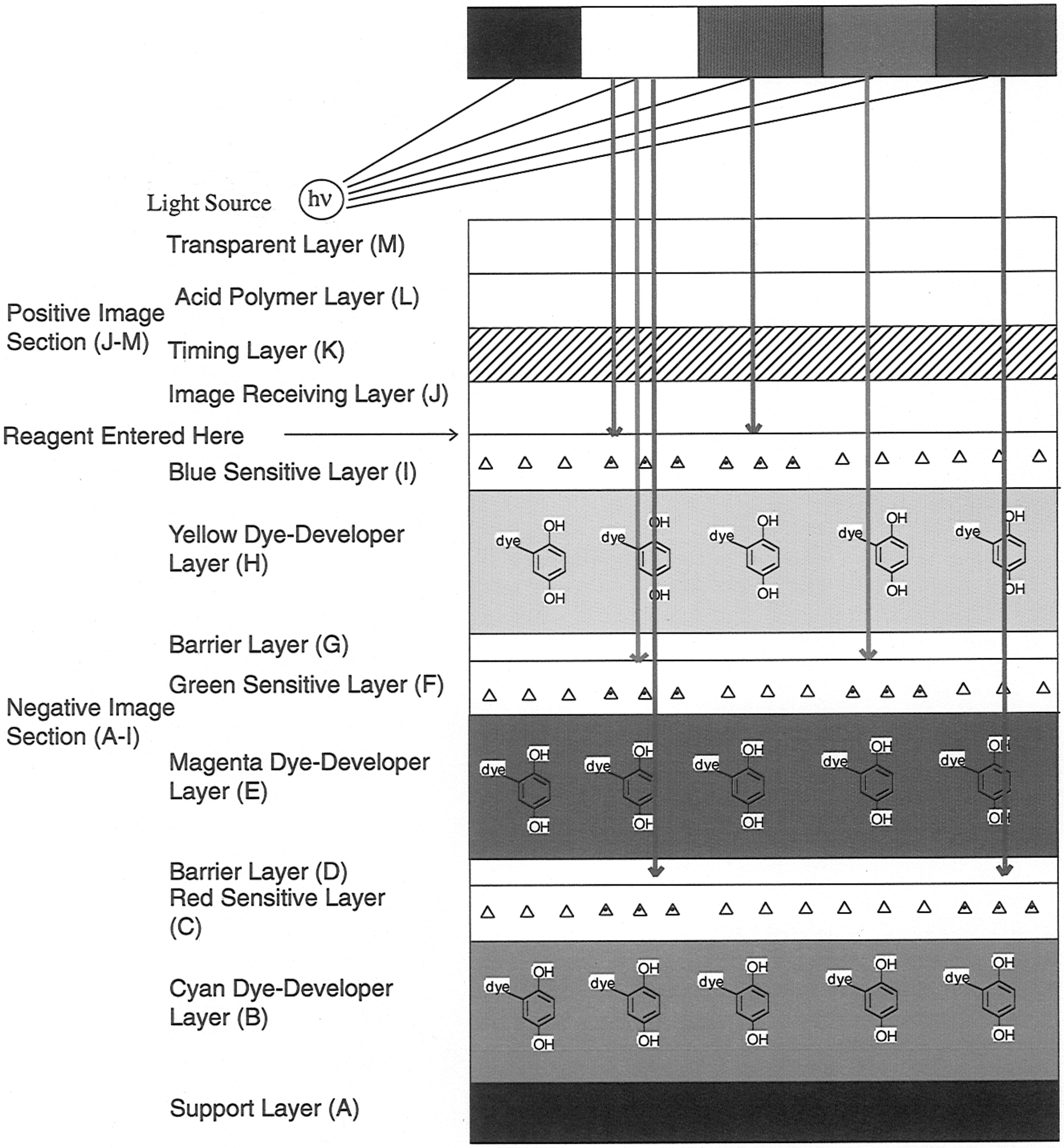
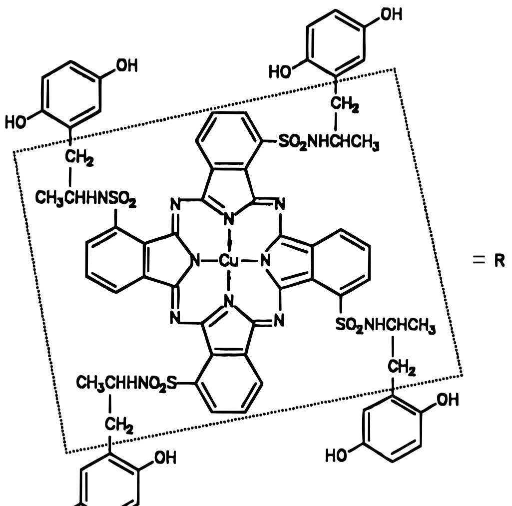


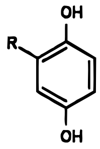
Figure 14. Cross section of the Polaroid SX70 instant color film during exposure. See compounds **53**−**55** for dye−developer structures. Symbols: (△) unexposed silver halide, (◬) exposed silver halide.

The negative section of the film comprises nine layers including the base material (Figure 14). The support (A) is composed of a black-pigmented polyester film, the purpose of which is to provide support to the layers above it and to absorb any residual light not absorbed by the sensitized layers. Above the support a cyan dye−developer coating (B) is applied. Besides the dye−developer, this layer contains either gelatin or a synthetic polymer such as cellulose acetate hydrogen phthalate. The dye−developer is dispersed in the gelatin. A copper phthalocyanine compound **53** is used[190,191] as the cyan dye−developer and has been found to be extremely stable to color degradation effects of light, humidity, and/or heat. The chain between the dye moiety and the hydroquinone group in compound **53** acts as an insulator to interrupt conjugation and thereby prevent color shifting associated with either pH changes or changes in the oxidation state of the hydroquinone group. A simplified structure of **53** is used in figures and schemes.

A red-sensitive silver halide emulsion layer (C) is coated over the cyan dye−developer layer (B). Red light will expose the silver halide grains in this layer. Typically the grains are of the iodobromide type and gelatin is often the matrix, i.e., carrier for the silver halide. This layer is separated from the magenta dye−developer layer by a spacer which is also called a barrier layer (D). Barrier layers (Figure 14) are composed of a transparent compound such as gelatin, polyvinyl alcohol, or polyacetate. Barrier layers function as spatial separators, provide a medium for reactions, and control the permeation rates.

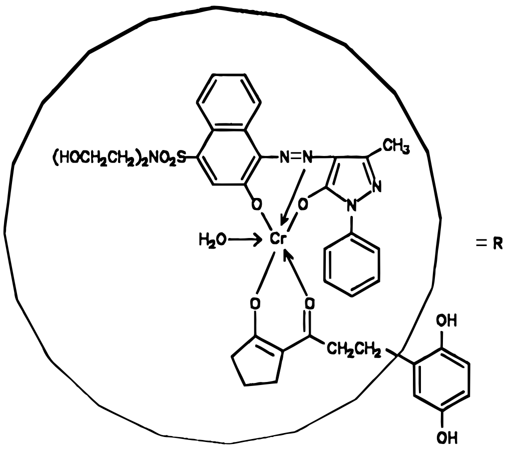


53



The structure used in figures and schemes to represent 53.

A magenta dye–developer layer (E) is coated over the spacer layer (D). The matrix is similar to that used for the cyan dye–developer layer. These layers often contain nonionic surface active agents to achieve a smooth uniform coating during the manufacture. The magenta dye–developer is a chromium complex of an azo pyrazolone of type **54**.[192] A simplified structure of **54** is used in figures and schemes. This chromium dye is characterized by a very high light stability.[193] The reducing agent moiety is typically of the hydroquinone type.



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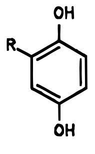
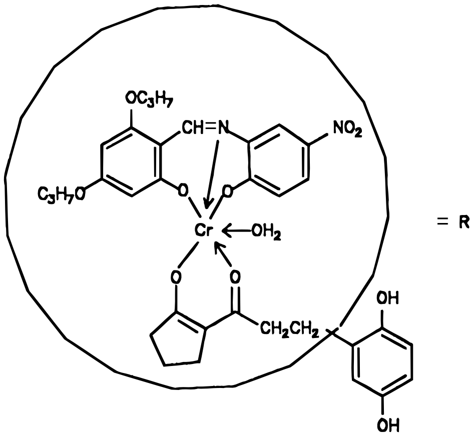


The structure used in figures and schemes to represent 54.

Coated just above the magenta dye–developer layer is the green-sensitive emulsion layer (F). Any green light will be absorbed by this layer. Other than its sensitivity only to green light, the composition of this layer is similar to that of the red-sensitive layer. Another spacer layer (G) separates the yellow dye–developer layer (H) from the green-sensitive layer. The yellow dye–developer in the SX-70 film is a chromium(III) complex of an azomethine type dye **55**. A simplified structure of **55** is used in figures and schemes.



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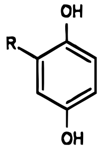


The structure used in figures and schemes to represent 55.

Chromium in the magenta and yellow dye–developers can form complexes with either one or two azo and azomethine dyes. Since the 1:1 complex had[192] the greatest "spectral purity", a colorless β-keto enolato ligand was introduced to occupy two of the remaining coordination sites in order to minimize reactions which might otherwise occur between the chromium cations and gelatin during diffusion of the dye through gelatin-containing layers of the negative.[189] The reducing agent moiety is attached through the keto enolato ligand in the chromium dye–developer complexes.

A blue-sensitive layer (I) is applied after the yellow dye–developer layer (H). A weak bond exists between this layer and the next upper layer since the alkaline reagent must enter at this point. All of the layers discussed so far are part of the negative section of the film.

The positive section of the film, the section in which the positive colored image will form, consists of 4 layers. An image-receiving layer (J) is coated over the blue-sensitive emulsion layer. The mobile dye–developers will be precipitated in this layer. The reduced forms of the dye–developers are immobilized by a reaction with poly-4-vinylpyridine which is contained in the matrix of the receiver layer and which functions as a quaternary counterion under alkaline conditions to the anionic dye–developers. The matrix may consist of either a nylon polymer, such as, *N*-(methoxymethyl) polyhexamethyleneadipamide, or gelatin, or polyvinyl alcohol.[194] Over this layer is coated a timing layer (K) for controlling the rate at which the pH drops by use of its permeability and thickness properties. The timing layer is positioned to separate the layer above it called the acid polymer layer (L).

The acid polymer layer (L) is composed of either carboxylic or sulfonic acid containing either polymers or acid-forming polymers such as anhydrides which neutralize the alkali as it diffuses through the timing layer. Diffusion is timed in such a way as to allow the dye—developer to completely diffuse to the image receiving layer before the pH drops. This lower pH is beneficial for image stability and also terminates the transfer process by mediating the conversion of the dye—developer from its ionized, mobile form, to its un-ionized, immobile form. Specific examples[195] of acidic polymers include *o*-sulfobenzoic acid, polyvinyl hydrogen phthalate, polyacrylic acid, and polystyrene sulfonic acid.

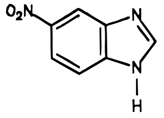
The top layer is a transparent polyester sheet (M) through which the positive image is viewed. Often an antireflection coating is applied to the surface of this layer to minimize flare. Figure 14 represents a schematic diagram of the cross section of this film.[189]

2. Processing Chemicals

The viscous alkaline solution squeegeed between the negative and receiver sections functions[185,194,196] in a number of important ways. Most importantly the alkaline solution supplies the alkaline components which solubilize the dye—developer, transforms it into an active reducing agent, and softens the emulsion to allow permeation of the various chemicals. Another function of the alkaline solution is to provide an opaque surface to prevent further exposure of the film during dye transfer and to allow a reflective backing which will provide a white background. Since this layer will remain after the process has been completed it must also form an adhesive bond between the negative and positive sections. The alkaline solution also serves as the carrier of the auxiliary developer. The auxiliary developer acts as an electron-transfer agent for the less mobile dye—developer.[185] Auxiliary reducing agents greatly accelerate the speed of the development process. Other less critical functions of the alkaline solution are to act as a development restrainer for unexposed silver halide and as a development accelerator for exposed silver halide. All of these functions will be discussed in greater detail with references to specific examples.

The alkaline solution is applied[184] as a viscous liquid which is contained in small pods concealed within the wide border of the film unit. After exposure the pods burst by the automatic withdrawal of the film through rollers, and the reagent is spread evenly between the negative and positive sections. Immediately the alkaline viscous gel permeates the various layers and initiates the mechanisms involved in the dye-transfer process.

This viscous solution is generally composed of[189] water, alkali, a white pigment, a polymer, a restrainer, an auxiliary developer, a development accelerator and other processing chemicals. The alkali may be either lithium, sodium, or potassium hydroxide or an amine such as diethylamine. Titanium dioxide is used as the white pigment and acts along with opacifying dyes of the phthalein type to make the reagent layer opaque. These phthalein dyes are highly colored at a high pH but become progressively lighter as the pH drops. Polymers of the acrylamide and carboxymethyl cellulose type are used as thickeners and adhesives. Restrainers such as potassium bromide, benzotriazole (**24**), 5-nitrobenzimidizole (**56**), and mercaptans such as 1-(4-hydroxyphenyl)tetrazoline-5-thione (**57**) are used to protect the unexposed silver halide grains from unselective reductions. The use of development accelerators, such as quaternary ammonium compounds reduces the charge barrier that might lengthen the time in which the developing agents act. One such compound is *N*-phenethyl-α-picolinium bromide (**58**).



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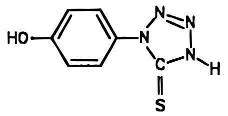

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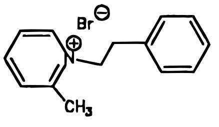

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Auxiliary developers have an important role in determining the reaction rates of the silver development process, i.e., the speed at which the dye—developer can act. Auxiliary developing agents may be included in either only one or all of the silver halide emulsion layers. However, they are often added to the alkaline reagent. Typical examples of auxiliary developing agents[194,196] include 1-phenyl-3-pyrazolidinone (**59**), substituted hydroquinones **60**—**62**, and derivatives of *p*- and *o*-aminophenols **63** and **64** (Figure 15). Hydroquinones are especially suitable since they are ineffective reducing agents at neutral pH. The mechanism for the ionization and electron transfer (Scheme 21) initially involves the

