Kirk-Othmer Encyclopedia of Chemical Technology.

PHOTOGRAPHY

The unique light-sensing properties of silver halide crystals have been recognized since the 1500s. In spite of many technical advances in nonsilver halide (eg, electronic) technologies, chemically based silver halide systems continue to dominate in the ability to record images (1–3) of superb image quality and archival characteristics. Photochemical reduction in which the silver ion, Ag^+, in the ionic silver halide crystal is reduced to elemental silver, Ag^0 (4–7) was first observed by the alchemist Fabricius in 1556. As photochemical reduction continues, elemental silver atoms aggregate and grow into clusters of a colloidal size sufficient to scatter light and produce hue shifts. The science of photography uses this photochemical property of silver halide to form images and record scenes. One of the earliest researchers to produce such a photochemical image was Schultze in 1727 (8). In these experiments, solutions of silver nitrate and white chalk were photochemically reduced to produce metallic silver images when the solutions were exposed through stencils.

The daguerreotype process, prepared by Daguerre in 1837, and the calotype process, produced by Talbot in 1841, were among the first photographic techniques to produce continuous-tone images as reproductions of scenes (9, 10). The steps of a typical daguerreotype process include polishing and cleaning a silver-plated copper plate; treating the silver side of the plate with iodine vapors to convert silver into light-sensitive silver iodide [7783-96-2], AgI; exposing the plate through the optics of a camera that projects and focuses a scene on the plate, ie, where light strikes these plates, silver ions are photochemically reduced to silver metal; and treating the exposed plate with mercury. The mercury reacts with silver metal to produce a silver amalgam. White silver amalgam appears in areas of the plate exposed by light; the unexposed areas remain dark, thereby producing a positive image.

Daguerrotype images were produced primarily by the action of light. For the production of satisfactory images, long exposures to light, on the order of minutes, were required because many absorbed photons were necessary to reduce photochemically enough silver ions to silver metal for visible imaging. In 1841, Talbot announced the calotype process, which could reduce exposure times to seconds and produce visible images without dependence on the action of light (11). In the calotype process, the exposure of silver halide produced an invisible latent image that was composed of only trace amounts of reduced silver. This acted as a catalyst for subsequent chemical reduction, ie, a nonphotochemical continuation of the light-initiated reduction process that eventually produced a visible silver image. In addition to being sensitive to much lower light levels, the calotype process was less expensive than the daguerreotype process and provided a negative–positive system that could generate several positive copies from a single negative original. The use of chemical amplification after low level image exposure is a conceptual approach applied in modern photography.

Unexposed silver halide in these early recorded images photolytically darkened upon repeated exposure to light, thus photographic images were not permanent. In 1839 Herschel discovered that unexposed silver halide could be dissolved with sodium thiosulfate and washed away, whereas metallic silver was relatively unaltered by sodium thiosulfate treatments (12). This process, called fixation, along with chemical and spectral sensitization, were necessary to the foundation of modern photography. Sensitization improvements led to the development of high sensitivity available-light photographic systems. Before such sensitivity improvements, high energy illumination was required to give enough exposure intensity.

Without special sensitizing treatments, silver chloride [7783-90-6], AgCl, microcrystals, which do not significantly absorb light having wavelengths greater than 400 nm, are virtually insensitive to visible light. Similarly, silver bromide [7785-23-1], AgBr, and Ag(Br,I) and Ag(Br,Cl,I) microcrystals popularly used in modern photography are effectively insensitive to electromagnetic radiation of wavelengths longer than 500 nm. Photographically these crystals are said to be blue sensitive, but green and red insensitive. Blue sensitivity refers to the intrinsic sensitivity of the silver halide crystals. To reduce the number of blue photons required to produce a developable latent image, ie, a catalytic center, the silver halide crystals are treated with materials called chemical sensitizers, that absorb to the crystal surfaces and may or may not react with them. Chemical sensitizers do not significantly alter the light-absorption properties of the silver halide crystals, but they do alter the efficiency with which the latent image is formed. Sulfur- and gold-containing compounds are among the most popular chemical sensitizers. In 1925 it was demonstrated that in certain samples of gelatin (qv), sulfur could increase the intrinsic sensitivity of silver halide microcrystals (13–15). Gelatin has been used since 1847 as a protective colloid to prevent the silver halide microcrystals from aggregating or coalescing before and after coating on paper, film, or glass supports. The use of gold salts as chemical sensitizers was discovered in 1936 at the Agfa film plant in Germany (16). However the mechanisms by which these salts enhance photographic sensitivity continue to be investigated (17–21).

To achieve photographic sensitivity in the green (500–600 nm) and red (600–700 nm) regions of the visible spectrum, silver halide crystals are spectrally sensitized with dyes (22) (see Dyes, sensitizing). In spectral sensitization, dye molecules are absorbed to the silver halide surfaces. The transition from glass plates to film bases for supporting light-sensitive emulsions represents the final step that made photography a popular and commercial success.

The first satisfactory photographic film was produced in 1888 when gelatin-dispersed microcrystals of silver halide were coated on celluloid sheets (23). Within a year George Eastman prepared and marketed roll films on a base produced by dissolving nitrocellulose with camphor and amyl acetate in methanol(qv).

A broad range of photographic materials exists in the 1990s including x-ray films (see X-ray technology), graphic arts films, microfilms, and complex multilayer coatings for color films that provide low granularity, available-light sensitivity, and rapid access. Many modern color films have more than 15 separate layers. For such films, coatings having as much silver as 10 g/m^2 and as many as one hundred different chemical compounds may be necessary to provide the desired image quality (granularity and sharpness), color reproduction, image permanence, and light sensitivity (see Color photography).

The modern preparation of photographic films, papers, and plates begins with the growth of silver halide microcrystals (Fig. 1). Commercially, reaction vessels having capacities as large as 2000 L are used to produce microcrystals (grains) ranging in size from tens of nanometers for microfilms up to micrometers for the highly sensitive crystals required in available-light photography. During the early stage of the grain growth process (precipitation), silver ions from a silver nitrate [7761-88-8] solution and halide ions from an alkali halide salt solution come together in a reaction vessel to form silver halide nuclei. After this stage, the nuclei are available as substrates for continued crystal growth. The crystals are generally precipitated in aqueous environments using a low concentration of added gelatin which, used as a protective colloid, prevents the grains from aggregating into clumps as ionic strength increases. After the precipitation, the counterions, eg, Na^+, K^+, and $NO^-{}_3$, are removed by a washing process. The resulting silver halide dispersion in gelatin is then chilled and allowed to gel (emulsion). The emulsion is usually stored in this chilled state for future use.

Later, the emulsion is melted, the emulsion grains chemically sensitized to enhance their intrinsic sensitivity, and spectrally sensitized using dyes to extend the intrinsic sensitivity into the lower energy regions of the visible spectrum. For certain applications, such as aerial reconnaissance, ecological land surveys, and recording laser diode signals from digital data, emulsions are spectrally sensitized with dyes that sensitize into the infrared region of the spectrum. Figure 2 shows absorptance spectra for AgCl, AgBr, and Ag(Br,I) grains with and without an adsorbed spectral sensitizing dye. Once the grains have been precipitated and chemically and spectrally sensitized, the emulsions are ready for coating on a support (Fig. 3). The choice of

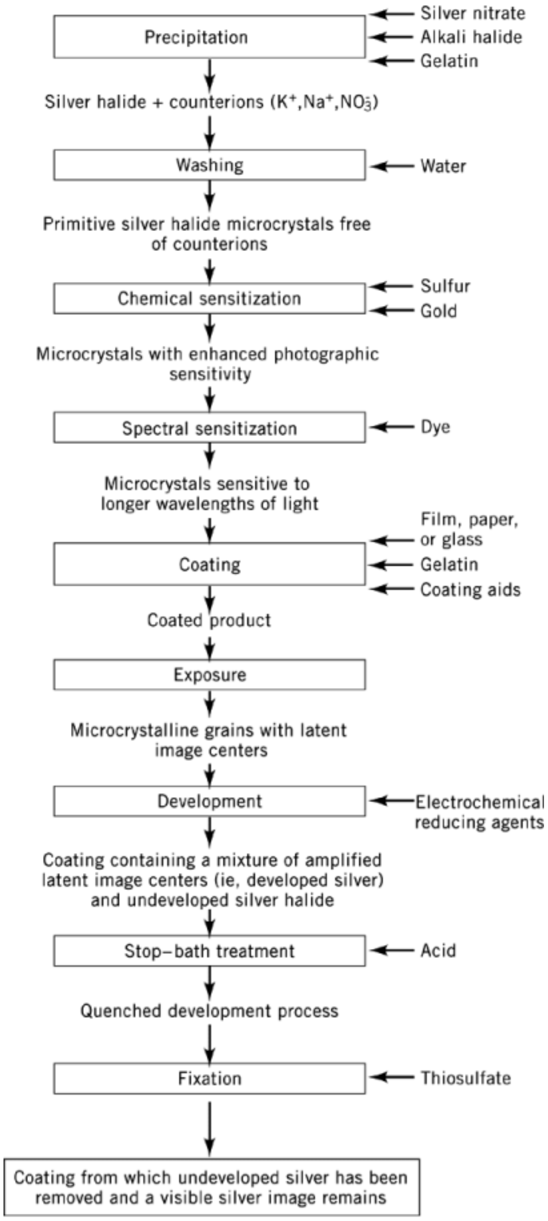
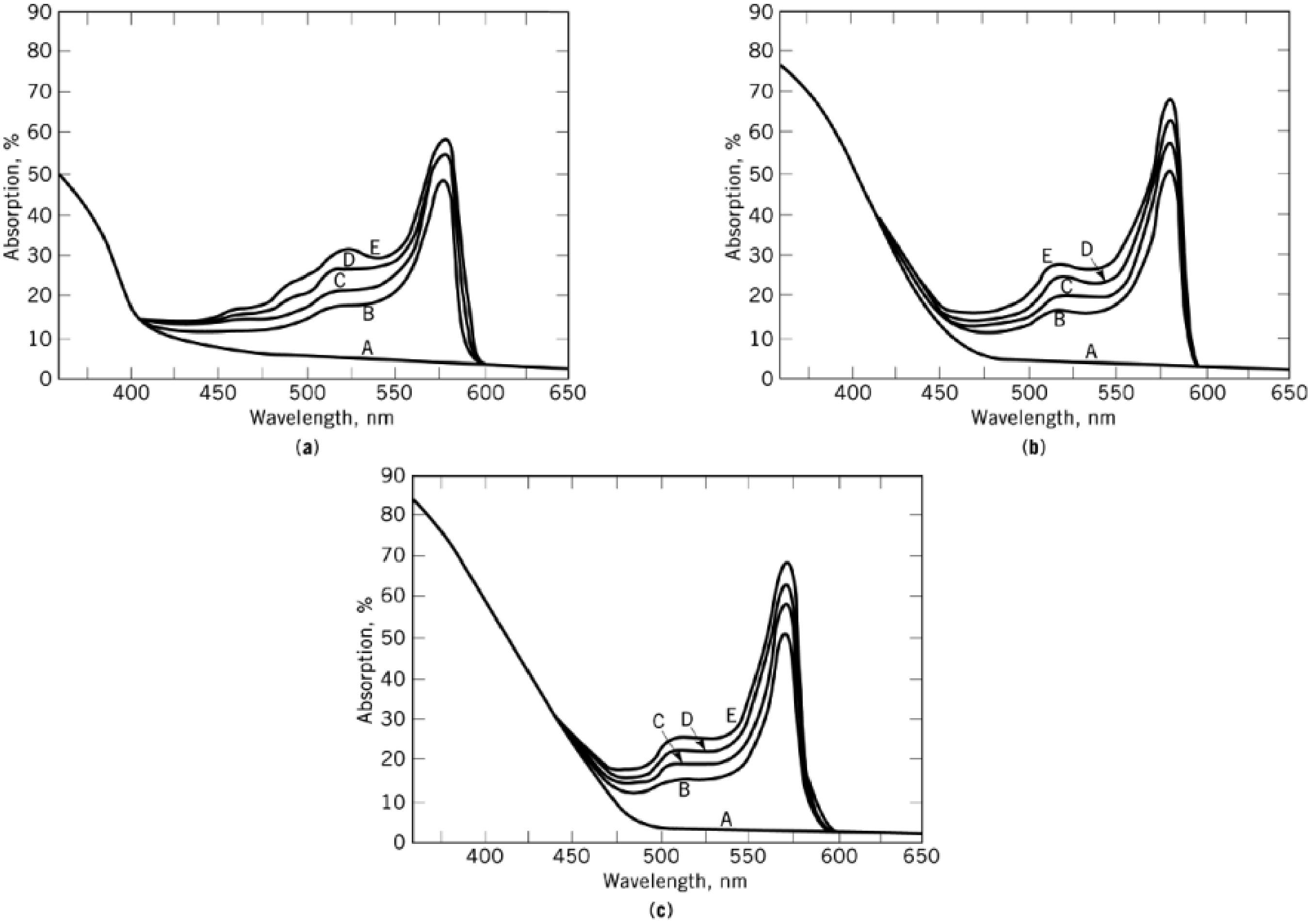


Fig. 1. Flow chart of the photographic process.

support depends on usage requirements. Paper, glass (qv), and polymeric films are most popular because of the dimensional stability, chemical inertness, archival properties, flexibility, and convenience they exhibit. Desired intergrain separations are achieved by coating silver and gelatin in appropriate concentration ratios. Before coating, spreading agents (surfactants) and high molecular weight polymers are added to the emulsions to facilitate coating operations, antifoggants are added to improve the signal-to-noise performance of the photographic film, hardeners are added to produce thermally stable gelatin matrices, emulsion stabilizers are added



(a)

(b)

(c)

Fig. 2. The effect of a sensitizing dye (1,1′-diethyl-2,2′-cyanine iodide) on the absorption spectra of (**a**) AgCl, (**b**) AgBr, and (**c**) Ag(Br,I) crystals (iodide content=ca 2.5%). The dye levels, ie, $A=0$, $B=3.3\times10^{-4}$, $C=4.4\times10^{-4}$, $D=5.5\times10^{-4}$, and $E=6.6\times10^{-4}$ dye mol/mol of silver, correspond to 0.5–1.0 dye mol/nm^2 of grain surface.

to extend shelf-life properties, and in the case of color photography (qv), organic compounds called couplers or dye-release materials are added to allow for the production of colored images.

Once coated, the photographic material is in an appropriate form to be exposed. The optics of the camera focus an image of a given scene onto the emulsion grains. When an exposing photon is absorbed by the silver halide grain, a mobile electron and a mobile hole are produced within the microcrystalline grain. The photoelectrons thus produced are available to reduce silver ions electrochemically to elemental silver. As the exposure continues, a stable cluster of silver atoms (a latent image) is eventually formed, and the signal is recorded. The number of atoms composing the latent-image center is below the detection limits of conventional light microscopy, yet the cluster is large enough to function as a catalytic center for the electrochemical reduction of more silver ions by developer molecules. Continuing advances in atomic force microscopy may eventually allow for detailed detection and analysis of sensitivity and latent-image centers (24, 25).

Development is an amplification stage following exposure in which the relatively small number of silver atoms comprising the latent-image center is magnified by factors as large as 10^{10}. Development can occur within

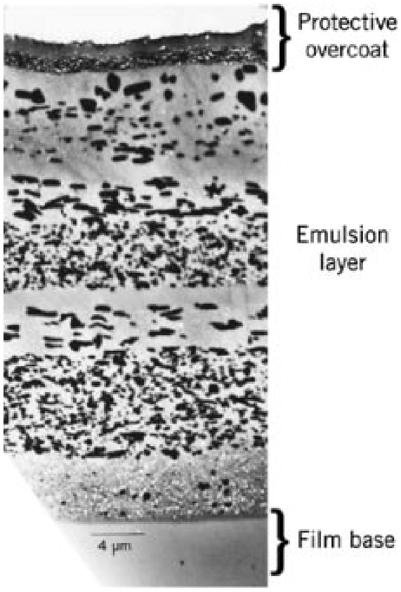


Fig. 3. Cross-section photomicrograph of a color-negative product showing the film base, the emulsion layer (the black specks are microcrystalline silver halide grains), and a protective overcoat. The emulsion layer and overcoat are $\sim 3.5 \times 10^{-5} m$ thick.

seconds after exposure, as in instant photography (26–30) (see Color photography, instant), or it can be months or years after exposure, as in conventional photography. When amplification occurs in the exposed regions of a negative film, a signal composed of elemental silver is produced; however, when amplification occurs in the unexposed regions of such a film, the relative signal intensity is diminished. Such unwanted amplification in the unexposed regions (or in the exposed regions of a reversal film) is called fog or D-min (minimum density). In a conventional black-and-white film, the developed silver produces visual darkening by scattering and absorbing light. This visual darkening is measured in units of optical density, the logarithm of the ratio of the incident-to-transmitted light for a transparent support, or the ratio of the incident-to-reflected light for a reflection support. After development the coatings are transported to a bath containing thiosulfate, where the remaining undeveloped silver halide is removed by fixation. During fixation, water-soluble complexes are formed between silver and thiosulfate ions, and are later washed from the coatings. The silver may be recovered for future use. After the undeveloped silver ions are removed, a stable silver record of the original scene remains. In instant color films there is no fixation.