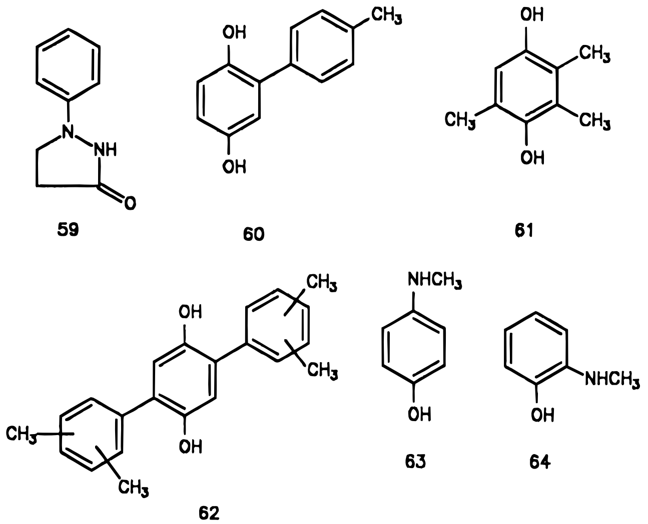
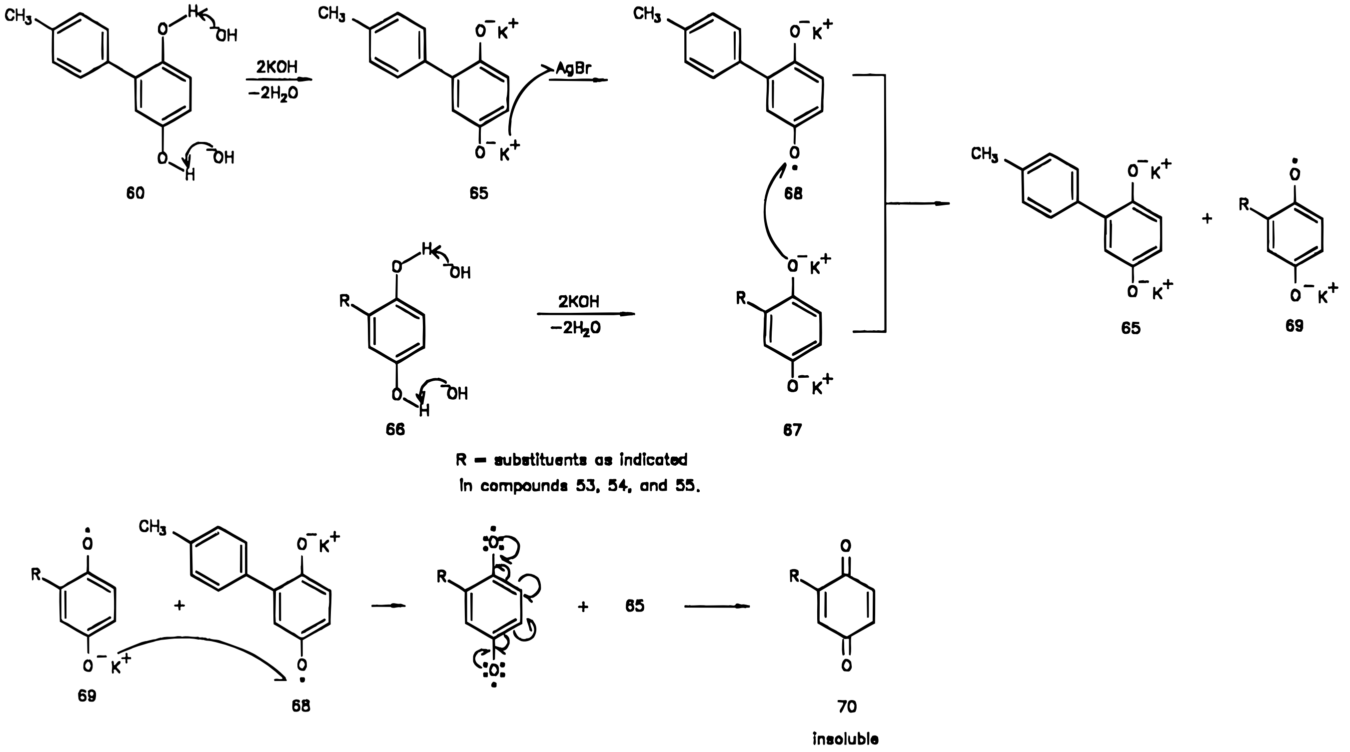


Figure 15. Auxiliary developing agents.

Scheme 21



formation of soluble salts of the auxiliary developer and the dye−developer.

Both the auxiliary developing agent **60** and the dye developers **66** are ionized by potassium hydroxide to their corresponding salts **65** and **67**, respectively. The highly mobile salt of the auxiliary developing agent **65** diffuses quickly to the exposed silver halide, reducing it to silver metal and thereby forming the semiquinone species **68**. The semiquinone species then receives an electron from the ionized dye−developer **67**, regenerating the ionized auxiliary developing agent **65** and oxidizing **67** to its semiquinone form **69**. Further oxidation occurs to produce the immobile quinone form **70** of the dye−developer. The auxiliary developing agent **65** is, therefore, replenished to its original state. Immobilization of the quinone **70** is apparently related, in part, to a change in the solubility of the dye developer on oxidation and, in particular, to its solubility in alkaline solutions. It may also be partly related to a tanning effect on the gelatin by the oxidized developing agent **70**, and further because of a localized exhaustion of alkali as a result of the development process.[195] In a more recent study using radioactive labeled picolinium salts, it was suggested[197] that an insoluble product results from a reaction between the quinone **70** and a picolinium salt.

Unexposed and partially exposed areas of the film contain unreacted dye−developer in the ionized form. These molecules **67** are mobile, although less mobile than the auxiliary developing agent, diffusing to the receiver layer where they are anchored. The pH begins to fall as the alkali is neutralized and a positive image remains. The Polacolor 2 process differs from the SX-70 in that the negative section is exposed prior to sandwiching of the positive to it by the alkaline reagent. In addition, the negative section is later peeled off and discarded. A schematic diagram of the SX-70 film after the reagent has been spread between the positive and negative sections is illustrated in Figure 16.[189]

B. Dye-Release Process

The name dye-release process stems from the fact that the major components required for a dye formation, are formed from the dye-releasing compounds. The dye-releasing compounds are insoluble species incorporated into the emulsion layers of the film and are designed to split into two portions on oxidation and hydrolysis. The oxidized portion of a dye-releasing compound remains as an insoluble moiety in the original layer, whereas the other portion, as a result of alkaline hydrolysis, diffuses to the image receiving layer where it becomes mordanted, i.e., immobilized. Diffusible portions of the dye-releasing compounds are constructed of soluble dye moieties and the nondiffusible portions of the dye-releasing compounds which are composed of a combination of reducing agent moieties and ballasting groups, the latter groups function to insolubilize the dye-releasing compounds. As defined previously, ballasting groups are usually long-chain organic substituents. In this process the substituents can range in length from eight to 32 carbons.[198] The structure and function of the dye-releasing compounds will be delineated in greater detail in the next section. In this review only the dye-release processes which are based on sequential oxidation and hydrolysis will be discussed. Release of a dye moiety from a dye-releasing compound can be achieved by reactions other than sequential oxidation and hydrolysis. Thus, reduction and hydrolysis,[199−202] silver metal-assisted cleavage,[203−208] oxidation followed by intramolecular ring closure,[209,210] and other methods[184] have been devised but will not be further elaborated.

Besides the use of a dye-releasing compound instead of a dye-coupled compound, the respective

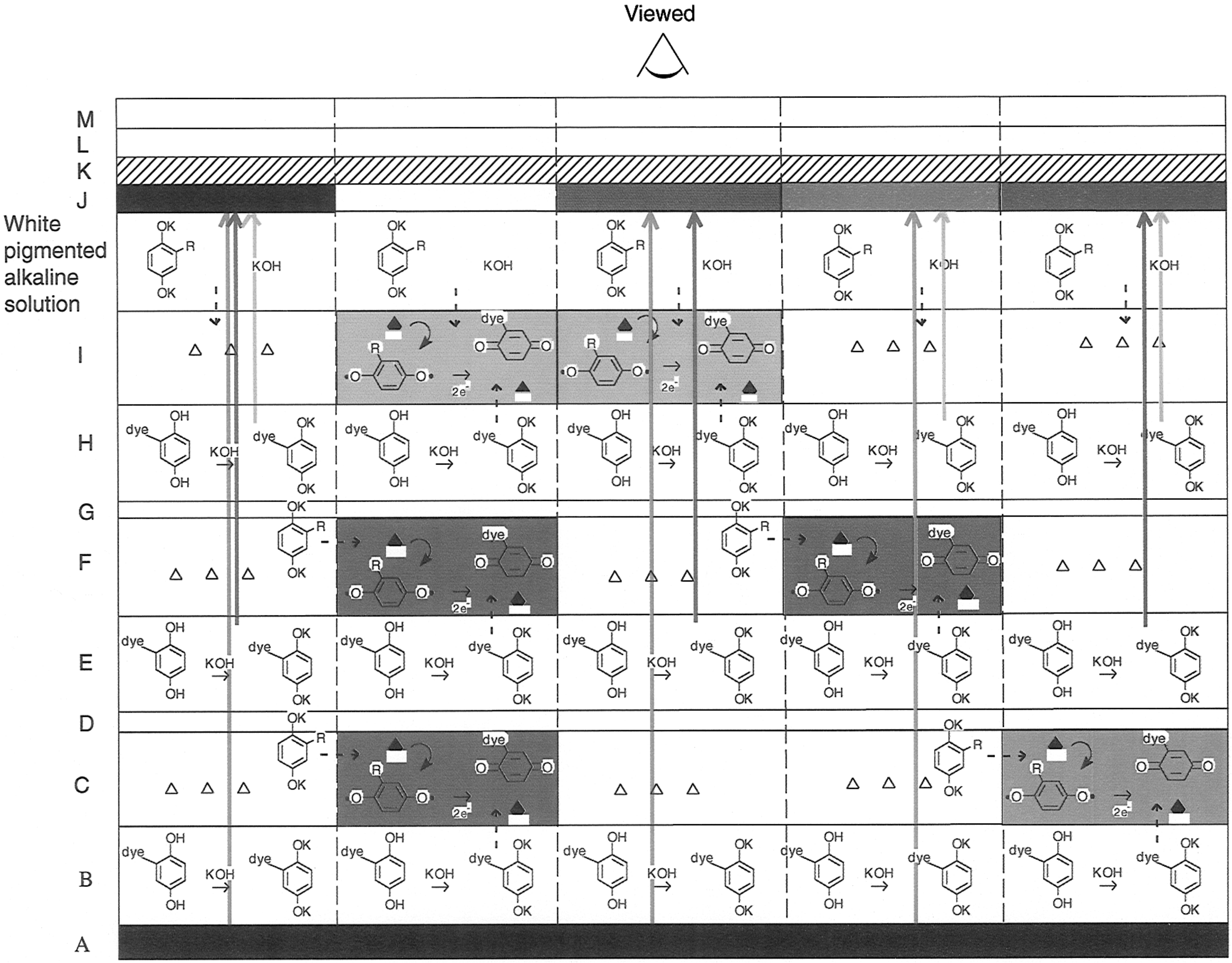


Figure 16. Polaroid SX70 film after application of the alkaline solution. See Scheme 20 for mechanistic details and Figure 14 for details on the function of each of the layers. Symbols: (△) unexposed silver halide, (▲) silver metal.

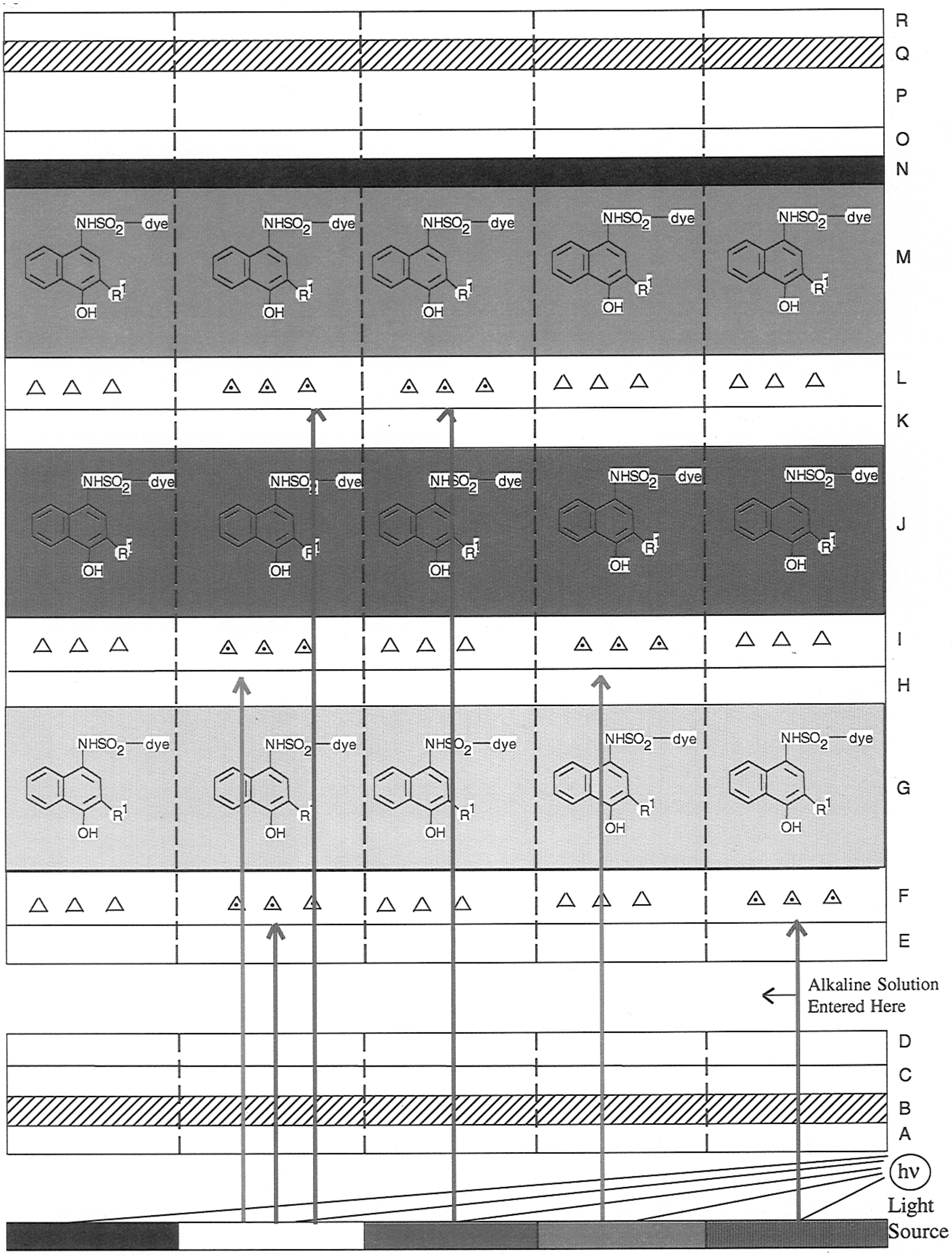


Figure 17. Cross section of the Kodak PR-10 film before application of the alkaline processing solution. See compounds **71a**−**c** (Figure 19) for dye-release structures. The various layers can be described as follows: backing layer (A), polyester support (B), acid layer (C), timing layer (D), UV absorbing layer (E), blue-sensitive layer (F), yellow dye-releasing layer (G), spacer layer (H), green-sensitive layer (I), magenta dye-releasing layer (J), spacer layer (K), red-sensitive layer (L), cyan dye-releasing layer (M), black layer (N), opaque reflective layer (O), image receiving layer (P), polyester support (Q), backing layer (R). Symbols: (◬) silver halide with *internal* latent image, (△) silver halide.

processes differ in another important way. In the dye-coupled process, the image dyes are formed in the unexposed regions of the film. Therefore, the film emulsion utilized in the dye-coupled process is termed a negative working emulsion. In the dye-release process, the image dyes are formed in the exposed regions of the film and the film emulsion employed is termed a positive working emulsion. Elaboration on how positive working emulsions and dye-releasing compounds function will serve as the next topic, using Kodak's PR-10 and Fuji's FI-10 films as representative examples of the dye-release process (Figure 17).