The extent of silver-ion reduction during development depends on the development time, the composition and temperature of the developer solution, and the level of the original exposure to light. The relation between the extent of development or amplification and the exposure is often expressed graphically in the form of a characteristic plot of the optical density, D, as a function of the logarithm of the exposure, log H (31–33). Figure 4 is an example of a negative-working characteristic curve. In the D-min region (fog), the exposure is below the detection limits of the system. As the exposure increases, the density increases up to the saturation–exposure region. The slope of the characteristic curve in the mid-scale region is defined as the contrast of the photographic response, and the exposure range from toe to shoulder measures the latitude of the response; both are important in determining how well a scene is reproduced. In addition to contrast and latitude, the image also is evaluated in terms of sharpness, granularity, and color reproduction (34, 35).

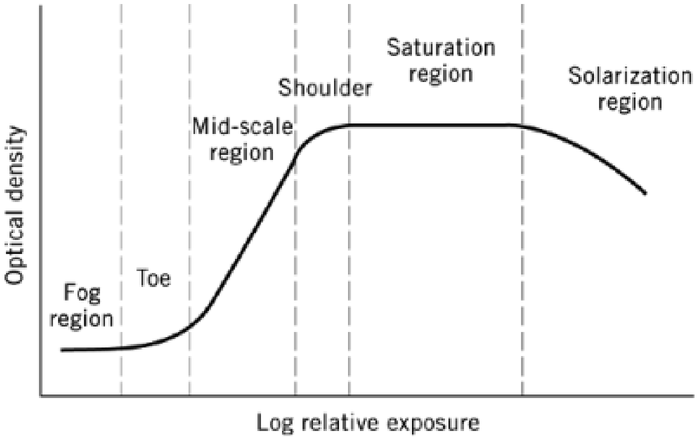


Fig. 4. A characteristic D-log H curve.

1. The Photographic Crystal

The preparation of light-sensitive photographic materials begins with the precipitation of silver halide grains. Various process control parameters are rigorously regulated during crystal growth to achieve the desired grain morphologies, size-frequency distributions, solid-state properties, light sensitivity, and catalytic activity (developability). In addition to the use of mechanical process control parameters, eg, flow and mixing rates, various chemicals are added during precipitation to control silver halide growth rates, ripening characteristics, stability, and even light sensitivity. Common to all precipitations is the controlled mixing of solutions of a halide, such as an alkali halide salt, and a silver salt, usually silver nitrate, in the presence of a peptizing agent. Gelatin is one of the best peptizing agents known; however, others have been used (36). During mixing, a chemical reaction occurs and a suspended solid phase, in the form of microscopic silver halide crystals, separates from the liquid phase. As the reactants are added to the reaction vessel, the concentrations of the soluble counterions (alkali cations and nitrate anions) increase. If the ionic strength of the solution in the reaction vessel is sufficiently high, the double-layer repulsion force (37) between grains can be reduced to less than the van der Waals attraction force, a condition that encourages the coagulation of the silver halide particles. The presence of a peptizing agent that adsorbs to the grain surfaces but does not inhibit continued growth is essential to prevent coagulation and to maintain a uniform dispersion of microcrystalline grains.

1.1. Techniques of Crystal Growth

Two commonly used precipitation techniques for crystal growth are the single-jet and the double-jet methods (38–40). In the single-jet approach an aqueous solution of the halide salt and peptizing agent is in the reaction vessel at thermal equilibrium before precipitation begins. The chemical reaction is initiated by the controlled addition of a silver nitrate solution. The silver ion activity increases monotonically throughout this process, whereas the ionic strength starts and remains at a high value. In double-jet precipitations, the halide and silver salts are added simultaneously to the reaction vessel, allowing the operator to control the silver ion activity as the reaction progresses. The ionic strength increases monotonically in this method. In addition to the use of gelatin, other approaches have been developed either to control or overcome the adverse effects of high ionic strengths during crystal growth. High amplitude mechanical vibrations (41) and high dilutions (42) during the precipitation are two procedures that have reduced or even eliminated the need for peptizing agents. Triple-jet precipitations, in which halide ions, silver ions, and silver halide seed crystals are simultaneously added to the reactor, have been described in the literature (43) and offer an approach for achieving grain size distributions not achievable by the other methods.

The silver ion activity during precipitation is an important parameter in determining the morphology of the resulting silver halide crystals. In general, high silver ion activities favor cubic structures bound by ⟨100⟩ crystallographic surfaces; lower activities promote the formation of octahedral grains bound by ⟨111⟩ surfaces. At very low ($10^{-9} - 10^{-11}$ M) silver ion activities, crystals having single and multiple twin planes are produced. When double parallel twin planes are generated in a given AgBr crystal, thin tabular crystal morphologies can be achieved. pAg, defined as $-\log\ [Ag^+]$, is often used as a parameter related to silver ion activity, ie, high pAg corresponds to low silver ion activity. The pAg in a reaction vessel determines the number and type of silver halide complexes, eg, Ag_2Br^+, $AgBr^-{}_2$, $AgBr^{2-}{}_3$, that are present (44) and thus strongly affects the silver halide solubility, which strongly influences crystal growth rates. Thus the solution *p*Ag in an emulsion precipitation reactor is an important control parameter, affecting both crystal size and morphology. Because of this silver ion activity effect, single-jet precipitations, which have low initial silver ion activities, generally produce ⟨111⟩ crystallographic surfaces.

Various organic compounds can be added to the reaction vessel during crystal growth to modify or control the resulting crystalline morphology. For example, silver chloride, which under most conditions grows with cubic structure (45), can be prepared with octahedral and dodecahedral morphologies if habit modifiers are used (46). Figure 5 shows electron micrographs of cubic, octahedral, and tabular silver bromide grains. Figure 6 shows the atomic arrangement within a silver halide unit cell and orientation of three important crystallographic surfaces: silver halide cubes are bounded by ⟨100⟩ surfaces, dodecahedra are bounded by ⟨110⟩ surfaces, and octahedra are bounded by ⟨111⟩ surfaces. The arrangement of lattice ions and the associated interlattice site distances (47–49) on perfect surfaces are exhibited in Figure 7. Newly developed analytical techniques, such as surface extended x-ray absorption fine structure (sexafs) and atomic force microscopy (afm), suggest that the structure and interionic separations on the surface of silver halide microcrystals are the same as in the bulk for ⟨100⟩ AgBr surfaces, but that some reconstruction may occur on ⟨111⟩ surfaces because of electrostatic effects (50, 51). In spite of the presence of gelatin during the growth of silver halide microcrystals, and coulombic forces driving reconstruction, the surfaces can be remarkably smooth. Atomically smooth ⟨100⟩ AgBr surfaces for thin-film epitaxial vapor deposition on cleaved NaCl substrates have been observed using afm (52) (see Thim films).

The ultimate size–frequency distribution of the emulsion grains depends on the rate of addition of reactants, halide type, temperature, and presence of growth modifiers or ripeners. Ripeners are compounds that form water-soluble silver salts or complexes and preferentially dissolve the smallest grains from a given population of crystal sizes to enhance growth in the larger grains. In addition to influencing grain growth kinetics, ripeners can also affect the surface structure of crystals (53). Ammonia (54, 55), sodium thiosulfate (56), sodium thiocyanate (57), certain thioethers, and thiourea (58) are effective ripening agents. Ripeners can be added to the reaction vessel after precipitation to produce post-precipitation digestion effects. Alternatively, ripeners can be introduced into the vessel during or even before the onset of crystal growth.

Silver halide crystals grown from a single halide type have received considerable attention in basic studies. Some studies have focused on the growth of AgBr (59–62) and others on AgCl (63). Although analyses of the growth processes for crystals of mixed halide content, eg, Ag(Br,I) and Ag(Cl,Br,I), have not been as extensively reported in the literature, mixed halide grains of various compositions commonly are used in practical photographic materials. In the preparation of mixed halide crystals, the various halide types may be added to the reaction vessel either simultaneously or sequentially. In the latter case, the most soluble silver halide crystal, ie, AgCl, is sometimes grown first, and through subsequent halide additions the silver halide is converted partly to a silver halide of lower solubility, eg, AgBr. Photographic (64–66), electron-microscopic (67), and x-ray diffraction studies (68–70) suggest that this conversion involves a surprisingly efficient intragranular anionic diffusion. If the least soluble silver halide crystals are grown first, epitaxial growth can be achieved. In epitaxial growth the second phase is crystallographically oriented on the substrate phase (71). For example,

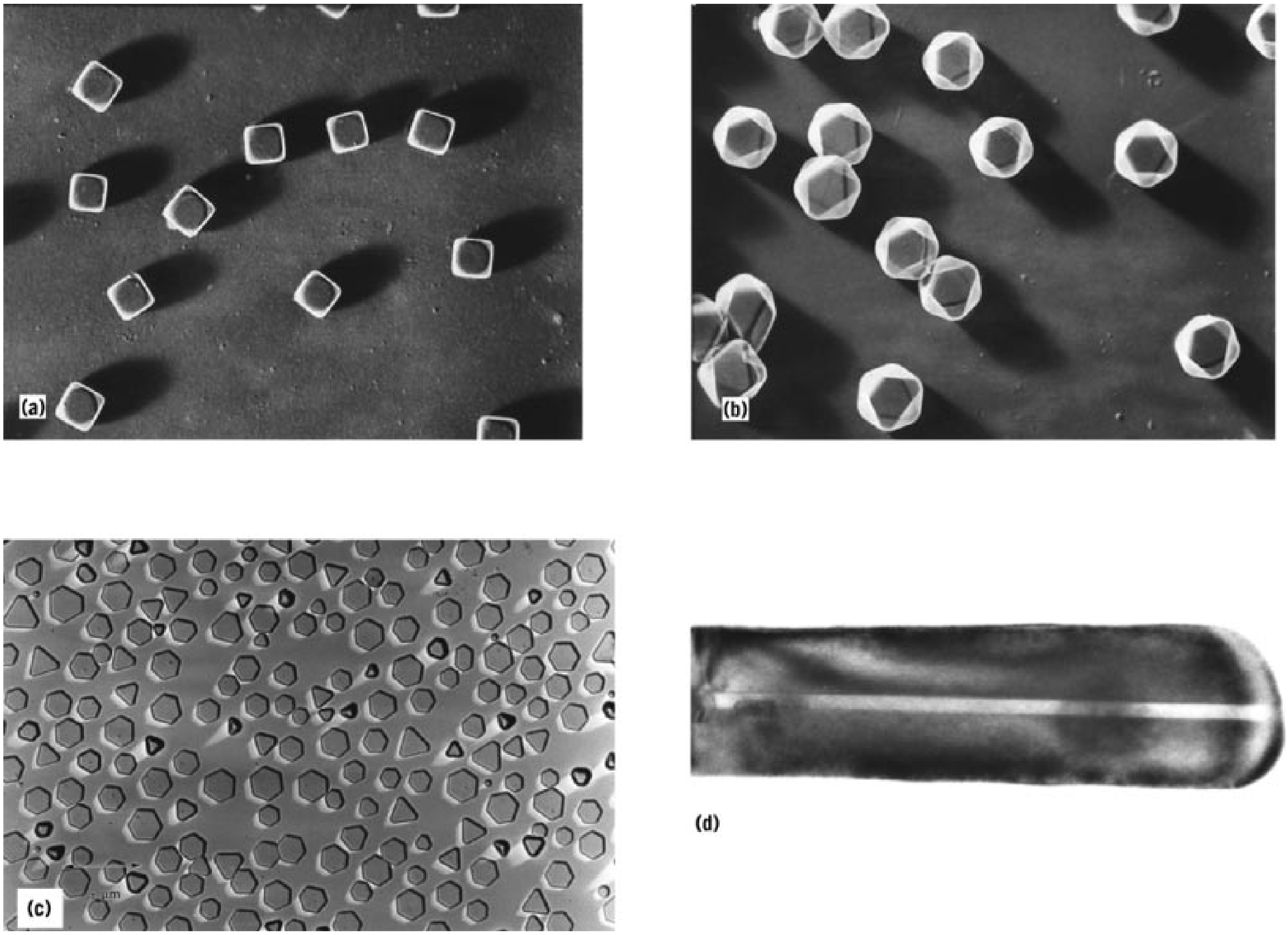


Fig. 5. Silver halide grain morphologies for (**a**) cubic, precipitated in an environment having a silver ion concentration, $[Ag^+]$, of ca 2.5×10^{-5} mol/L; (**b**) octahedral, ca 6.0×10^{-9} mol/L; and (**c**) tabular microcrystals, ca 1.0×10^{-10} mol/L. A cross section of a tabular grain revealing double parallel twin planes is shown in (**d**).

AgCl growth on preformed β-AgI microcrystals has been reported (72). The two phases (AgCl and AgI) of the epitaxial crystals are in electrical contact. In fact, mobile photogenerated electrons produced in the AgI phase have been shown to migrate into the AgCl phase.

The growth of silver halide crystals can be viewed as a collection of subprocesses, including nucleation, dissolution, ion diffusion, surface integration of ions, aggregation (73), and growth, which occur concurrently and/or sequentially. According to the Gibbs-Thomson equation, sometimes referred to as the Kelvin equation, a small spherical particle having an associated small radius of curvature, r, has a higher solubility, C_r, than the bulk thermodynamic equilibrium solubility, C_∞, measured over a flat macrosurface. The solubility, C_r, of spherical crystals is given by

$$C_r = C_\infty \exp\{2\sigma V_m/rRT\} \qquad (1)$$

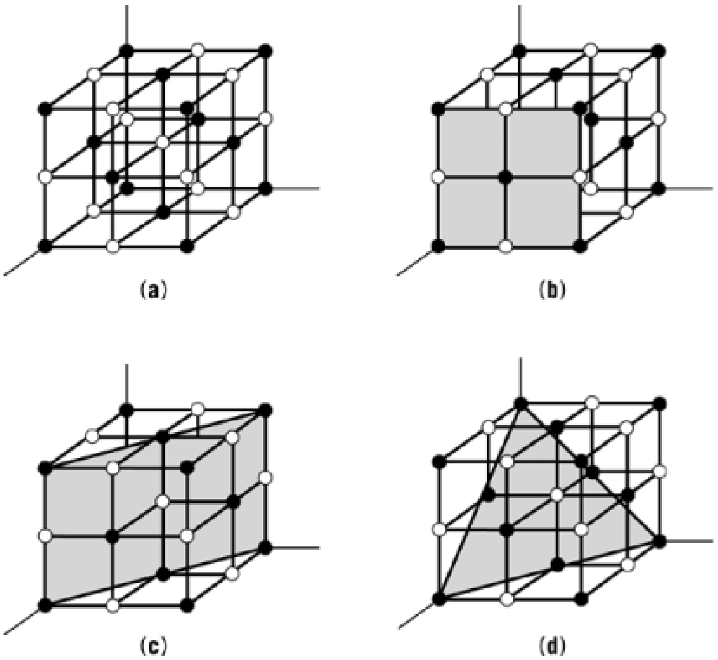


Fig. 6. Unit cell for silver halide where shaded areas represent crystallographic planes, (○) halide ions, and (•) silver ions. (**a**) Complete cell; (**b**) showing a $\langle 100\rangle$ surface; (**c**), a $\langle 110\rangle$ surface; and (**d**), a $\langle 111\rangle$ surface.

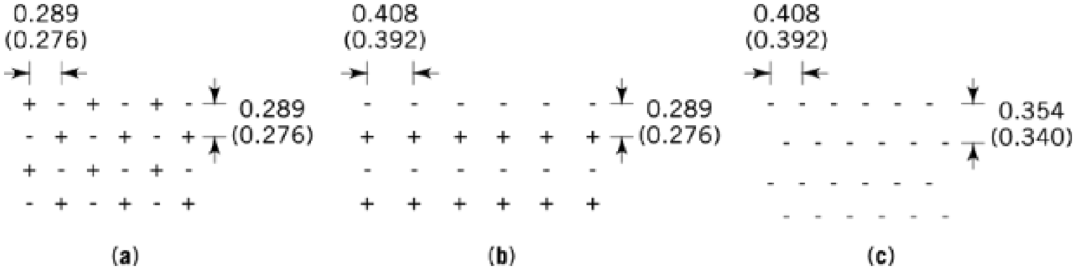


Fig. 7. Ionic arrangements on different (**a**) $\langle 100\rangle$, (**b**) $\langle 110\rangle$, and (**c**) $\langle 111\rangle$ crystallographic surfaces. The interionic separations are given in nanometers for AgBr and in parentheses for AgCl. Values are larger for AgBr because of the relative ionic radii of bromide and chloride.