1. Emulsion

The PR-10 film (Figure 17) which was introduced[211−213] by Eastman Kodak in 1976 and the FI-10 film which was introduced[184] by Fuji in 1981 were competitive products and similar in composition. The two films and the chemistry of their processing will be discussed as comparable products but differences will be noted where they exist. Kodak's PR-10 film was composed of 18 layers not including the alkaline solution layer which, like the Polaroid SX-70 film, discussed in the section on the dye-coupled process, was spread between two layers from pods after exposure. There were three sections in this film: a transparent support, a light-sensitive section, and an image-receiving section. The light-sensitive section contained the positive working emulsion layers.[214] As a consequence of a special manufacturing process[215] the normal recording of light is reversed. During exposure and processing of a positive working emulsion, the silver halide which is unexposed by light is reduced by the auxiliary developing agent to silver metal and the exposed silver halide remains as silver halide after processing the film in the alkaline solution. The special manufacturing process which allows a reversal in the classical sensitivity of the silver halide is called chemical nucleation or chemical fogging. Fogging agents, such as hydrazines, hydrazides, hydrazones, and certain quaternary compounds are added to the emulsion during manufacture and are in intimate contact with the silver halide.[14] On exposure, an *internal* latent image is formed in the exposed silver halide grains. This exposed silver halide differs from the unexposed silver halide in that the unexposed silver halide forms a *surface* latent image after nucleation by the fogging agent. In addition, electrons are transferred from the fogging agent to the exposed silver halide grains, but in this case the electons are funneled to the internal latent image. The reducing agent, so-called auxiliary developing agent, contained in the alkaline solution is utilized in the reduction of the unexposed, surface latent imaged silver halide grains. The exposed grains with their internal latent images cannot be reduced. An illustration of the mechanism for chemical nucleation or fogging is shown in Figure 18.[14]

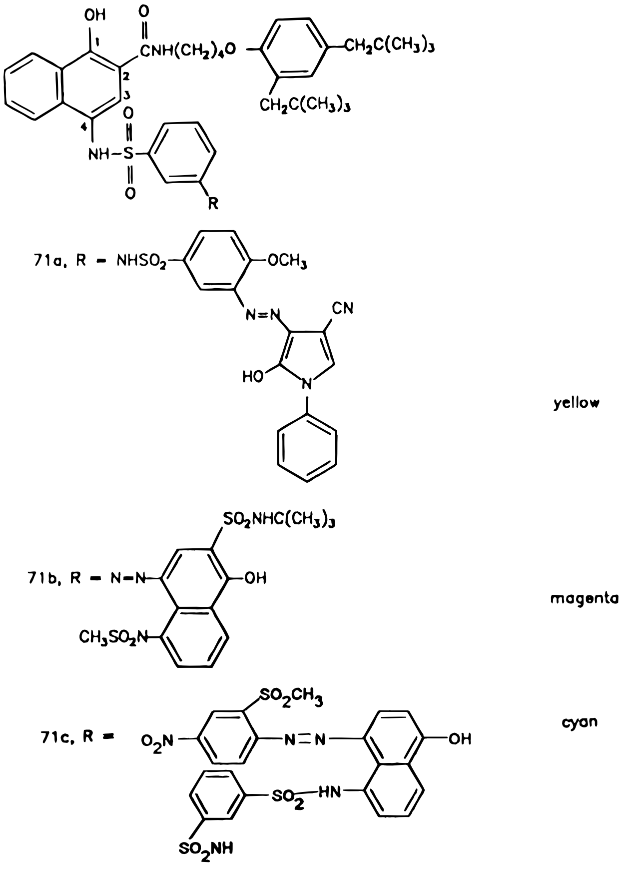


Figure 19. Dye-releasing compounds used in Kodak instant color films.

The silver halide grains described in Figure 18 are present in the blue- (F), green- (I) and red-sensitive (L) layers of the PR-10 film (Figure 17) and are coated next to their corresponding dye-release layers (G, J, M). Spacer layers (H and K) separate the dye-release layers from each other and compounds contained within spacer layers function as scavengers for any oxidized auxiliary developing agents which failed to react with the dye-releasing compounds. A UV-absorbing layer (E) is present containing special UV-absorbers to stabilize the colored image dyes by absorbing ultraviolet light.

The dye-releasing compounds are incorporated[216,217] in the PR-10 film in separate layers G, J, M (Figure 17) as aqueous alkali-insoluble 4-sulfonamidonaphthols with azo dye moieties for yellow **71a**, magenta **71b**, and cyan **71c**, attached through the C4 sulfonamido groups (Figure 19). The 2-amido substituents serve as ballasting groups which immobilize the dye-releasing compounds by making them insoluble in the gelatin and in the aqueous alkaline solution.

4-Alkoxy-2-sulfonamidophenol dye-releasing compounds are utilized[218−221] in the Fuji instant color films (Figure 20). The azo dye moieties yellow **72a**, magenta **72b**, and cyan **72c** are also attached through

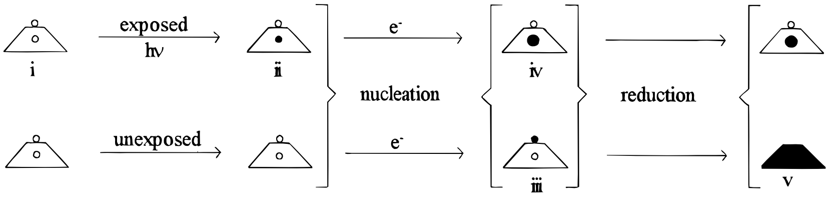


Figure 18. Process of chemical nucleation and effect on the development: (i) silver halide grain; (ii) internal latent image from light exposure; (iii) external latent image from nucleation; (iv) internal latent image from nucleation and light exposure; (v) reduction of silver grain by auxiliary developing agent.

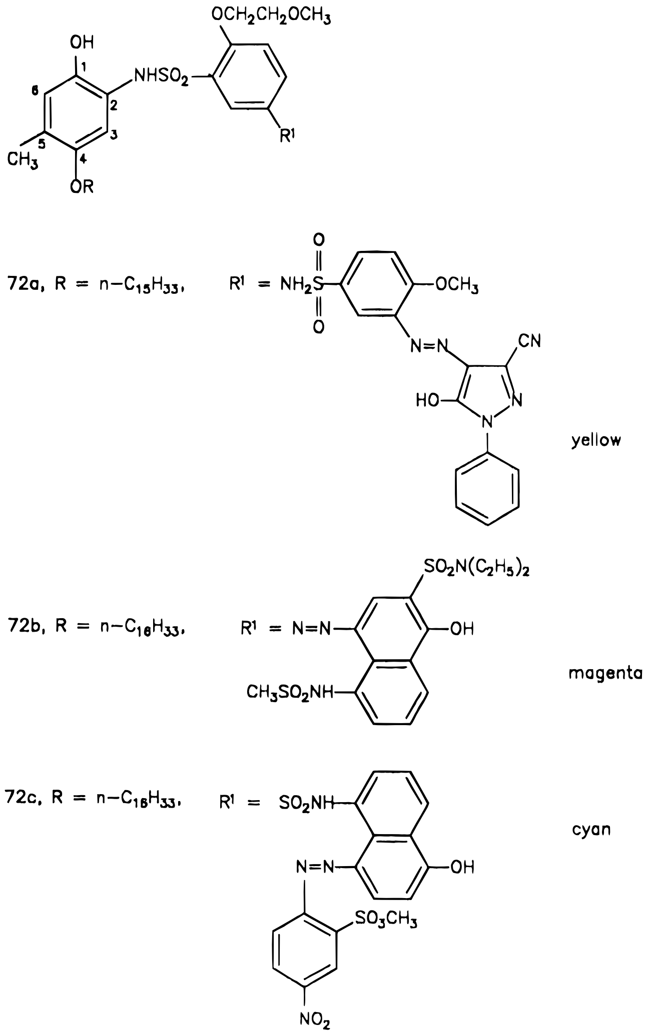


Figure 20. Dye-releasing compounds used in Fuji instant color films.

the C2-sulfonamido groups. However, unlike the Kodak dye-releasing compounds, these species have ballasting groups attached at the C4-position as long alkoxy moieties, which insolubilize the compounds. The naphthol and phenol groups in the dye-releasing compounds of the Kodak and Fuji films, respectively, function as reducing agents by transferring electrons to the oxidized auxiliary developer. Mechanistic aspects of the dye-release process will be discussed in the next section.

In addition to the light-sensitive section already mentioned, the PR-10 film (Figure 17) also contains a transparent support which is composed of a timing layer (D), an acid layer (C), a polyester support (B) and a backing layer (A). The purpose for the first three layers is similar to that discussed earlier in the emulsion section of the dye–developer process. A backing layer is included to function as a noncurling layer in order to secure planarity of the film. The alkaline solution is introduced between the transparent support (A–D) and the light-sensitive section (E–M).

The image-receiving section (N–R) is the last part of PR-10 film. It is attached to the light-sensitive portion of the film by a black opaque layer (N) which, along with the white opaque reflective layer (O), serves as a light barrier during processing. A barrier to light is required since processing occurs after the film is ejected from the camera. Without this barrier, exposure of the film by either sun or room light would continue, thus destroying the integrity of the image. The black layer (N) is composed of carbon black and gelatin and the white layer (O) of titanium dioxide and gelatin. The remaining layers include the image-receiving layer (P), the support (Q), and a backing layer (R). The image-receiving layer (P) contains gelatin and a mordant of the quaternary type. The support (Q) is a polyester and the backing (R) functions in the same manner as the backing (A) on the opposite side of the film. A schematic representation of the PR-10 film is illustrated in Figure 17.

2. Processing Solution

Spreading of the alkaline solution, i.e., the processing solution, begins the process of silver halide reduction and initiates the dye-release process. The alkaline solution is spread between two layers by the bursting of pods containing the reagent (Figure 21). The alkaline processing solution is composed of a solvent which is usually water, and an alkaline compound, such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, or an amine, to raise the pH in excess of 11.0. One or more auxiliary developing agents, such as hydroquinone, *tert*-butylhydroquinone, *N*-(methylamino)-phenol, 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-(hydroxymethyl)-4-methyl-3-pyrazolidone, ascorbic acid, and aminophenols are usually present.[216] If two auxiliary developing agents are present, then a hydroquinone and a 1-phenyl-3-pyrazolidone type auxiliary developing agents are usually included, although each type of reducing agent may be present alone. A thickening agent is incorporated and is usually of the carboxy cellulose type which increases the viscosity and allows a uniform spreading of the alkaline solution. An opacifying agent is added to the alkaline processing solution to prevent exposure of the film during processing. This opacifying agent is most often carbon black. Other components may be added to the alkaline solution, such as preservatives and restrainers. An example of the components and concentrations of an alkaline processing solution is shown as follows.[222]

Processing Composition

potassium hydroxide	56.0 g
4-(hydroxymethyl)-4-methyl-1-phenyl-3-pyrazolidone	8.0 g
5-methylbenzotriazole	2.4 g
tert-butylhydroquinone	0.2 g
sodium sulfite (anhydrous)	2.0 g
carbon	40.0 g
hydroxyethylcellulose	25.0 g
water to make 1.0 L	

The dye-release process involves, in general, reduction of unexposed silver halide, oxidation of the dye-releasing compounds, and subsequent release of the dye moieties for diffusion to the image receiving layer. After exposure the alkaline solution is applied. Application of this fluid results in the reduction of

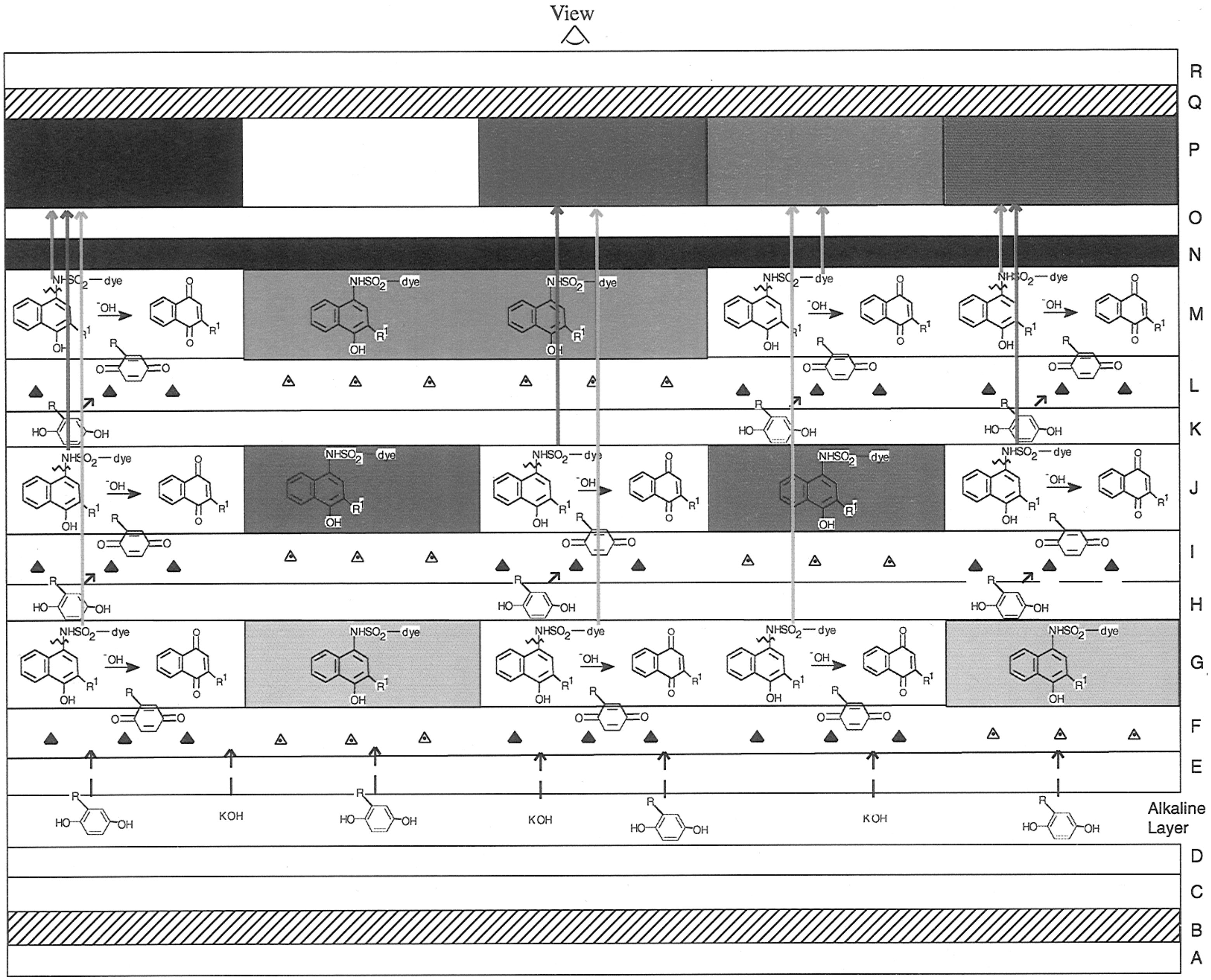
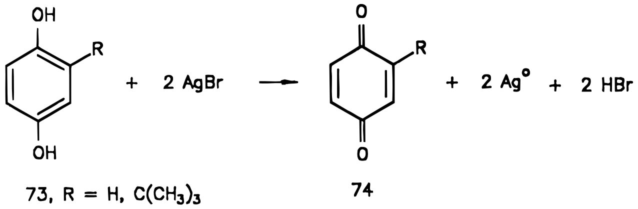


Figure 21. Cross section of the Kodak PR-10 film after application of the alkaline processing solution. See Figure 17 for a description of the function of the various layers. Symbols: (〰) bond cleavage resulting in various, migrating, colored image dyes (for structural details, see Figure 19), (△) silver halide with internal latent image, (▲) silver metal.

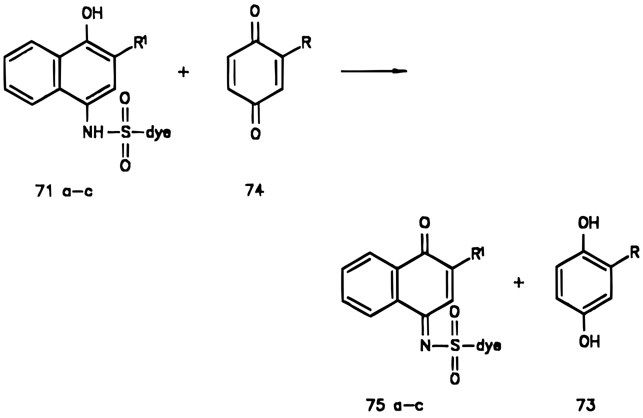
the unexposed, i.e., nucleated silver halides by an auxiliary developing agent such as **73** (Scheme 22).

Scheme 22



The oxidized auxiliary developing agent **74** in the unexposed areas is reduced by the reducing moiety of the dye-release compounds **71a**–**c** (Scheme 23).

Scheme 23



The oxidized dye-release compounds **75a**–**c** are then hydrolyzed by potassium hydroxide in the reagent (Scheme 24). The hydrolysis of the oxidized dye-release compound **75** frees the dye moiety **77** to diffuse to the image receiving layer where it is insolubilized by the reaction with a quaternary compound. The oxidized portion **76** of the dye-release molecule is anchored by the insoluble substituent at the C2 position of the naphthol ring. The dye-releasing compounds **71** in the exposed areas of the film are also fixed in place by the insoluble substituents, so-called ballasting groups, at the C2 position of the naphthol ring. The mechanism for the Fuji dye-releasing compounds **72a**–**c** is similar to the mechanism for the Kodak dye-releasing compounds **71a**–**c** but compounds **72a**–**c** undergo[223–225] hydrolysis at the C2-position on the phenol ring.

To complete the dye-release process the timing layer (D), along with the acid layer (C), are made to slowly decrease the pH of the film layers to terminate the process. The final print is viewed from the opposite side of exposure. The dye-released method is claimed to be an improvement over the dye-developed method since the active reducing agent moieties are not present in the former method during diffusion. A schematic representation of the film after transfer is illustrated in Figure 21.

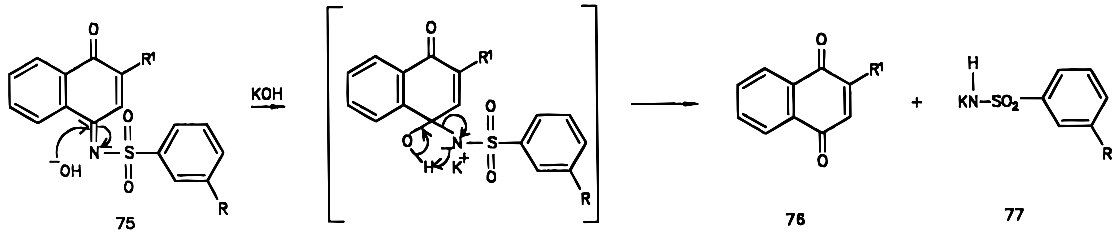
C. Silver-Transfer Process

In contrast to the dye–developer and dye-release processes which are subtractive color photographic processes employed to produce an instant color photograph, the silver-transfer process[184,226] is an additive process designed to produce 35mm transparent slides. Instead of transferring a dye, as in the case of the two previous processes, in the silver-transfer process silver ions are transferred. The alkaline processing solution is applied by bursting of pods by pressure rollers as the film is either automatically or manually wound in a cassette called an autoprocessor. After a brief interval, the film is rewound and the portion of the film containing the negative image is separated from the positive image to produce the colored slide. Polachrome CS and Polachrome HS films are the only commercial products using an additive system. Because the additive primaries remove two-thirds of the white light spectrum, the resulting 35-mm films, used for production of colored slides, results in dimmer images than those based on subtractive systems.

1. Film

Polachrome film[227] consists of seven layers plus a polyester support (A) (Figure 22). A layer (B) of minute lines of alternating red, green and blue dyes is coated over the support (A). The lines of the additive screen layer (B) form the “filter” through which light will pass and, thus, the light will be either absorbed by the dyes in the additive screen or be transmitted to the emulsion containing the silver halide. In Polachrome film there are about 1200 colored lines per centimeter. Over the additive screen an alkali guard layer (C) is coated to prevent penetration by the alkaline processing fluid to the dye screen and protecting the screen from damage. A positive image receiving layer (D) is coated over the screen protective layer (C). The positive image receiving layer (D) functions as a silver complex precipitating layer by the incorporation of nuclei which deposit silver complexes as they diffuse to the receiving layer (D). Over the image receiving layer (D) is an image-protecting layer (E) that will serve as a surface barrier after processing and separation from the portion of the film containing the negative image. The image-protecting layer (E) also contains an image-stabilizing compound which functions as a

Scheme 24



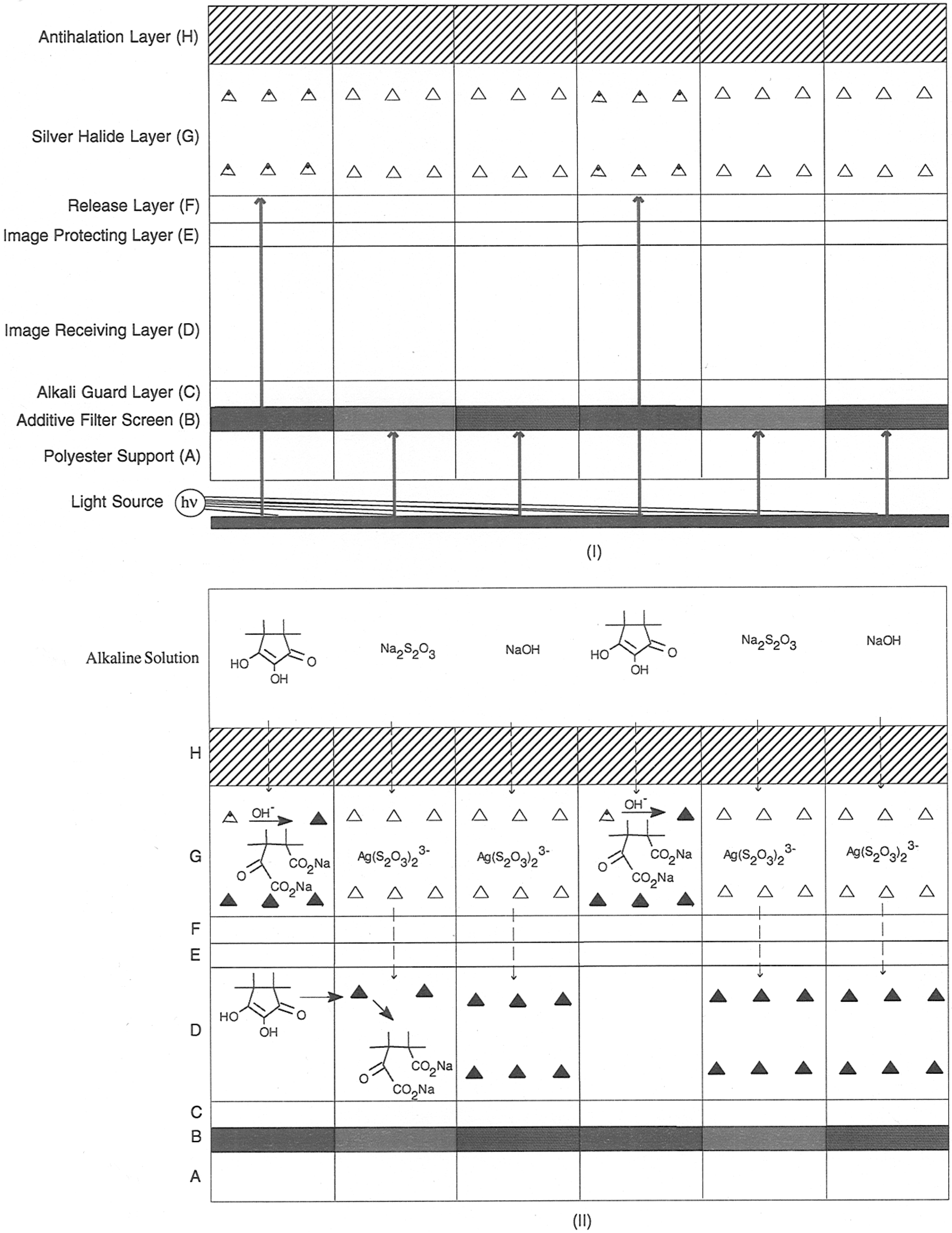
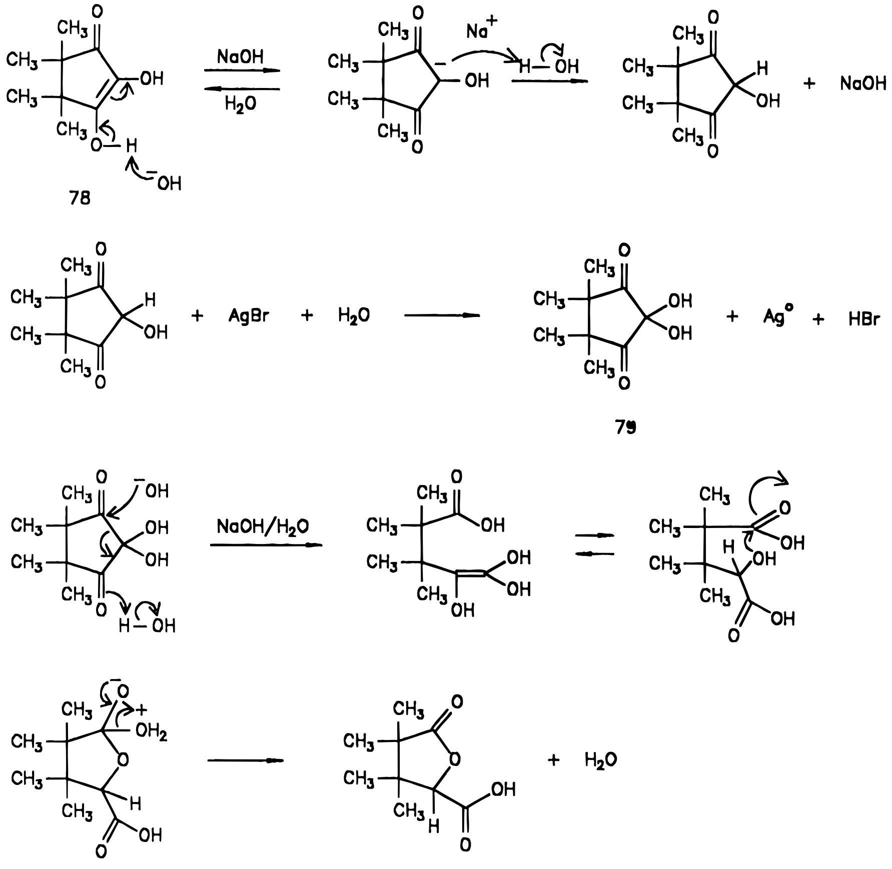


Figure 22. Polachrome film and process. **(I) During an exposure:** For example, red light is reflected off the red object and passes through the color screen. Only passage through the red stripe will result in exposure of the silver halide. **(II) After the reagent has been applied:** The latent image silver halide (◬) is reduced, and the unexposed silver halide is complexed causing it to diffuse into the receiver layer where it is reduced to silver metal. Symbols: (△) unexposed silver halide, (◬) exposed silver halide, (▲) silver metal.

silver metal preservative, protecting the silver from atmospheric degradation and from degradation caused by residual processing chemicals. Over the image-protecting layer (E) a release layer (F) is coated and

Scheme 25



separation of the negative image portion of the film from the positive portion of the film will occur between these two layers (E and F). The next layer forms the photographically sensitive silver halide emulsion layer (G). The light-sensitive emulsion layer (G) contains silver halide grains dispersed in a gelatin emulsion. The final layer of the film is an antihalation layer (H), designed to absorb stray light not absorbed in the photosensitive layer, and thus to prevent reflections of the stray light. After exposure, the alkaline processing fluid is spread over the antihalation layer and, hence, reduction of the latent silver halide and also the transfer of the unexposed silver halide is initiated by the application of the processing solution.

Key components of the film include the additive screen (B), the receiver nuclei, silver halide, an antihalation dye, and an image-stabilizing compound. The additive color screen is a microscopically fine tripack pattern consisting of red, green, and blue lines[228] arranged in a repetitive sequential distribution in a side by side relationship. These lines are so fine that they cannot be seen when projected. Light is passed through the screen to the silver halide. Latent image silver halide reduction occurs after the processing solution is applied. In unexposed areas the silver halide forms soluble silver complexes, and these complexes diffuse to the image receiving layer where they are precipitated by nuclei contained in the image receiving layer (D). Metallic sulfides and selenides which function as nuclei are dispersed in a permeable, transparent gel, such as, gelatin, polyvinyl alcohol or cellulose ethers.[229]

Once the silver ions have been deposited as a result of precipitation by the nuclei, the silver ions are reduced to metallic silver by the reducing agent contained in the alkaline processing solution. Stabilizing compounds migrate to the silver and react to produce a more stable image. These stabilizing agents,[229,230] including gold 2-mercaptobenzimidizole, gold 2-mercaptobenzothiazole, and platinum 1-phenyl-5-mercaptotetrazole, are composed of an organic complexing ligand and a noble metal less reactive than silver. It is thought[229] that a partial replacement of elemental image silver in the image receiving layer by gold provides a decrease in the reactivity of the silver image with residual processing reagents and atmospheric components, thus enhances the preservation of the image. As these reactions proceed the colored antihalation dye is converted to a colorless form by the processing fluid.

2. Alkaline Processing Solution

The alkaline processing solution is designed to reduce the exposed silver halide grains and to transfer the unexposed grains to the image receiving layer where the silver ions are also reduced. The components of the processing solution include a reducing agent, a silver halide solvent, a thickener, an alkali, a solvent, a reducing agent preservative, and a restrainer to minimize indiscriminate reduction of silver halide. Preferred reducing agents suitable for the silver-transfer process are reductic acid derivatives and in particular tetramethylreductic acid (**78**). Tetramethylreductic acid (**78**) is very

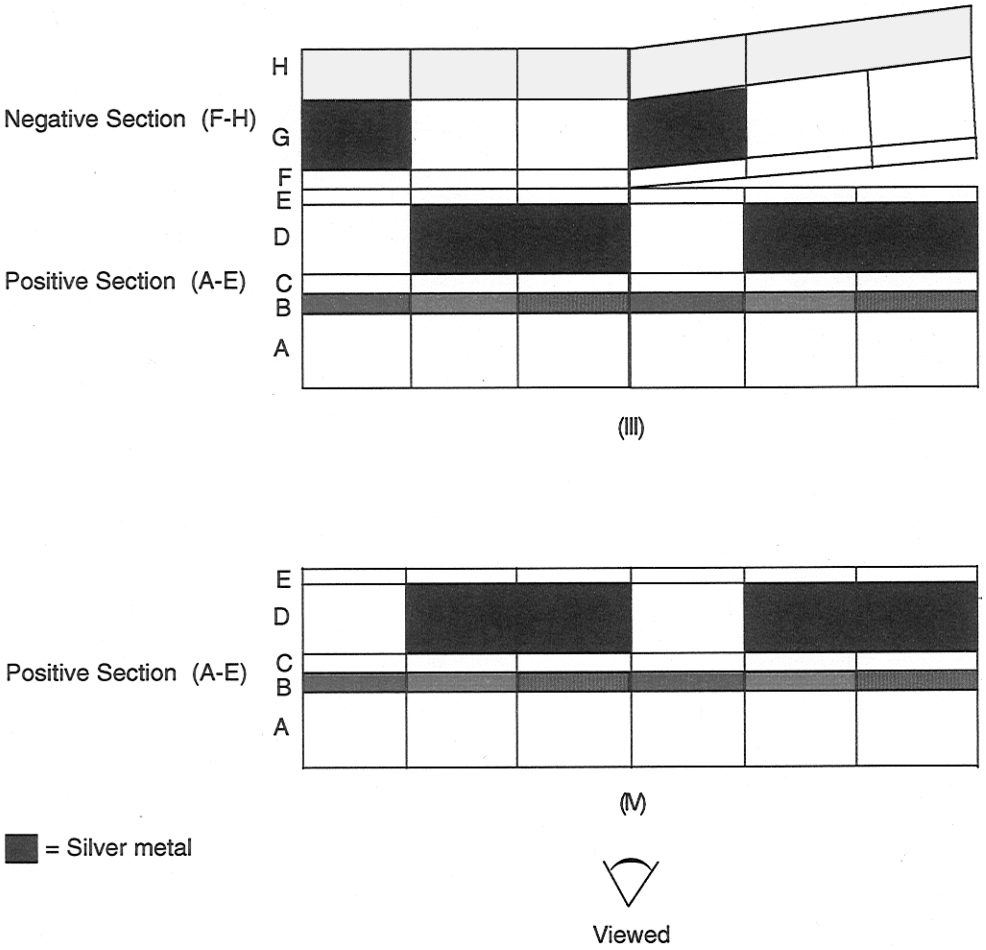


Figure 23. (III) Polachrome film as the negative section of the film, which is discarded, is being peeled off. (IV) The final positive image.

stable in alkaline solution, in the absence of oxidizing agents. When employed as a reducing agent for silver halide, compound **78** is much more discriminate and effective than other common reducing agents.[231] The oxidation of tetramethylreductic acid (**78**) also results in a colorless product **80**. The structure of tetramethylreductic acid (**78**) and reactions[184,231] which occur during and after development are illustrated in Scheme 25. Thus, the reduction of the exposed silver bromide by tetramethylreductic acid (**78**) results first in the formation of the triketone hydrate **79**. Hydrolysis of **79** by hydroxide ions from the alkaline processing solution generates[232] the γ-lactone **80**.