where ς is the partial surface free energy ($\partial G/\partial$area) of the crystal and is by analogy related to the surface tension at a liquid–vapor interface, V_{m} is the crystal molar volume, R is the gas constant, and T is the temperature. Accordingly, small nuclei having small values of r are relatively soluble and dissolve if the solution concentration is not greater than C_{r}. In the beginning of a double-jet precipitation the concentrations of silver and halide ions continue to increase until a condition of sufficiently high supersaturation is achieved, the adverse free energy effects described by equation 1 are overcome, and nucleation occurs. The reaction to form a silver halide crystal is initiated by nucleation (74), which is the initial formation of a solid silver halide phase. Once the nuclei are formed, a substrate or surface is available for continued growth, and the growth stage is initiated. The transition between nucleation and growth does not necessarily occur at a specific time during the precipitation or even over a specific time range. Indeed, under certain conditions, eg, in localized regions of supersaturation, nucleation may continue throughout precipitation (59, 75). The surface integration process does not appear to be rate determining for double-jet precipitations of AgBr crystals (76) but may play an important role during the formation of twinned planes which are essential for the production of tabular crystals (77), as shown in Figure 5**c**. Growth models based on diffusion, the Gibbs-Thomson effect, and mass balance have been developed that can predict the number of nuclei formed and the ultimate grain sizes (78, 79). Using such a model the number of crystals, Z, grown is given by

$$Z = (FRT\,(a/r_c - 1))\,/8\pi\sigma V_m D C_\infty \qquad (2)$$

where F is the molar addition rate of the reactants (Ag^+ and Br^-); D is the diffusion constant for these ions; C_∞ is the equilibrium solubility which is a function of pAg, T, and halide type; a is the average effective crystal radius; and r_c is the critical crystal size (see eq. 1) which depends on the supersaturation condition, C/C_∞, and therefore on the molar flow rate to which this ratio is proportional. Equation 2 is consistent with the observation that larger crystals, ie, fewer nuclei, are achieved with low molar addition rates and high solubility conditions.

In addition to nucleation, growth, halide conversion, and epitaxy, the Ostwald ripening crystallization process must be considered (59, 60, 80–82). Ostwald ripening occurs when there is a range of grain sizes within the reaciton vessel. From equation 1, the solubility of the smaller grains is greater than that of the larger grains and thus the small grains tend to dissolve and contribute to accelerated growth of the larger grains. This dependency of solubility on size revealed by equation 1 is an important property contributing to the ability to produce relatively monodispersed size-frequency distributions. In double-jet precipitations, nucleation has been observed to occur continuously throughout the growth process, yet the total number of crystals does not change after the first few minutes (59, 78) because the newly formed nuclei dissolve and redeposit on existing crystals according to the size-dependent driving forces suggested in equation 1. Ostwald ripening can be divided into at least three mechanistic steps: dissolution of small grains, ionic diffusion through the aqueous phase, and redeposition of ions on large grains. The rate-limiting step depends on environmental conditions. However, in general, ripening is promoted by temperature increases and addition of ripening agents which complex with silver forming water-soluble silver salts.

Since the mid-1980s, tabular crystals (Fig. 5**c**) have become increasingly popular in color as well as black-and-white photographic products. The popularity is a consequence of the relatively high surface-to-volume ratios attainable with the tabular morphologies. For tabular grains having sensitizing dyes adsorbed to their surfaces, the high surface-to-volume ratios render them particularly sensitive to spectral regions of the visible spectrum. Thus, high signal-to-noise (ie, photographic light sensitivity to granularity) signals can be achieved.

It is generally believed that tabular crystals are produced when faults in the buildup of successive lattice layers occur during early stages of crystal growth and parallel twin planes are produced (83–86) (Fig. 5**d**). Studies indicate that tabular crystals having high aspect ratios can be produced even when the crystals have only a single twin plane (87). Other research has focused on diffusion-controlled lateral growth (88–90) which must predominate over thickness growth to preserve tabular morphology. These models can predict the rate of change in grain diameters and how these rates depend on diffusion coefficients, supersaturation, and time.

1.2. Impurity Incorporation

For some applications, inorganic impurities are intentionally added to emulsions during precipitation to achieve certain desired photographic responses. These impurities or dopants are usually incorporated into the silver halide grains at very low (ie, in the ppm or ppb range) concentrations. In spite of these low concentrations, dopants can have significant effects on the solid-state properties of the grains as well as on light sensitivity, contrast, and developability. By the use of photoluminescence (91–93), dielectric loss (94–96), spectrophotometry (97), conductivity (97, 98), diffusion (99, 100), ionic thermocurrent (101–103), electron spin resonance (104, 105), and Auger spectroscopic (106) measurements, dopants have been found to influence the ionic and electronic properties, light absorption, and catalytic properties of silver halide crystals. For example, polyvalent cationic dopants can reduce the interstitial silver ion concentration, influence trapping phenomena associated with mobile conduction band photoelectrons and mobile valence band photoholes, and alter electron–hole recombination probabilities. Some key elements capable of providing these solid-state effects include Ir (107–109), Pb (110, 111), Zn (112), Ce (113), Cd (114), Rh (115–118), Cu (119), Fe (119), Os (120, 121), and Pd (122). Many of these elements, even in the cationic state, are present as trace level impurities in a variety of raw materials and in the general environment. Because these materials all can have substantial effects on the fundamental processes associated with the photographic sensitivity of emulsion grains, great caution must be exercised in the manufacture of photographic products.

1.3. Emulsion Washing and Concentrating Procedures

After crystal growth is completed, the resulting photographic emulsion is a dispersion of silver halide microcrystalline grains in an aqueous gelatin phase. Precipitation by-products such as counterions, ripeners, and others are also present in solution. If these by-products are not removed, adverse crystallization may occur when the emulsion is coated on a support and dried, and certain by-products may interfere with subsequent chemical and spectral sensitization. When photographic materials are coated on a paper support, some of the by-products are adsorbed on the fiber matrix of the paper, which can minimize or eliminate the adverse effects of reaction by-products. However, for many photographic products, such as those coated on film, glass, and water-impermeable resin-treated paper, the adsorbent properties of the substrate are not sufficient, and the amount of water present after crystal growth is often inconveniently high for coating operations.

Several washing procedures have been devised to remove water and water-soluble by-products. The most common of these procedures are noodle washing, flocculation washing, and ultrafiltration (qv). In noodle washing, additional gelatin is added to the emulsion after precipitation causing the emulsion to solidify into a jelly upon cooling. In the jellied state the emulsion can be fragmented into noodles that are washed with circulating water. Noodle washing is often inconvenient because of high gelatin content and the length of time required to leach by-products.

Flocculation washing requires less time for efficient by-product removal, does not require addition of extra gelatin, and provides a more concentrated emulsion through removal of the water used during precipitation. In flocculation, precipitation gelatin is made to coagulate either by adjusting the pH to the isoelectric point of the protective gelatin colloid (123–125) or by adding salts, eg, inorganic sulfates, which promote coalescence by increasing the ionic strength (126). When the gelatin floccules settle to the bottom of the reaction vessel, they carry the silver halide grains with them. The water-soluble by-products and supernatant that are left behind can be removed by decantation. A sequence of redispersal with water, flocculation, and decantation can be repeated until the silver halide emulsion has the desired purity. Variants of this process have been developed to accelerate settling rates of the floccules (127) and to improve the photographic response of the washed emulsions (128) (see Flocculating agents).

Ultrafiltration is the most modern method for washing and concentrating photographic emulsions (129). In this method, the emulsion is pumped into contact with a semipermeable membrane. A maintained pressure drop across the membrane drives water, counterions, and other low molecular weight precipitation by-products through membrane pores of an optimized size, leaving behind the silver halide crystals and gelatin in a purified and concentrated state suitable for subsequent sensitizing and coating operations.