Silver halide complexing agents suitable for complexing unexposed silver halide include thiosulfates such as sodium thiosulfate, thiocyanates such as ammonium thiocyanate, and cyclic imides such as uracil. These compounds form soluble complexes in alkaline solution with silver ions. Usually water is used as the solvent for the alkaline-processing solution. A thickener provides the desired viscosity and spreadability for the processing fluid. Thickeners, which were employed in the dye–developer and dye-transfer processes are also suitable for use in the alkaline solution of the silver-transfer process. The alkali must provide a high pH in excess of 12.0, and common alkaline compounds which satisfy this requirement include sodium hydroxide and potassium hydroxide. Preservatives for prevention of the aerial oxidation of the reducing agent are often present. Usually, sulfite compounds, such as sodium and potassium sulfite, are added. Restrainers, such as sodium and potassium bromide, may be present in addition to surfactants and reducing agent accelerators. An example of the components of a typical processing solution is shown as follows.[230]

Processing Composition

water	11.125 L
carboxymethyl cellulose	600 g
sodium hydroxide	625 g
sodium sulfite	648 g
sodium thiosulfate	1600 g
surfactant (reaction product of nonylphenol and glycidyl)	720 g
nitrobenzimidazole	42 g
tetramethyl reductic acid	700 g

As can be seen in Figure 22, the color screen allows only red light through the red-colored portion of the screen. The silver halide is exposed and developed behind this screen. The blue and green lines absorb the red light so that silver halide behind these lines is unexposed. The negative section of the film is separated from the positive section to produce a positive color image (Figure 23).

VII. Dye–Bleach Process

The silver dye–bleach process[233–235] requires the fragmentation and dissolution of azo dyes, which originally were incorporated in the emulsion, in proportion to the amounts of silver metal which are formed in the image areas of the film. The exposed

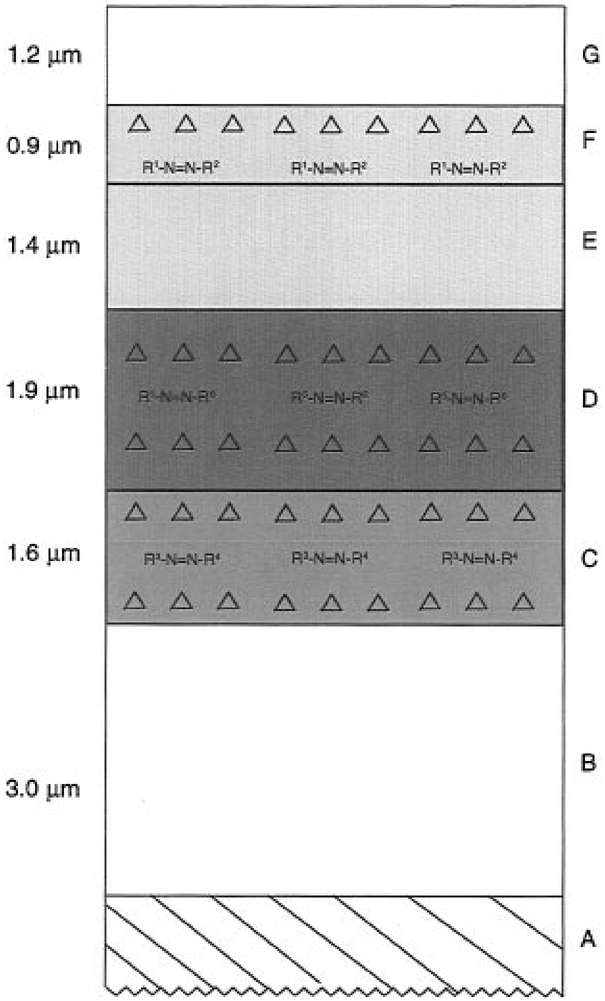


Figure 24. Cross-sectional view of a typical silver dye–bleach photographic paper used in rapid processing. The various layers can be described as follows: (A) support, (B) gelatin layer, (C) red-sensitive layer, (D) green-sensitive layer, (E) yellow filter layer, (F) blue-sensitive layer, (G) protective layer. Dyes are noted by the following: R^1-N=N-R^2, yellow azo dye (**81a**); R^3-N=N-R^4, cyan azo dye (**82a**); R^5-N=N-R^6, magenta azo dye (**83a**). Symbols: (△) silver halide grains.

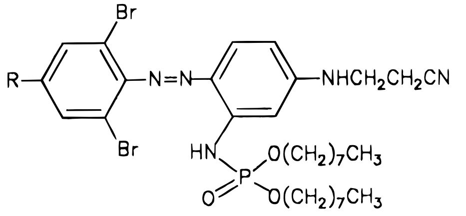
silver halide is reduced when the film is submerged in a developing solution which contains a developing agent. The insoluble silver metal which is formed, in turn, functions as a reducing agent in the presence of a catalyst and a strong acid to reduce the azo dyes to colorless amines. In the areas of the film where the silver halide is not exposed, the azo dyes remain to form a positive image. The dye–bleach process is inherently a positive process; consequently, it is used to produce color transparencies and color prints. The silver dye–bleach process results in colored images with dyes of superior properties to those produced by chromogenic, i.e. color-forming, development. Color images produced by the silver dye–bleach process are superior in brilliance, luminescence, and stability.[16] Azo dyes which are used for the dye–bleach images are more stable to light and acid gases, such as atmospheric sulfur dioxide, than the subtractive dyes produced by the dye-coupled, chromogenic process.[16]

The print paper (Figure 24) employed[236] in the dye–bleach process, represented by material patented by Ciba-Geigy and sold for years under the tradename Cibachrome, is composed of six to nine layers coated over a paper support. Processing of the paper requires four solutions, such as a developing solution, a bleaching solution, a fixing solution, and a washing bath. The latent image silver halide is reduced in the developing solution, the azo dye is “bleached”, i.e. the azo-bonded nitrogens reduced and, thus, solubilized in the bleaching solution by the aid of the formed silver metal, and the residual silver halide is removed in the fixing solution. Discussion of the function and composition of each emulsion layer of the print paper and the three formulated processing solutions which are used in the silver dye–bleach process will follow.

A. Print Paper Emulsion

Several structural versions of the Cibachrome material and methods for processing have been patented[236–242] and published in journals.[233–235] Two distinct types of Cibachrome paper are apparent from analysis of this literature, i.e., conventional materials and materials for rapid processing. Conventional materials provide higher quality prints than the materials for rapid processing, but the processing time is approximately 4–5 times longer.[233] Processing time for the materials for rapid processing may be as short as 5–7 min to produce a color print.[233] A photographic paper for rapid processing is typically constructed of six layers, whereas a conventional photographic paper is constructed typically of nine layers. For the sake of simplicity only the construction and composition of the material designed for rapid processing will be discussed although the chemical reactions which occur are similar to both types of photographic materials. Commonly, the composition of the support distinguishes the material as either a photographic film (transparency) or a photographic print (paper). The transparent film and opaque paper supports are composed of materials, such as cellulose triacetate, and polyester as transparent supports and coated paper and synthetic papers made from either polystyrene or nylon fibers as opaque supports.[236] Over the support (A) is coated a layer of gelatin (B) which functions as an adhesion layer for the remaining layers (Figure 24). Over the gelatin layer (B) is coated a red-light sensitive silver halide emulsion layer (C) containing a cyan dye. Coated over layer (C) is a green-light sensitive silver halide emulsion layer (D) incorporating a magenta dye. Over layer (D) is spread a yellow filter layer (E) which contains a yellow azo dye together with emulsified silver halide. The yellow filter layer prevents excess blue light from exposing the layers beneath. The yellow dye in the yellow filter layer and the silver/silver halide are removed during processing. A blue light-sensitive silver halide emulsion layer (F) containing a yellow azo dye is coated over the yellow filter layer (E). The blue light-sensitive layer (F) is coated by a protective layer (G) of gelatin which shields the underlying layers from abrasion. A schematic cross-sectional view of a typical photographic print paper which is used in rapid processing is illustrated in Figure 24.[236]

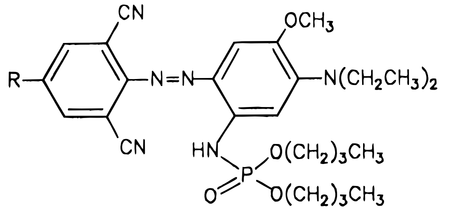
Azo dyes of the *N*-phenylphosphoramic acid diester types are incorporated in the various layers because these types of dyes are very stable and result in brilliant colors with good color rendition. Examples of yellow, cyan, and magenta dyes (**81–83**, respec-



81 R = H, CH$_3$

R^1–N=N–R^2 yellow

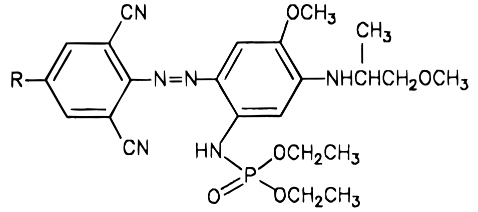
81a



82 R = CN, NO$_2$, CH=C(CH$_3$)$_2$,
CH=C(CN)CO$_2$CH$_2$CH$_3$

R^3–N=N–R^4 cyan

82a



83 R = Cl, CH$_3$

R^5–N=N–R^6 magenta

83a

Figure 25. Examples of *N*-phenylphosphoramic acid diester type yellow, cyan, and magenta azo dyes (**81**–**83**, respectively) which are used in the emulsion layers of silver dye-bleach materials. Structures **81a**, **82a**, and **83a** are shown in figures and schemes to represent **81**, **82**, and **83**, respectively.

tively) which were patented[237] for use in silver dye–bleach processing films and papers are shown in Figure 25.

The azo dyes **81**–**83** are not water soluble; therefore, they are dissolved in an organic solvent, such as ethyl acetate, and a surface active agent is added to improve the dispersibility of the dye in the aqueous colloid of the coating composition. Suitable surfactants include naphthalenesulfonic acids and alkyl phosphates, such as dibutylnaphthalenesulfonic acid and tricresyl phosphate, respectively. Gelatin is commonly employed as the protective colloid; however, other water-soluble protective colloids, such as polyvinyl alcohol or polyvinylpyrrolidone can be used.[238]

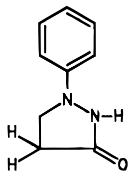
Silver halides, such as silver bromoiodide, are generally incorporated into the gelatin emulsions. Since emulsions of high sensitivity are required in silver dye–bleach material, a part of the incident light is inherently absorbed by the azo dyes during exposure.[236] In addition to silver halides, other emulsion additives are usually required, such as hardening agents and optical sensitizers.

B. Processing Solutions

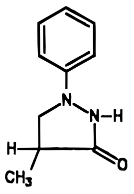
Processing of the sensitized material is achieved by four solutions,[233] i.e., a developing solution, a bleaching solution, a fixing solution, and a wash water bath. Extending the life of the solutions can be realized by the use of wash water baths between each solution. The exposed silver halide is reduced to silver metal in the developing solution. The image dye is then converted to a colorless amine in the strongly acidic bleaching solution. Residual silver metal is also oxidized to silver ions in the bleaching solution, but the silver ions thus formed and the unexposed silver halides are solublized in the fixing solution by the formation of soluble silver complexes. Finally, a wash is employed to remove all of the residuals left in the film. Each of these solutions will be discussed in greater detail.

A developing solution, commonly employed for black on white papers, is also utilized in this case as the first processing solution. Much of what was already discussed on the developing solution formulations in the dye-couple section applies to the developing formulations in this section. However, a short recount is in order.

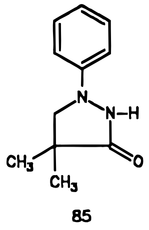
Developing solutions contain a variety of components. Water is always used as the major solvent; nevertheless, organic solvents, such as glycol ethers and alcohols, are sometimes added as components of the formulation to facilitate dissolution of developing agents which have low water solubility. Pyrazolidinones **59**, **84**, and **85** are the developing agents; however, since these developing agents alone are not very effective, they are employed in conjunction with hydroquinone type derivatives. The highest contrast is obtained with the developing agent **59**. With compound **84** an intermediate contrast and with compound **85** the lowest contrast are obtained. Pyrazolidones have limited solublity at the relatively low pH of dye–bleach-type developers; therefore, organic solvents which are misible with water are usually incorporated in the formulations.



59



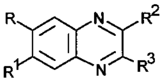
84



85

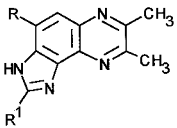
Buffering becomes much more important at the characteristically low pH of these developing solutions, which are used in the silver dye–bleach process, since developing agents, such as hydroquinone, become inactivated at a pH below ap-

Table 2. Examples of Catalysts Which Are Used in the Silver Dye–Bleach Process[239]



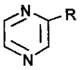
86

R	R¹	R²	R³
H	H	CH_3	CH_3
H	CH_3	CH_3	CH_3
OCH_3	H	CH_3	CH_3
OH	H	CH_3	CH_3
OCH_2CH_2OH	H	CH_3	CH_3
$OCH_2CH_2CH_2SO_3Na$	H	CH_3	CH_3
CH_3	NH_2	CH_3	CH_3
H	NH_2	CH_3	CH_3
H	CH_2OH	CH_3	CH_3
H	CH_2SO_3H	CH_3	CH_3
H	$NHCOCH_3$	CH_3	CH_3
$NHCOCH_3$	CH_3	CH_3	CH_3
H	$NHSO_2CH_3$	CH_3	CH_3
$NHSO_2CH_3$	CH_3	CH_3	CH_3
OCH_3	OCH_3	H	CH_3
OH	CH_3	CH_3	CH_3
OCH_3	OCH_3	CH_3	CH_3
OCH_3	CH_3	CH_3	CH_3
CH_3	CH_3	CH_3	CH_3
OCH_3	NH_2	CH_3	CH_3
OCH_3	$O(CH_2)_3SO_3NH_4$	CH_3	CH_3
OCH_3	OCH_3	CH_2SO_3Na	CH_3
OCH_3	$O(CH_2)_2SO_3NH_4$	CH_3	CH_3
OCH_3	OCH_3	CH_2OH	CH_3
OCH_3	OH	CH_3	CH_3



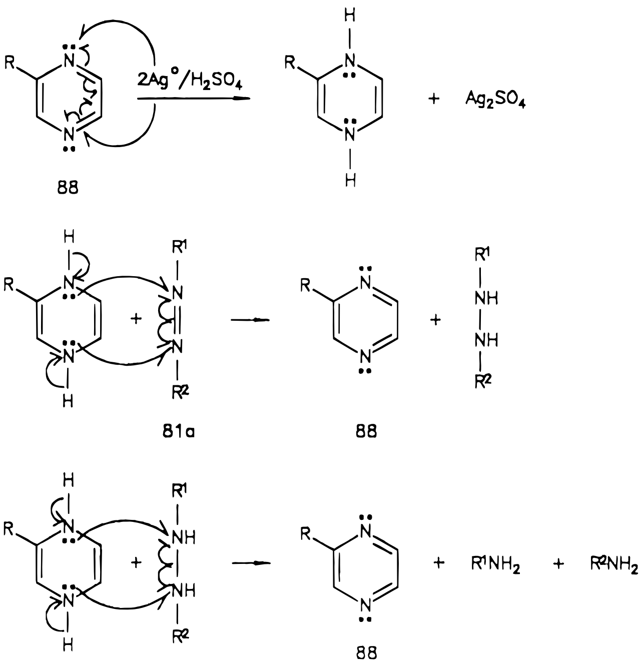
87

R	R¹
H	H
H	CH_3
OCH_3	H
OCH_3	OCH_3



88 R= H, CH_3

Scheme 26



proximately 9.0. Carbonates and borates are commonly incorporated as buffering agents. Restrainers, such as sodium bromide and iodide, are employed either alone or in combination with such organic compounds, as benzotriazole (**24**) and 6-nitrobenzimidazole (**25**). Sodium or potassium sulfite is usually incorporated in the developing formulations as a preservative for minimizing aerial oxidization of the developing agents. An alkaline compound, such as potassium or sodium hydroxide is often added to developing solutions to reach a desirably high pH. Other components, such as chelating agents, hardeners, development accelerators, and bleach catalysts may be added to the developing solution.