1.4. Crystal Properties

Silver halide crystals have been the photosensitive materials of choice in most photographic materials since the pioneering efforts of Daguerre, Niépce, Talbot, and Herschel in the early 1800s. This preeminence of silver

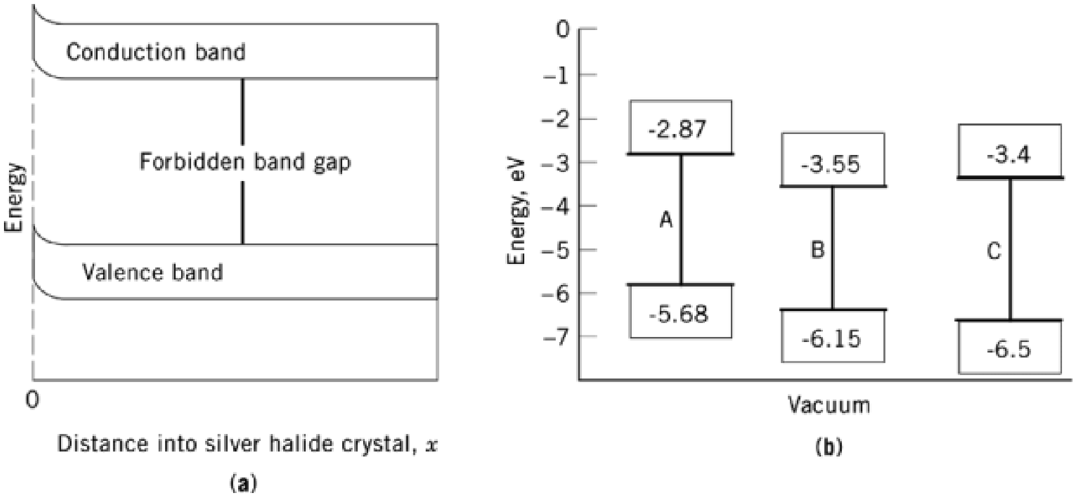


Fig. 8. (**a**) Energy levels for the band model of silver halide crystals. The band bending at the surface (– – –) is exaggerated. The extent of bending is at most 0.1 of the band gap. (**b**) Energy positions relative to vacuum of the conduction and valence bands within crystal bulk. The band gap for β-AgI. A=2.81 eV (4.52×10^{-19} J); for AgBr, B=2.6 eV (ca 4.17×10^{-19} J); and for AgCl, C=3.1 eV (4.99×10^{-19} J) (133, 134). See text.

halide in photography is the result of a unique collection of physical and chemical properties. The low aqueous solubility and range of silver halide complexes are important during crystal growth. Solubility products, K_{sp}, for the silver halides are as follows:

Temperature, °C	AgCl, M^2	AgBr, M^2	AgI, M^2
25°	1.77×10^{-10}	4.85×10^{-13}	8.28×10^{-17}
50°	1.30×10^{-9}	6.45×10^{-12}	2.49×10^{-15}

Optical absorption properties, mobility of both ionic and electronic charge carriers, and electronic energy structure are all essential features of silver halide grains during latent-image formation. The catalytic properties of the small silver specks constituting the latent image are required during development. The dissolution characteristics of silver halide crystals permit stabilization during fixation. Because of the outer electronic shell structures for silver and the halogens, ie, Ag, $5s^24d^9$; Cl, $3s^33p^5$; Br, $4s^24p^5$; and I, $5s^25p^5$, the silver halides are often referred to as ionic crystals. Silver has a relatively ionizable electron that it sacrifices to a halogen atom which has a relatively large electron affinity. However, the large dielectric constants, high insolubility in water, and high mobility of interstitial silver ions are not predictable based on an ionic crystal model. These values are all high compared to the values for the alkali halides (130, 131).

Figure 8**a** shows a schematic representation of the electronic energy structure of silver bromide. Because of the periodicity of the lattice positions in silver halide crystals, quantum-mechanical analysis dictates an energy-band scheme (132). In this scheme bands of allowed and closely packed electronic energy levels are separated by forbidden energy gaps. The highest energy band in which all of the electronic energy states are occupied is the valence band; the band that is energetically directly above the valence band is the conduction band. In the absence of external excitation energy, the electronic energy states comprising the silver halide conduction band are unoccupied. During exposures of sufficient energy, a photon is absorbed and simultaneously an electron is promoted from the valence band into the conduction band. Such an intrinsic absorption produces a positive mobile hole in the valence band and a mobile electron in the conduction band. The electron and hole thus formed are free to move through the crystal independently and contribute to a photoinduced electrical conductivity. The forbidden gap is temperature dependent because of phonon-assisted transitions which reduce the photon energy required to effect promotion of an electron into the conduction band. At 298 K, the forbidden energy gap for silver bromide is $\sim 4.2 \times 10^{-19}$ J (2.6 eV) (133–136). Therefore, to excite an electron from the valence band into the conduction band, a minimum photon energy of 4.2×10^{-19} J is required. This energy corresponds to the intrinsic silver bromide absorption edge near 475 nm (see Fig. 2).

The energy positions for the conduction and valence bands in bulk β-AgI, AgBr, and AgCl are provided relative to vacuum in Figure 8**b**. The energy gap for silver chloride is significantly greater than the gap for either silver iodide or silver bromide, as can be correlated with the long-wavelength absorption edges shown in Figure 2. Because these band gap energies are large compared to thermal energy, silver halide crystals do not exhibit dark conductivity resulting from electronic motion. In silver halide crystals, electronic conductivity must be photoinduced. The photoinduced charge carriers produced upon exposure to light initiate the latent image formation in photographic materials. Once formed, the mobile electronic charge carriers do not necessarily remain free, but rather are likely to be trapped at localized sites within the crystal interior or on the crystal surface. The concentration and nature of the trapping centers in nominally pure silver halide crystals, although not completely understood, have been extensively studied (19, 137–141). An electron trap is an unoccupied electronic energy state that is energetically below the bottom edge of the conduction band. On the other hand, a hole trap is an occupied electronic energy state above the top edge of the valence band. These traps may result from impurities; surface defects, eg, kink sites; interior defects, eg, jogs on dislocation lines; or intentional dopant additions during or after crystal growth. The depth, cross section, and concentration of such traps determine in part the lifetimes and mobilities of the photoinduced charge carriers.

The ultimate trapping site for a photoelectron is influenced by the high dielectric constant of silver halide (ca 12.5, 11.15, and 7.15 for AgBr, AgCl, and β-AgI, respectively), the negative surface charge, and relative trap depths. Interior traps located at point defects on dislocation lines are probably not as deep as surface traps at positive kink sites because of the high dielectric constant of silver halide. However, the negative surface charge of the microcrystals appears to repel the photoelectrons and thereby enhances the probability of internal trapping (142). The relative photographic sensitivity of the interior of silver halide microcrystalline grains is consistent with such an effect from a negative surface charge. Many emulsion grains have been designed to shuttle photoelectrons and photoholes in opposite directions to avoid inefficiencies in photographic sensitivity associated with electron–hole recombination (143–147). By creating relatively iodide-rich regions during crystal growth, a driving force that directs photocarrier motion is established within the microcrystal. It is generally believed (134) that both the valence and conduction band edges are higher in iodide-rich regions (Fig. 8**b**); thus electrons in the conduction band attempt to minimize their energy by moving toward the iodide-poor regions, and holes in the valence band associated with the iodide-depleted regions migrate in the opposite direction. The band positions relative to vacuum in Figure 8**b** may shift somewhat due to ionic migration of interstitial silver ions and vacancies when two iodide phases are brought into electrical/thermal contact (134, 148, 149).

Although there are no mobile electrons in the dark, silver halide crystals do have a dark conductivity that results from ionic motion. Thermally activated ionic mobility at room temperature contributes to latent-image formation during exposure to light. The ionic motion can result from one of two sources in pure silver halide crystals: movement of silver ions in interstitial positions and the motion of silver ion vacancies. A vacancy is created when a silver ion lattice position becomes unoccupied. Vacancy motion results from successive hopping in which lattice silver ions and adjacent vacancies exchange positions. Of the two ionic charge carriers, the interstitial ions are the more mobile and usually considered the main ionic actors in latent image formation. The concentrations of interstitial ions and vacancies are governed by mass balance equations. A dynamic equilibrium (the Frenkel equilibrium) is established in silver halides such that the mathematical product of the two activities is constant at any given temperature (150).

$$K_f(T) = \left[\mathrm{Ag}_i^+\right]\left[V_{\mathrm{Ag}^+}\right]$$

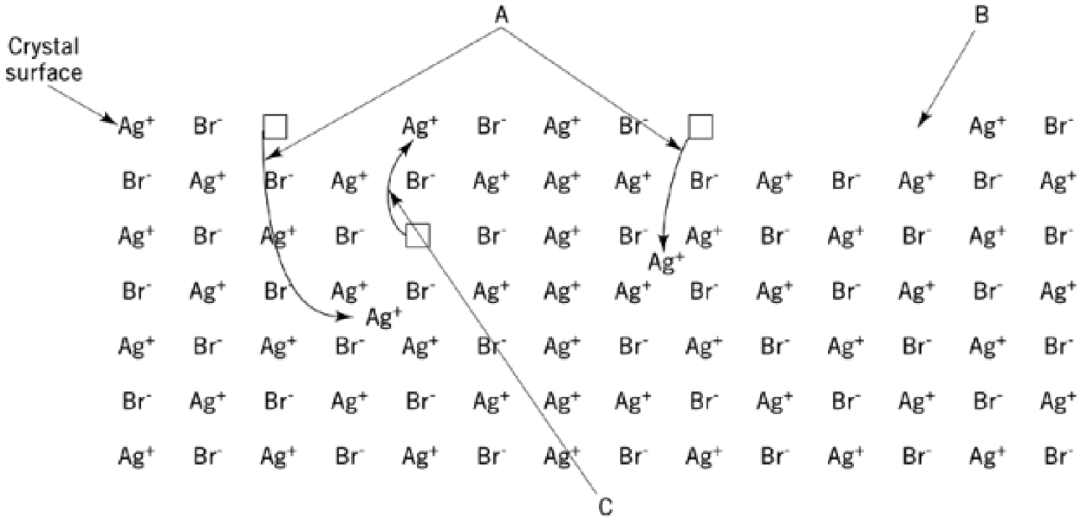


Fig. 9. Schematic of a two-dimensional cross section of an AgBr emulsion grain showing the surface and formation of various point defects: A, processes forming negative kink sites and interstitial silver ions; B, positive kink site; and C, process forming a silver ion vacancy at a lattice position and positive kink site on the crystal surface.