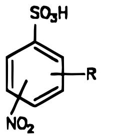
Bleach catalysts **86–88** (Table 2)[239] are most often present in the bleaching solution where the catalysts are activated by a strong acid. These catalysts, employed in amounts ranging from 0.05–10 g L^{-1}, serve as mobile agents by migrating between the insoluble silver metal and the insoluble azo dye. This process involves a series of redox reactions. Thus, the bleach catalyst is reduced at the silver surface, and, as the latent catalyst migrates through the gelatin layer, a redox reaction occurs with the azo dyes whereby the azo dye is reduced and the latent catalyst is reoxidized to its original form. A very simplified mechanism is shown in Scheme 26[233] for **81a**. Analogous schemes for **82a** and **83a** are not shown.

The pH of a bleach solution is typically below 1.0. In order to obtain such low pH levels, strong acids, such as sulfuric and sulfamic acids are incorporated. In addition to a bleach catalyst and a strong acid, the presence of a source of suitable silver ligands is required. The redox potential of silver metal is lowered to zero or to negative values as measured against the normal hydrogen electrode by the presence of ligands which form insoluble silver salts.[233] Iodides, such as potassium and sodium iodide, are frequently employed but the use of iodides has certain disadvantages, such as liberation of iodine during storage, and formation of silver iodide during processing. Furthermore, silver iodide is removed only with difficulty from the emulsion layers of the film by the fixer solution. Nevertheless, when formation of silver iodide is unavoidable, antioxidants can be added to preserve the iodide from oxidizing during storage. Reductones, water-soluble mercaptans, aldehyde–bisulfite adducts and water-soluble phosphines are examples of suitable antioxidants. Ascorbic acid, thioglycerol, formaldehyde–bisulfite and sodium salt of bis(2-cyanoethyl)-2-sulfoethylphosphine serve as specific examples of each category. When mercaptans are employed they function not only as antioxidants, but also as corrosion inhibitors for the metallic parts commonly used in the mechanized film processors. The incorporation of phosphines as antioxidants have an additional advantage as well. Phosphines also function as bleaching accelerators by lowering the charge barrier of the gelatin, and thus allow a more facile penetration by the bleaching solution into the various emulsion layers.

Whenever acceleration of the bleaching process is desired, in the absence of phosphines as antioxidants, quaternary nitrogen compounds can function as bleaching accelerators. Some specific examples of such bleaching accelerators include tetraethylammonium iodide and *N*-methylpyridinium iodide. Quaternary nitrogen bleaching accelerators may or may not be present in the bleaching solution but when present they are added to the formulation in concentrations of from 1 to 5 g L^{-1}.

Another component of the bleaching solution is a water-soluble oxidizing agent which participates in the conversion of residual silver metal to silver ions.

Aromatic mononitro and dinitro compounds **89**, such as 2,4-dinitrobenzenesulfonic acid, 2-amino-4-nitrobenzenesulfonic acid, and 1-hydroxy-4-nitrobenzene-2-sulfonic acid, are often employed for this purpose in amounts ranging between 1 to 30 g L^{-1}. The reduction of nitrobenzene in acid media was believed to occur by a series of two electron steps.[243] A plausible sequence for a stepwise reduction of the nitro group in **89**, involving metallic silver in the presence of sulfuric acid, is shown in Scheme 27. In order to separate the oxidizing agents from the reducing agents during storage, the bleaching solution is usually packaged in two parts. One part of the bleaching solution contains the bleaching catalyst, the iodide, the antioxidant, and the accelerator. The other part contains the oxidizing agent and the acid. Both parts may also contain solvents for solubilizing the organic components in the aqueous solutions. Often concentrates of the bleaching solutions are employed. The ready for use bleaching solutions are either prepared by simply combining the two bleach parts without further dilution with water, or water is added to the concentrate at the time of use.



89 R = H, CH_3, Cl, NO_2, NH_2, OCH_3, OH

Catalysts for the bleaching process are usually either quinoxalines of type **86** and **87** or pyrazines of type **88** (Table 2),[239] although other catalyst classes, such as phenazines and naphthazines have been mentioned[233] in the literature. A disadvantage of pyrazine derivatives is that they often have a strong bleaching effect on adjacent layers which causes color distortions, and phenazine and naphtazine derivatives are usually colored species, and thus may cause staining as a result of the absorption by gelatin. In contrast, quinoxaline derivatives, such as 2,3-dimethylquinoxaline and 2,3,4-trimethylquinoxaline, are more suitable with regard to diffusion and absorption.[233] In practice, two types of quinoxalines with different redox potentials are usually employed.[233] Preferred compounds include 2,3,6-trimethylquinoxaline with a redox potential of +2 mV and 6-hydroxy-2,3,7-quinoxaline with a redox potential of −46 mV.[239] The two catalysts of the quinoxaline type are required to have at least a redox potential difference of 15 mV in order to be effective as a catalyst combination.

The mechanism for the reduction of quinoxaline type catalysts has been studied[244−248] and found to be a series of reversible reactions, resulting in two products of types **90** and **91** (Scheme 28), one of which is a poor reducing agent for azo dyes. The tautomeric reaction of the 1,4-dihydro species **90** to the 1,2-dihydro species **91** is fast in the forward direction and slow in the reverse direction. The azo dyes are bleached only by the 1,4-dihydro compound **90**.

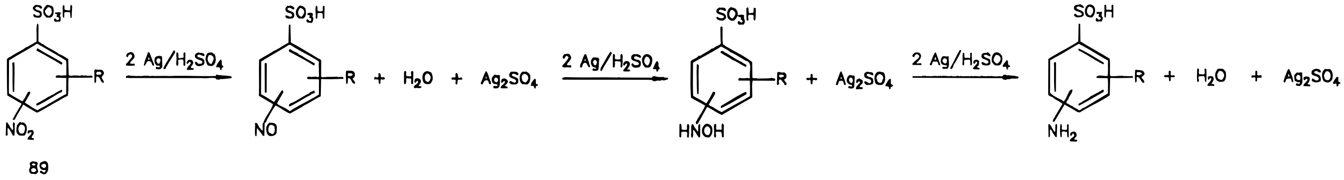
The half-life for the 1,2-dihydro compound **91** is at least 60 times longer than that of the 1,4-dihydro compound **90**. Consequently, interlayer bleaching is minimized. The 1,2-dihydro compound **91** could accumulate for hours or even days in the solution if left unchecked; hence, to prevent wandering of the 1,2-dihydro compound **91** from the layer in which it was generated, an oxidizing agent is incorporated into the interlayers of the emulsion. A simplified mechanism for the azo dye decomposition is illustrated in Scheme 29. The composition of a typical bleach is as follows.[237]

Cibachrome Bleaching Solution

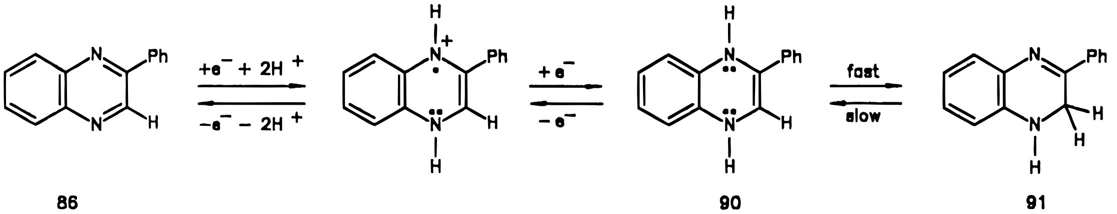
water	1950 mL
sulfuric acid, concentrated	56 mL
4-mercaptobutyric acid	2 mL
sodium iodide	18 g
disodium salt of 1-hydroxy-4-nitrobenzene-2-sulfonic acid	12 g
6-methoxy-2,3-dimethylquinoxaline	2 g

After the bleaching step of the silver dye−bleach process, the next step is the removal of the silver halides. A fixing solution is employed to solubilize all of the silver halide, and as a result of transfer of the highly acidic bleaching solution into the fixing bath, a high pH fixer is necessary. If the pH of a fixing solution containing thiosulfate is allowed to drop below a pH of around 4.0, sulfur precipitates will then form from decomposition of the thiosulfates in the fixing solution. A wash bath between the fixing solution and the bleaching solution significantly reduces the transfer of bleaching components and thus allows the use of a “normal” fixer, i.e., with a lower pH. Sulfites, such as ammonium and sodium

Scheme 27



Scheme 28



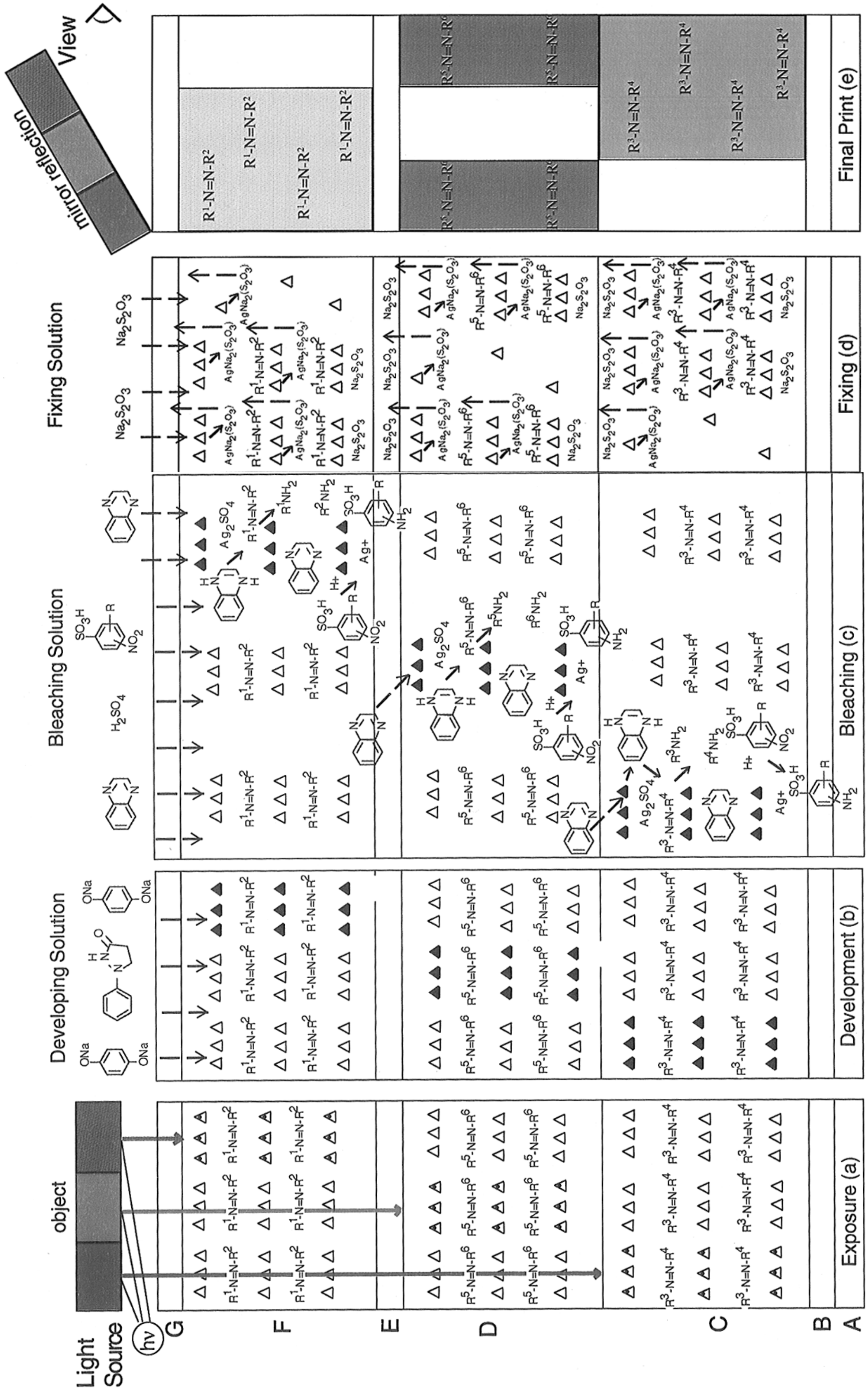
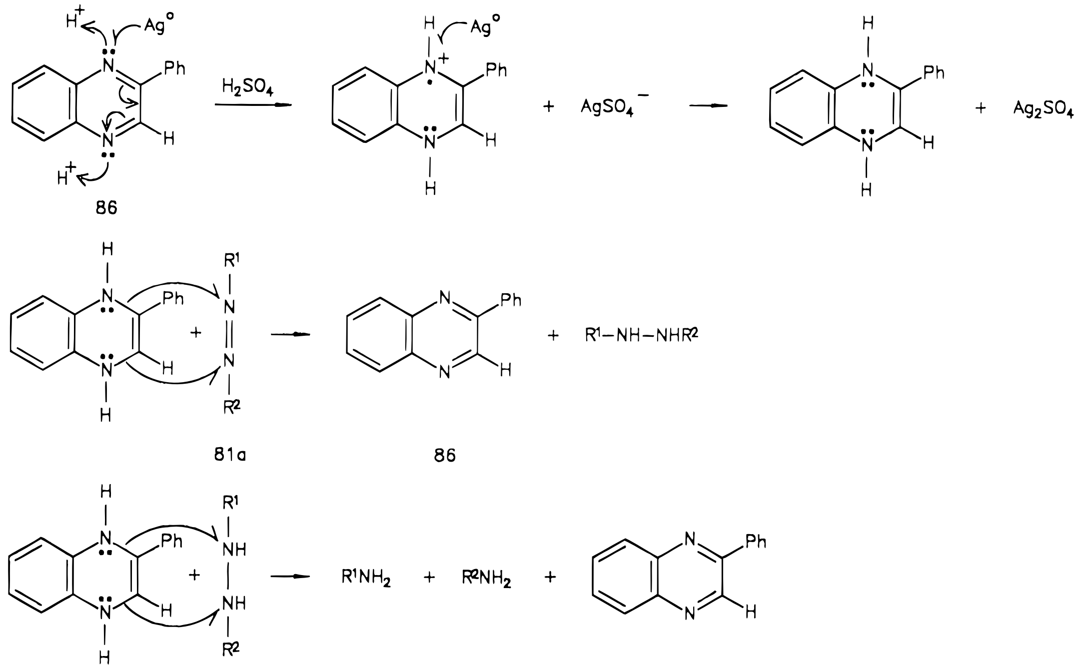


Figure 26. Dye–bleach print paper during various stages of processing. (a) The paper contained in the camera is exposed after reflection of light off a colored object. (b) The paper is removed from the camera and submerged sequentially in the three processing solutions, i.e. developer (b), bleach (c), and fixer (d). When the print is viewed either directly, or by reflection from a mirror, the colors add to reproduce the original colors of the object (e). See Figure 25 for the chemical structures of **81a**, **82a**, and **83a**: R^1-N=N-R^2, yellow azo dye (**81a**); R^3-N=N-R^4, cyan azo dye (**82a**); R^5-N=N-R^6, magenta azo dye (**83a**).

Scheme 29



sulfite, are also present as preservatives for thiosulfates. Thiosulfate, such as sodium and ammonium thiosulfate, are often employed as sources of ligands for the formation of soluble silver complexes. Buffering agents, such as sodium acetate, sodium borate, and sodium citrate, are added to retard the rate at which the pH of the fixer is lowered as a result of the transfer of the bleaching solution into the fixing solution. Water is usually employed as a solvent and often chelating agents are added in the case that hard water is encountered.

Minerals in water coat the automated processor, i.e., the mechanized device which transports the film into the various processing solutions, by forming insoluble compounds. Even worse, the insoluble compounds may coat the final print. Hard water residues may also cause scratches to the emulsion. Nevertheless, it is recommended to use regular tap water when washing processed films. The final washing bath of the process is more critical than expected since washing with soft, distilled, or deionized water may result in prints with red-brown, muddy black areas, and red-brown streaks, variations from print to print in red or magenta, including black areas, and physical damage such as a peeling off of the emulsion or a very soft, easily damaged print surface.[249] The final wash is designed to remove all undesirable residues remaining in the emulsion layers after completion of the processing cycle. The stepwise processing sequences of the silver dye–bleach process, and the chemical reactions which occur during processing to form a colored reproduction are illustrated in Figure 26.

The biggest disadvantage of the silver dye–bleach process has been its slow speed. Because of the presence of azo dyes in the film, light, which would otherwise expose silver halide, is absorbed by the colored dyes. This absorption results in a reduced film speed.

VIII. Electronic Photography

Electronic photography[20] (Figure 27) involves the conversion of light from an object into an electronic signal, and use of that signal to either produce a photograph or to distribute the electronic information for later reference. In conventional photography, the image information is "stored" in the silver halide emulsion of a film. In electronic photography, the image information is "stored" either on magnetic tapes or disks. To obtain a color reproduction, in conventional photography, requires processing of the film in either a solution or a series of solutions, as has already been discussed. To obtain a color reproduction in electronic photography requires an electronic printer. Thus, electronic photography requires a means to "capture", "store", and convert the image information into a color photograph.

An electronic camera is employed to "capture" and "store" the image information. The components of the camera which convert and store the image information are the imaging device, the recording circuitry, and the memory device. The photons from an image are absorbed at the photosensitive sites, called pixels, on a photosensor, and thus electrons are generated as an image signal. Pixels are tiny dots which map out the image on a solid-state chip, i.e., the photosensor. The electronic signal is stored on either a disk or a tape which can be inserted into a player to be either viewed on a video screen or made into color prints by use of a processor, copier, or printer. The most common devices which generate color pictures from the image signal stored on a disk employ the principles of either thermal ink transfer, electrophotography, ink-jet printing, or conventional photography.

Replacement of silver-based films with electronic recording devices represents a major breakthrough in the science of color photography. The advantages of electronic imaging make it an attractive alternative to conventional photography. Benefits include

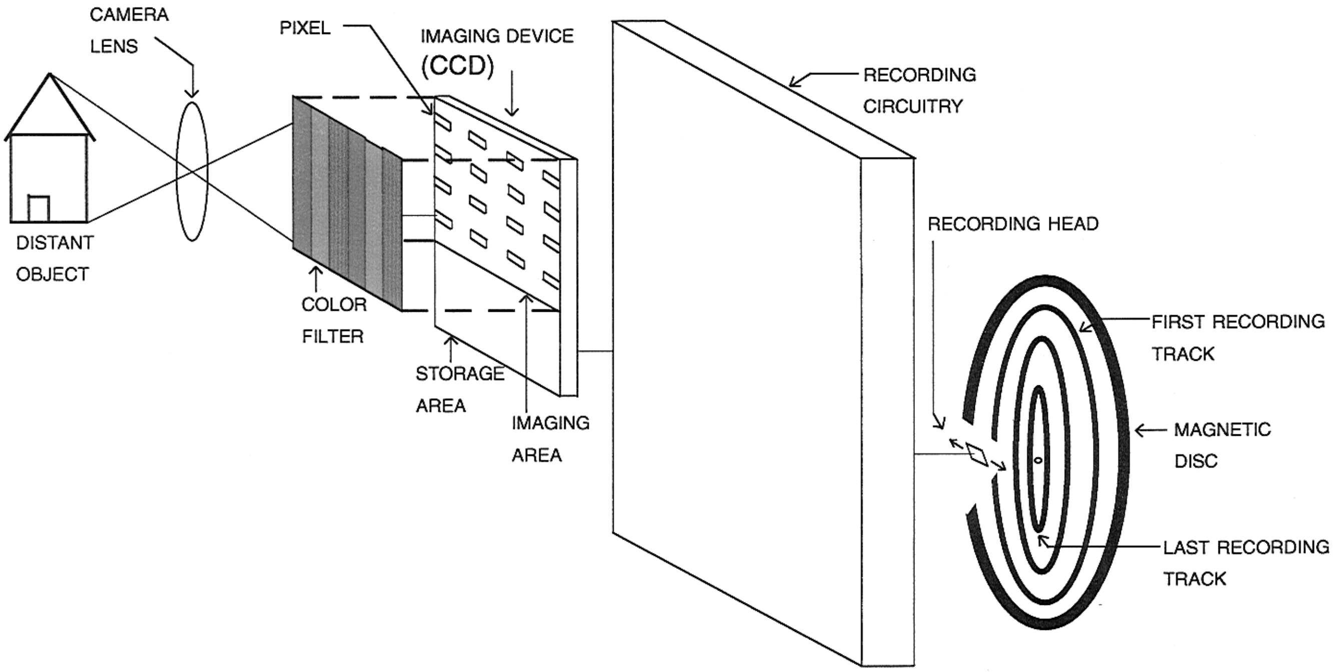


Figure 27. Rendition of image capture and storage using an electronic still camera.

a decrease in time and effort to generate a color print with acceptable quality. A decrease in the amount of space and time required to store and retrieve image information. And finally, the option of distributing image information around the world in a few minutes via electronic communications.[250] These advantages, among others, as well as disadvantages, will be recognized as the details of electronic photography are discussed.

A. Electronic Still Camera

In 1981, Sony introduced the first amateur electronic camera for still photography, called the MAVICA (Figure 27). Since this pioneering product was unveiled, other companies have developed similar electronic photography products.[20] In fact, many color digital cameras, such as the Kodak DCS, the Fuji DS, the Casio QV, and the Ricoh RDC series of cameras among others[251] are commercially available at prices under $500. However, the original Sony camera will serve as an example of electronic photography since its components have been explained[252] in some detail. The MAVICA, i.e., *ma*gnetic *vi*deo *ca*mera, consisted of three major components, i.e., an imaging device for capturing the optical image, recording circuitry for converting the imaging information into an electronic signal, and a memory device for storing the signal for playback. Although a magnetic disk is mentioned as the means of image storage, other types are possible.[20] The WORM (write-once read-many) technology is an example of storing optical color image information.[253]

The original imaging device was composed of a chip measuring 11.0 × 12.1 mm, divided into two sections, the imaging area and the storing area. The imaging area measured 6.6 × 8.8 mm and contained 570 horizontal and 488 vertical pixels. Over the image area was coated a colored filter striped with red, green and blue lines. The storing section of the imaging device functioned as a temporary storage area for the image signal generated in the image area. The image information was temporarily stored in the storage area until the recording circuitry could accept it. The imaging device in the MAVICA contained a solid-state charge coupled device (CCD).[252]

Analog circuitry with frequency modulation was used for the recording circuitry. The circuitry was designed to accept the color signal from the CCD and to convert it into two signals, i.e., a luminance signal and a chrominance signal. The luminance and chrominance signals were then recorded, in the form of frequency modulation (FM) signals, on a magnetic disk.

The FM signals were stored on the magnetic disk either for immediate or for future playback. The flat, round disk was composed of a polyester base coated with a metal alloy powder. A protective plastic casing covered the disk. The entire size of the disk measured only 60 × 54 × 3 mm and weighed only 8 g.[252] The ferromagnetic coating was a smooth, uniform layer of particles which had very few surface irregularity. A smooth, uniform surface was required to produce a high signal to noise ratio which translated into a picture of acceptable quality. The recording pattern began on the outer most track and then moved across the radius of the disk, recording subsequent images. A total of 50 pictures were recorded on one disk.[252]

The disk could be inserted into a playback unit which displayed the pictures on a television screen. The pictures could then be scrutinized to determine which pictures should be printed. Despite improvements in this system the resolution in a solid-state imager is still lower than in conventional photography.[254] Increasing the number of pixels, from 280 000 to 600 000,[20] which are contained in the image area, has improved the quality of the electronically imaged pictures, however, the picture quality is also related to the quality of the printer.

B. Electronic Printers

Electronic printers are designed to convert an electronic signal into a color print. With non-silver halide based printers, color reproductions can be made with either colored inks or colored powders. Silver halide photographic papers can also be used to generate a color print from an electronic signal. The most commonly employed non-silver halide based printers are thermal transfer printers, electrophotographic printers, and ink-jet printers. Conventional printers are designed to utilize silver halide-based papers and films like those already discussed. Each of these types of printers will be explained briefly.

1. Thermal Transfer Printers

In thermal transfer printers,[20,255−258] a solid waxy ink is transferred from a donor ribbon to a receiver sheet by application of heat to the donor ribbon (Figure 28a).[257,259] Although there are a number of related thermal transfer methods,[257,258] the method of dye diffusion has come closest to matching the quality of conventional photographic reproductions and, for this reason, will be used to illustrate thermal transfer printing. Three major components of the thermal printer are necessary to produce a colored print, i.e., a thermal printhead, an ink containing donor ribbon, and a receiver sheet. The thermal printhead receives the electronic signal and converts it into heat. In thermal transfer printers usually a thermal printhead is employed which consists of a row of resistive heating elements measuring the width of the paper. Each element in the printhead corresponds to one pixel in the printed image and energy pulses from the elements are applied to the donor ribbon.[256]

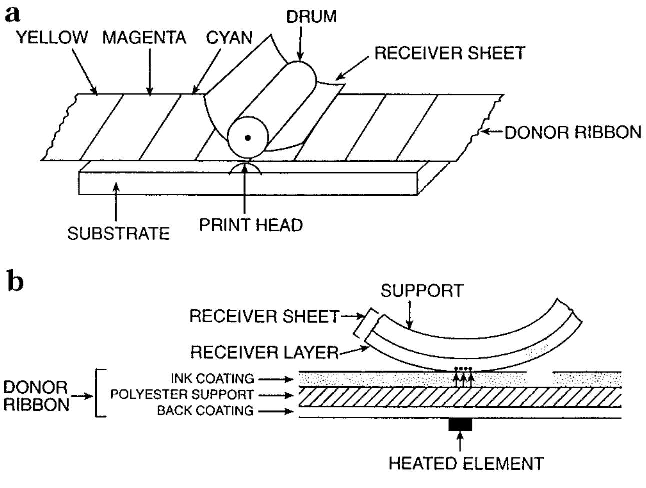
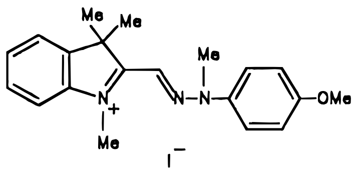


Figure 28. (a) Mechanics of a thermal transfer printer and (b) transfer of ink from donor ribbon to receiver sheet as a result of heat transfer from heating element contained in printhead.

Application of heat to the donor ribbon by the heating elements causes the ink in the donor ribbon to melt and to transfer by diffusion to the receiver sheet as the receiver sheet comes in contact with the donor ribbon (Figure 28b). The ink solidifies in the receiver layer of the receiver sheet to form the image. The donor ribbon is usually composed of a support material made of polyester, but high-density condenser paper and cellophane are also utilized.[256] Over this support is coated a thin layer of waxy ink. The ink layer typically contains dyes and binders, such as, polyvinyl butyral,[260] cellulose acetate butyrate,[261] and carboxy methyl cellulose.[262] Examples of yellow, magenta, and cyan dyes (**92**−**94**, respectively) employed as colorants in the ink coatings of the donor ribbon are shown in Figure 29.[263] A heat-resistant back coating made of polyurethane[264,265] is often present to serve as a barrier between the support and the heating element. The receiver sheet is usually composed of a white support and a receiver layer. The support is typically either a paper-based, plastic-coated material or a white-pigmented plastic. The receiver layer is normally a clear, thin layer composed of either polyester or polycarbonate.[257] A color print is obtained by sequentially printing images in the three subtractive primary colors, yellow, magenta, and cyan.[256] The receiver sheet is repositioned after the first color is applied and the next color superimposed on the previous.



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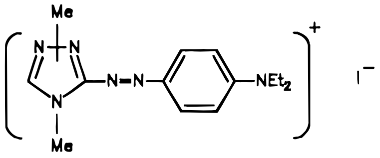

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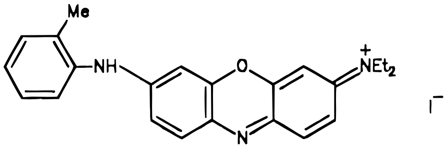


94

Figure 29. Examples of yellow, magenta, and cyan dyes (**92**−**94**, respectively) employed as colorants in thermal transfer printing.

In order for the ink to adhere preferentially to the receiver sheet rather than the donor ribbon, manipulation of the wetting coefficient and the chemical compatibility of the ink with the receiver layer is necessary.[256] In addition, the inks must be selected so that they adhere well to each other as they are applied vertically in layers.

The simplicity, reliability, quiet performance, and print quality of the thermal transfer printer has made it a popular choice among users. The thermal transfer printer is generally useful for text and graphics but not for high quality color prints. To reproduce color photographs, pixels with 6−8 bits (64−256 levels) per color at resolutions greater than or equal to 200 pixels per inch are required. Thermal diffusion transfer printers such as the Kodak 8600 family of printers represent this class of printers. The design of these printers is similar to the thermal wax printers except controlled levels of power are applied at each resistor in the head to drive controlled quantities of a diffusible dye into the receiver sheet. These printers are used in digital print stations and as small format printers for home use as video printers.

2. Electrophotography

Electrophotography[257,266,267] involves the interaction of light and an electrostatic charge to produce an image. The process requires a uniformly applied electrostatic charge to a photoconductive surface, such as arsenic triselenide, coated on either a metal drum or belt. The surface charge may be either positive or negative. Exposure of the charged surface, for example, by a laser beam, dissipates the charge wherever the radiation strikes the photocoductor surface (Figure 30). As an imaged surface is passed by the toner roller, the toner particles adhere to the image areas and are subsequently transferred to a receiver sheet. The toner on the receiver sheet is fixed in place by fusing the particles to the receiver with heat. Colored copies are achieved by sequential but separate application of the three primary subtractive colors plus black to the receiver.

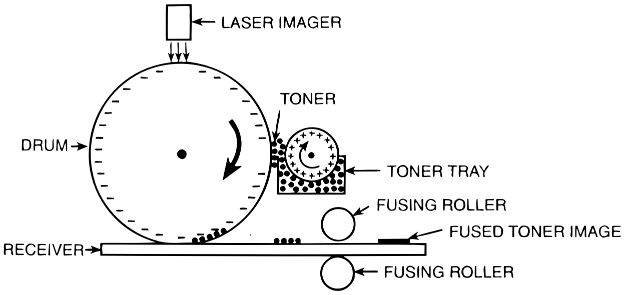


Figure 30. Electrophotographic printer process.

Colored toners are typically composed of a colorant, a charge control agent, and a resin. Dry toners are most prevalent but liquid toners result in higher resolution prints. Toners contain either pigments or dyes as colorants. Examples of a yellow pigment **95**, a magenta pigment **96**, and a cyan pigment **97** are illustrated in Figure 31.[268] One advantage to using pigments is that they do not readily diffuse during the fusing step as is often the case with dyes.[257] Examples of a yellow dye **98**,[269] a magenta dye **99**,[270] and a cyan dye **100**[271] are illustrated in Figure 32. Toners based on dyes rather than pigments often result in prints with a better color rendition.[257]

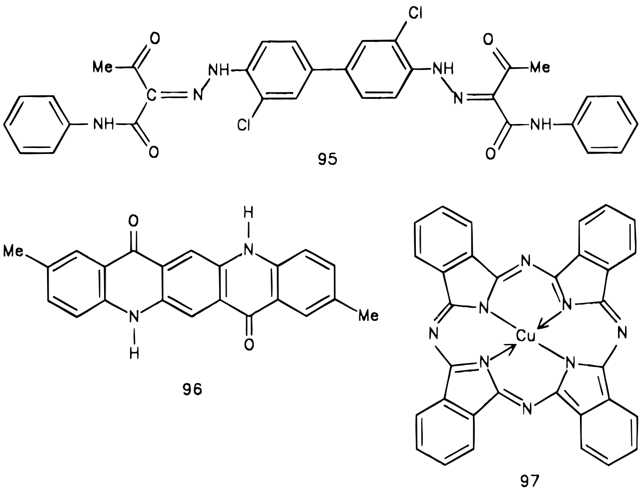


Figure 31. Yellow, magenta, and cyan pigments (**95**−**97**, respectively) used in electrophotographic toners.