Therefore, any perturbation acting on the crystal to increase or decrease the concentration of one species must have the opposite effect on the concentration of the other species (142).

In addition to being affected by polyvalent impurities, the interstitial ion concentration is also influenced by other factors, eg, crystal environment, temperature, species adsorbed to the crystal surface, halide ion, crystallographic morphology (141), and surface space charge (151–154). In fact, the concentration of interstitial silver ions is considerably higher in microcrystals than in bulk silver halide, presumably because of the high surface-to-volume ratios which enhance surface space charge effects. These surface effects occur because the Gibbs free energy required to transport a surface silver ion to an interstitial position is less than the energy necessary for moving a lattice silver atom to the surface, leaving behind an internal silver ion vacancy (155) (Fig. 9). Therefore, thermal equilibrium results in negatively charged surfaces, subsurface space charge regions with high interstitial silver ion concentrations relative to the bulk, and the associated band bending (see Fig. 8**a**). In spite of their high surface-to-volume ratios, tabular grains have lower ionic conductivities than do cubic crystals and both tabular and cubic microcrystals have significantly lower ionic conductivities than the octahedral crystals. This is presumed to be the result of interstitial silver ion localization at twin planes (141).

2. Response Enhancement

2.1. Chemical Sensitization

After the photographic microcrystals are precipitated but before they are coated on a support, the crystals are treated to enhance their sensitivity to light. Chemical sensitization is a process which improves that ability of the emulsion grains to use the absorbed photons, independent of the wavelength. Various methods of post-precipitation chemical sensitization have been developed to reduce the number of photons required to produce a developable latent-image center.

During exposure to light, photons are absorbed by silver halide microcrystalline grains and concurrently photoelectrons and photoholes are formed. These mobile charge carriers then interact with interstitial silver ions in a chemical sequence of mechanistic steps to produce centers of metallic silver called latent-image centers. There is some disagreement about the order of the steps and the identity of the rate-determining step in latent-image formation (130, 142, 156–167), but the basic scheme for the growth of the silver center and various sources of inefficiencies are widely accepted. The overall desired result of the sum of the various mechanistic steps is the reaction of photoelectrons with silver ions to form localized clusters of silver atoms. There are at least two well-defined loss processes that interfere with this chemical reduction of silver ions: recombination of photoelectrons with photoholes, and reoxidation of silver atoms upon attack by photoholes. In a practical sense, the topography (location) of latent-image center formation on or within the microcrystal can also influence the effectiveness of the latent-image center as a catalytic site for subsequent amplification during development (7, 168–170). Chemical sensitizers increase the light sensitivity of the microcrystalline grains by separating photoholes from photoelectrons and from the site of latent-image formation. Furthermore, chemical sensitizers can determine the topography of latent-image formation and improve the stability of the latent-image center once formed. Typical chemical sensitizers include sulfur-containing compounds such as thiourea and sodium thiosulfate (171–178), gold-containing complexes such as gold thiocyanate and potassium tetrachloroaurate (17, 18, 179, 180), and chemical reducing agents such as hydrogen gas and *tert*-butylamine borane [7337-45-3] (181–184). These sensitizers can be used either alone or in combination to increase sensitivity, and produce optimum photographic properties when used in trace amounts, ie, μmole sensitizer per mole Ag. At these low concentrations the sensitizers have advantageous effects on the solid-state phenomena during exposure without adversely affecting subsequent amplification processes during development.

Before the discovery of chemical sensitizing compounds, certain samples of gelatin were found to enhance the native sensitivity of silver halide grains. Subsequent investigation (171) revealed that these active gelatin samples formed silver sulfide, Ag_2S, by reaction with silver ions. Silver sulfide is generally considered to be the active chemical species resulting from sulfur sensitization treatments with either sodium thiosulfate or thiourea.

The reaction of thiosulfate with silver halide crystals to form adsorbed sulfide on the grain surfaces is activated thermally. If the reaction is allowed to continue too long before quenching or if excessive concentrations of sodium thiosulfate are used, the emulsion grains become spontaneously developable, ie, no exposure is required to induce catalytic activity, and image discrimination is lost. The sulfiding reaction is a two-step process that involves physical adsorption followed by a thermally activated chemical reaction.

$$(\mathrm{AgBr})_n + \mathrm{S_2O_3^{2-}} \longrightarrow (\mathrm{AgBr})_{n-1}\left[\mathrm{Ag}\,(\mathrm{S_2O_3})\right]^-_{\mathrm{ads}} + \mathrm{Br}^- \qquad (3)$$

$$(\mathrm{AgBr})_{n-1}\left[\mathrm{Ag}\,(\mathrm{S_2O_3})\right]^-_{\mathrm{ads}} + \mathrm{Ag}^+ + \mathrm{H_2O} \longrightarrow (\mathrm{AgBr})_{n-1}\,\mathrm{Ag_2S} + \mathrm{SO_4^{2-}} + 2\ \mathrm{H}^+ \qquad (4)$$

Radiotracer studies (see Radioactive tracers) (176) have shown that the outer-sphere sulfur atom in the thiosulfate anion is the active sulfur sensitizing agent remaining on the emulsion grains in equation 4. Actual chemical sensitization resulting in enhanced photographic sensitivity appears to require a third step in which adsorbed Ag_2S molecules aggregate to form crystalline clusters (21, 185).

$$m\,\mathrm{Ag_2S} \longrightarrow (\mathrm{Ag_2S})_m \qquad (5)$$

Based on radiotracer data, spectrophotometric analysis, and proton-monitoring experiments, the sulfiding reaction (eqs. 3 and 4) is first order in the concentration of thiosulfate and less than first order in the concentration of silver ions. This reaction proceeds with an activation energy of 84–126 kJ/mol (20–30 kcal/mol) (176, 178, 186–188). On the other hand, the overall sensitizing reaction, including the third step (eq. 5) which confers enhanced photographic sensitivity to the grain, appears to be one half order (185). Compounds that strongly

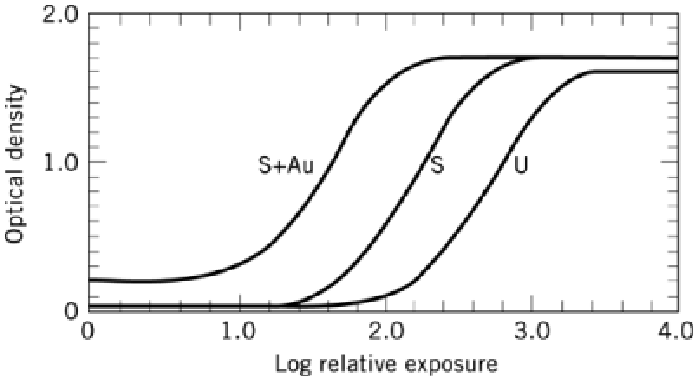


Fig. 10. Characteristic curves demonstrating the effects of chemical sensitization where curve U represents the photographic response of an unsensitized emulsion, and curves S and S $_+$ Au demonstrate the effects of sulfur and sulfur-plus-gold sensitizations. The emulsion is composed of 0.4 μm cubic AgBr microcrystalline grains coated with a gelatin binder on a film base to produce a Ag coverage of 1.25 g/m^2 of coating surface. After a 1.0 s exposure using tungsten light, the coatings are developed for five minutes in a standard black-and-white developer, fixed, washed, dried, and analyzed with a densitometer.

adsorb to silver halide surfaces, eg, tetraazaindene, interfere with the aggregation process in equation 5 and prevent optimum photographic sensitization even if the sulfiding reactions in equation 3 and 4 have gone to completion (189, 190).