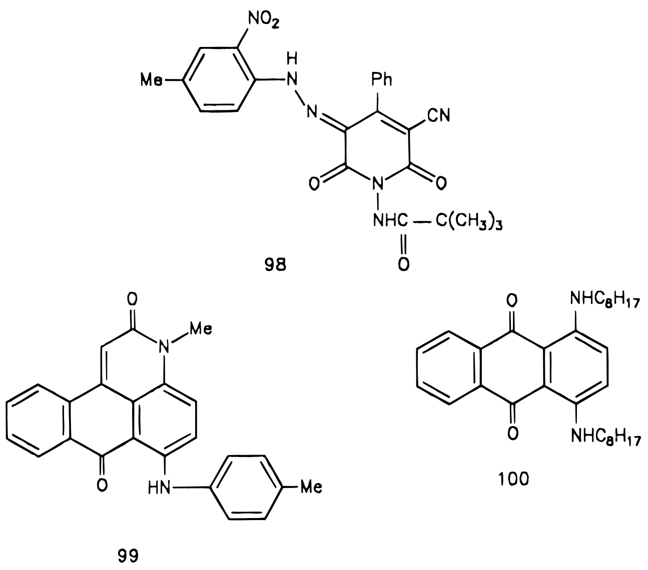


Figure 32. Yellow, magenta, and cyan dyes (**98**−**100**, respectively) used in electrophotographic toners.

In addition to a colorant, toners often contain a charge control agent to impart an electrostatic charge. Chromium complexes of aromatic *o*-hydroxy carboxylates[272−274] and quaternary ammonium compounds[275−283] are typical examples of charge couple agents used in color toner formulations. Toners also contain a resin usually composed of a styrene acrylate.[257] Liquid toners additionally contain hydrocarbon dispersants, such as Isopar G and Isopar H.[267]

The major disadvantage to the electrophotographic process is that it requires three passes or four passes, if black is also applied, to achieve a colored print. In contrast, the related electrophoretic process[266,267] of producing a colored image requires only one pass. The electrophoretic printing process[284] functions by a migration of charged solid particles in a fluid bed when an electric field is applied (Figure 33). The electric field is applied by a line of recording electrodes, containing 120 electrodes per millimeter. The toner suspension is pumped into the gap between the recording electrode and the drum by a supply nozzle, and the excess is removed by a suction nozzle positioned on the opposite side of the recording electrode. In this way a continuous flow of toner is supplied to the image area.

The toner suspension is composed of positively charged, colored toner particles and positive and negative ions, which are dispersed in a highly insulating carrier liquid. By applying a positive voltage to the recording electrode, toner particles are deposited on the image carrier.[284] Higher voltage results in greater color density. Higher toner particle concentration also results in greater image color density. Generally, toner concentrations in the suspension vary from 0.1 to 0.3%.[284]

A collecting roller removes nonadhering residual toner before the image is transferred to a paper receiver. The image transfers by application of a charge to a transfer roller which is behind and in contact with the receiver paper. An example of the

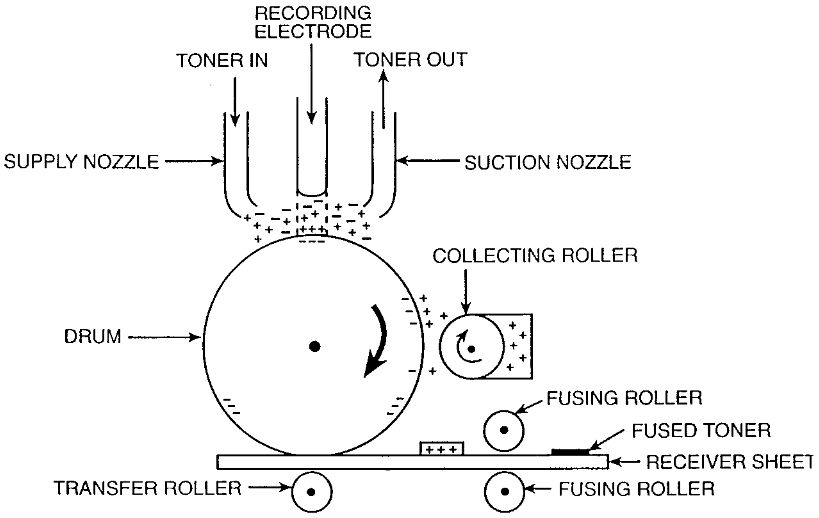


Figure 33. Electrophoretic printing process.

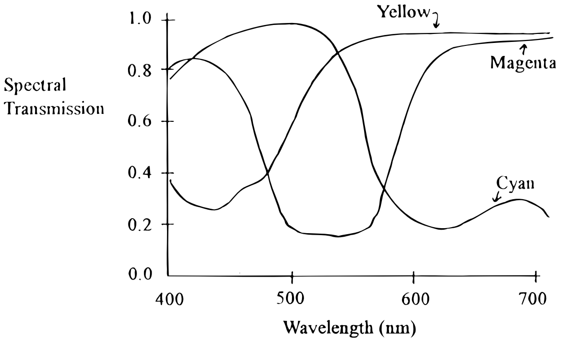


Figure 34. Spectral transmission of yellow, magenta, and cyan toners after electrophoretic application.

spectral transmission of toners used in this process is shown in Figure 34.[284]

It is apparent from Figure 34 that electronic color correction and masking techniques will be necessary to match ideal spectral transmission curves for the subtractive dyes. Increasing the number of electrodes per millimeter would help in the future to produce images of improved resolution.

3. Ink-Jet Printers

Ink-jet printing[20,257,285] involves direct deposition of ink on to a receiver sheet by means of a spray of microscopic ink droplets. An electronic signal causes a pressure wave to be applied to a capillary tube containing ink. This sudden contraction increases the pressure inside the capillary, and thus forces out a drop of ink directed toward the receiver sheet. An image is obtained by a matrix of dots. There are two basic types of ink-jet printers, i.e., impulse and continuous printers. The so-called impulse or drop-on-demand printer differs from the continuous stream printer in one fundamental aspect. The continuous ink-jet printer (Figure 35) contains ink which exits the capillary orifice as a continuous stream. This stream can be broken up into ink drops at a distance from the orifice. An electric potential is established between the ink and a ring-shaped control electrode. The electrode is positioned at the point of drop formation near the ink jet orifice. The spray is generated as a result of electrostatic repulsion between the drops of the jet and the ring-shaped electrode.[286] By varying the voltage, the flow of ink can be altered between linear and spray mode. The continuous printer deflects the flow of ink when there is no image, and drains it to either a reservoir or gutter for either recycling or discarding. A transverse deflection field is generated by the deflection plates which causes the ink stream to be diverted.

Where the continuous ink-jet printer has its flow of ink deflected when there is no image signal, the flow of ink is stopped with the impulse printer (Figure 36). In impulse printers, pressure control is achieved by the combined action of surface tension of the ink in the orifice of the capillary and the pressure generated by deflecting the elastic walls of

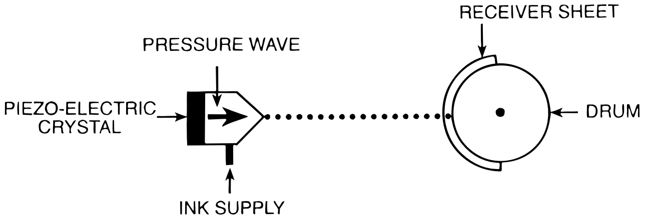


Figure 36. A diagrammatic presentation of an impulse printer.

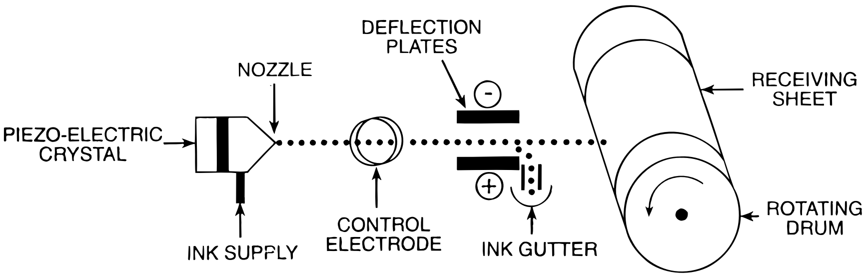
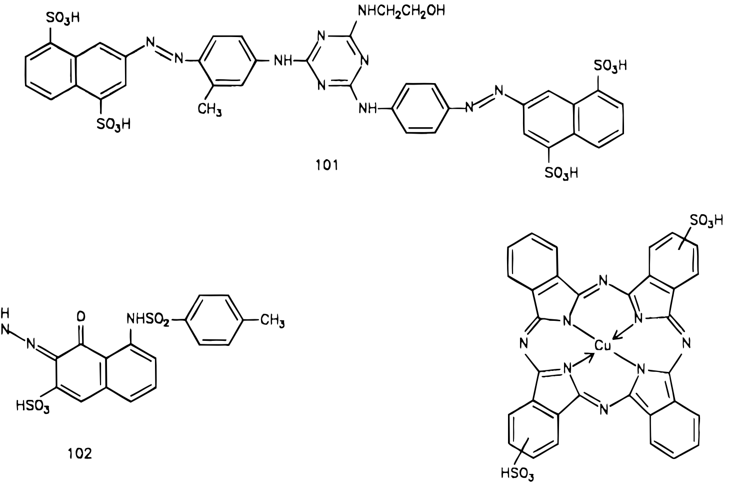


Figure 35. A diagrammatic presentation of a continuous ink-jet printer.


101

102

103

Figure 37. Yellow, magenta, and cyan dyes (**101**−**103**, respectively) employed as colorants in ink-jet printing.

the ink chamber.[287] A so-called piezoelectric crystal is often employed to generate the wall deflection.

Inks designed for ink-jet printing are very specialized. They generally are composed of dyes instead of pigments, have low viscosity, high surface tension, and are usually aqueous-based.[288] A typical example of a yellow dye **101**,[289] a magenta dye **102**,[257] and a cyan dye **103**[290] employed as colorants in aqueous-based ink formulations are shown in Figure 37. Pigments are not used as colorants in inks because they tend to clog the ejection nozzle. Humectants, such as glycerine and diethylene glycol, are added to ink formulations to retard the evaporation of water from the ink, and thus reduce a clogging of the nozzle.[285] Other components, such as organic solvents, biocides, and chelating agents, are sometimes incorporated in the ink formulations. A closely related ink jet technology that is being employed today is the so-called "bubble jet" printer. The ink in a bubble jet printing head is rapidly heated by a resistive element, the ink is vaporized, and the high pressure of the boiling ink results in ink droplet ejection from the nozzle of the printing head.[291,292]

Ink-jet printers offer quiet operation, high speed, and compatibility with a range of receiver sheets, such as paper, film, cardboard, and metal.[285] Ink-jet printers are already prevalent as devices for computer printouts, and photorealistic color prints have also been produced.[20]

4. Conventional Photographic Printers

Electronic photography has not totally divorced itself from the silver halide emulsions. Dominant companies in the field of conventional photography have also sought[20] to find a niche in the market of electronic reproduction by exploiting the poorer quality of the other unconventional methods.

Hence, printers have become common[293−296] which were designed to use conventional photographic papers and films. In these printers (Figure 38) cathode ray tubes (CRT) coated with phosphors as light sources are mainly used to sensitize the silver halide materials. For example, the P45 phosphor can be used as source for both blue and green light and the P22-RE3 phosphor can be used as a source of red light.[293] Blue and green colored filters are placed over the P45 phosphor to reduce spectral overlap of the emissions. A red filter is placed over the P22-RE3 phosphor for the same purpose. In conventional printers the film is either scanned by a moving lens of the CRT, or the film is transported to provide a latent image on the silver halide based paper or film. Interpolation methods were developed to make the scanning line structure invisible, resulting in a smoother picture. Instant photographic films[295] are useful for providing colored prints since they do not require elaborate processing solutions.

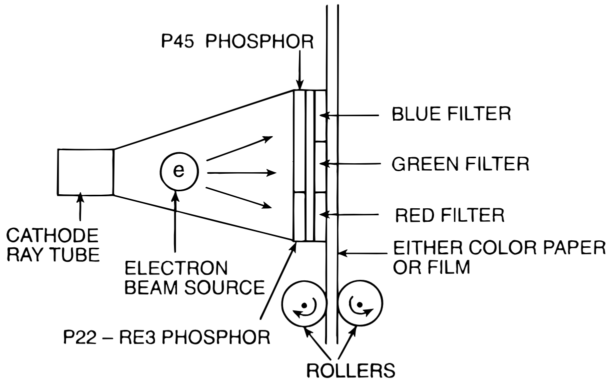


Figure 38. Exposure of a conventional photographic material by cathode ray tube/phosphor emission.

At the present time a much higher resolution can be obtained with conventional printers. Thus, an image on 35mm format film has the equivalent of 20 million pixels.[297] When considering that the maximum number of pixels possible for the best unconventional printer is one-tenth that of conventional photographic type printers, non-silver halide-based methods have a long way to progress before they match the quality of silver-based methods. However, the silver-based materials are more expensive, and in general, the processing is more complicated than that of the unconventional process.

Printer quality can only be as good as the TV signal, and at the present time, conventional televisions lack the necessary resolution to produce higher quality color prints. With the introduction of the high definition television, the amount of image information will be approximately 5 times that of the conventional TV.[298,299] When this occurs the quality of hardcopy prints from frozen TV scenes will improve dramatically.

IX. Conclusion

Color photography has come a long way since Antonius de Dominis first postulated that light was composed of three colors. Color picture processing has become faster and more efficient, yielding more stable and higher quality prints than those produced by du Hauron in 1862. Silver halide-based films have dominated the color reproduction market for over 100 years. The major silver halide processes, i.e., the dye-coupled, dye- or silver-transfer, and dye−bleach have been the dominant methods. A new method is evolving which may soon end this dominance. Electronic photography, although not yet achieving the quality of silver halide prints, is growing in popularity.

Much has been achieved to perfect the reproduction of color, however, there are areas which still require improvement. Whether it be silver halide films or electronic printouts, they both require dyes or pigments which must be stable for extended periods, and which are spectrally pure. Higher resolution, greater speed, more convenience, and less expensive methods are all areas on which future research will be centered.

Which process can best achieve these expected improvements will only be determined with time. However, it appears that electronic photography is presently the area where most research effort has been expended. Although amateur picture taking will continue to be based on advancements in silver halide technology in the foreseeable future, including systems such as the Advanced Photo System[300,301] that combine magnetic data storage with silver halide based films, many commercial and industrial imaging needs will probably be satisfied with alternative processes such as electronic capturing and printing.[302]

The introduction of the electronic still camera by Sony in 1981 has contributed greatly to advancing the prospects of electronic photography. Features of this process allow for communication of color images to locations all over the world. Signals then can be printed to produce hard-copy color pictures.

Future chemical research will still be required for electronic photography as well as silver halide photography. Shifts from liquid-state to solid-state chemistry will become more prevalent. All in all the future of color photography is evolving into simpler methods in which electronics will take on an increasingly significant role, changing the process dramatically from its present form.

X. Summary

The dye-coupled process of color development is the most widely used of modern times. In this process the subtractive theory of color reproduction is utilized. To obtain an image, the light exposed silver halide results in a latent image, the latent image silver is reduced to silver metal, and the oxidized developing agent is reacted with a coupling agent to produce a permanent dye. Both silver metal and silver halide are leached out from the emulsion to give the image a certain degree of permanence.

Another widely used process involves the production of instant photographs by the dye-transfer process. In this process, introduced by Polaroid, insoluble colored compounds in the emulsion layers of the film are fragmented by a series of chemical reactions. The colored portions of the insoluble compounds are solubilized as a result of these reactions and diffuse to a receiver layer to form the colored image. The developing “solution” is considered to be dry in so far as it is applied as a viscous fluid in pod form. The chemical transformations are internal, since they occur in the camera or between opaque sheets.

A dye destruction process called dye-bleaching is also used today and is considered to be the most resistant to the effects of dye degradation on storage of the finished picture. As opposed to the dye-couple method, which is a dye-forming process, the dye−bleach method is a dye-removal process. Image-wise removal of the dyes is accomplished by using the developed silver metal as a reducing agent in the presence of an acid and a mobile catalyst. The azo dyes are thus converted to soluble amines which are leached out from the emulsion layers into the fixing and washing baths. The remaining silver is converted to ionic silver in the fixing bath.

The last process discussed in this review is considered to be the wave of the future, since it does not involve silver salts in film emulsions. Electronic photography has been marketed but is still not widely used. It features electronic technology to image, store, and print the recorded image for color reproduction. The principles on which these processes are based took centuries of exploration into the understanding of light and how to manipulate it. The historical sequence of events leading up to modern color photography forms the foundation for today’s processes.

XI. Acknowledgments

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