The mechanism by which silver sulfide enhances sensitivity of silver halide grains is related to improved efficiency during latent-image formation. It has been suggested that sulfur sensitization increases the depth of individual electron traps (139, 191, 192); however, sulfur may reduce the repulsive potential energy associated with the surface space charge and thereby facilitate the approach of a photoelectron to the surface for subsequent latent-image formation (193). These models share the common notion that sulfur sensitization enhances electron-trapping propensities at sites where latent image formation can occur. On the other hand, other experiments have suggested that under certain conditions sulfur sensitization can enhance hole-trapping probabilities (19, 156, 194–196) or can have a dual role, trapping either of the photocarriers depending on the size and/or location of the silver sulfide cluster (197–199).

Gold is often used in combination with sulfur for an additional increase in sensitivity, particularly for high intensity exposures. The role of gold in chemical sensitization is at least twofold (17, 18, 200, 201). Gold enhances catalytic activity of the latent image center with which it is associated. In this capacity, gold reduces the total number of photochemically reduced atoms (Ag and/or Au) required for developability and therefore increases the light sensitivity of the grain. Furthermore, in association with a nucleating Ag center, gold appears to stabilize the cluster and thereby enhance the efficiency of the latent-image formation process (20, 202). Gold also may assist in the sulfiding processes (eqs. 3 and 4) (202). Ag_3AuS_2, Au_2S, and AgAuS species have been detected spectroscopically and calculations suggest that clusters of either of the first two species may have vacant electronic orbitals below the bottom edge of the AgBr conduction band and may therefore behave as traps for photoelectrons (199) and contribute to the efficiency of latent-image formation. The photographic responses for unsensitized, sulfur-sensitized, and sulfur-plus-gold-sensitized octahedral silver bromide grains with 0.7-μm edge length are shown as characteristic D-log H curves (Fig. 10).

Treatment of emulsion grains with chemical reducing agents also enhances sensitivity. Reduction sensitization can be achieved by high pH treatments (203), low pAg treatments (204), or treatment with chemical reducing species such as H_2, stannous ions, or hydrazine [302-01-2] (qv) (205–207). Reduction sensitization contributes to enhanced sensitivity by either hole-trapping processes, electron-trapping processes, or some combination thereof, depending on the particular technique used (207–210). The hole-trapping process can provide substantial sensitivity enhancement by hole removal which reduces electron–hole recombination processes (eq. **6**), and by releasing an extra electron into the conduction band which could contribute to latent-image formation. The thermal regression of atomic silver associated with the latter process is described in equation **7**.

$$Ag_2 + h^+ \longrightarrow Ag_2^+ \longrightarrow Ag^0 + Ag_i^+ \qquad (6)$$

$$Ag^0 \longrightarrow Ag_i^+ + e_{CB}^- \qquad (7)$$

In this process a photohole, h^+, and a reduction-sensitization center combine to produce two interstitial silver ions, $Ag^+{}_i$, and a conduction band electron, e_{CB}^-. All of these products are reactants in the latent-image forming process and thus can impact favorably on photographic efficiency. However, reduction treatment of any of these types must be controlled carefully because excessive chemical reduction may produce atomic silver centers of sufficient size or activity to catalyze spontaneous development (sensitization fog). Such oversensitization can reduce sensitivity and increase the developed density in the unexposed regions of negative films. The controlled use of iodide to produce hole traps and/or as a means to establish phase boundaries which can encourage electron–hole separation has contributed significantly to the sensitivity advantages of commercial tabular grains (147, 211).

2.2. Spectral Sensitization

The intrinsic absorption, and therefore the intrinsic photographic sensitivity, of silver bromide and silver iodobromide microcrystals falls off rapidly for wavelengths greater than 500 nm (see Fig. 2). In fact, silver chloride crystals have almost no sensitivity in the visible regions of the spectrum. The need to extend silver halide sensitivity into the green (ca 500–600 nm) and red (ca 600–700 nm) regions of the visible spectrum is obvious for the production of color photographic products. Furthermore, even in black-and-white materials, extension of the photographic response beyond 500 nm is necessary for optimum effective light sensitivity. The process of expanding the wavelength sensitivity beyond the intrinsic region is called spectral sensitization.

As in chemical sensitization, spectral sensitization is usually done after precipitation but before coating, and usually is achieved by adsorbing certain organic dyes to the silver halide surfaces (47, 48, 212–229). Once the dye molecule is adsorbed to the crystal surface, the effects of electromagnetic radiation absorbed by the dye can be transferred to the crystal. As a result of this transfer, mobile electrons are produced in the conduction band of the silver halide grain. Once in the conduction band, the electrons are available to initiate latent-image formation.

Most mechanistic models of spectral sensitization include an electron-transfer step. Upon absorption of light by the dye molecule, an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye. If in this excited state the electron is energetically above or close to the bottom edge of the conduction band, the electron can transfer from the dye molecule to an energy state within the conduction band of the crystal. The electron-transfer process is depicted in Figure 11. During the transfer, the dye molecule becomes oxidized and is left with a photohole trapped in the highest occupied molecular orbital. Many dyes have been discovered in which the lowest unoccupied molecular orbitals are appropriately disposed so as to promote such an electron transfer. In addition to the obvious importance of the position of the electronic energy levels, ie, HOMO and LUMO energies, structural packing, aggregation, and orientation of the adsorbed dye molecules are also factors in determining the practical photographic efficacy of spectral sensitizing dyes. In fact, such structural properties may explain why only about 30 of a possible 50,000 dyes commonly are used in the photographic industry (215).

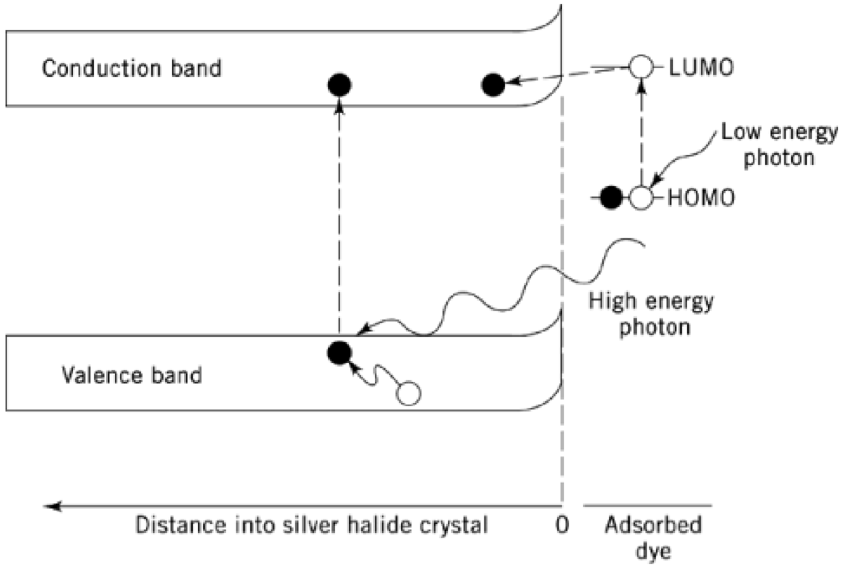
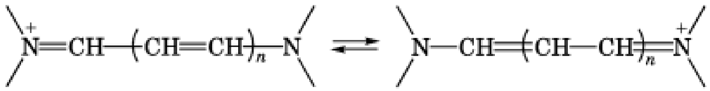


Fig. 11. Mechanism of electron transfer from an excited dye molecule to a silver halide crystal where HOMO and LUMO are highest occupied and lowest unoccupied molecular orbital, respectively.

Many spectral-sensitizing dyes can be classified according to molecular structures (228). The structural part of a dye molecule that enables the molecule to absorb visible or infrared radiation is called a chromophore. The resonance structure for three common chromophores is shown.

Amidinium ion system



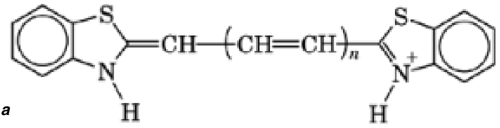
Carboxyl ion system

Dipolar amidic system

The resonance within the chromophore corresponds to electronic motion along the length of the conjugated chromophoric chain. The terminal groups of the chromophore chain are often included in heterocyclic rings. The structure in Table 1 shows an amidinium ion system bound by two benzothiazole nuclei. If the bridge between the heterocyclic nuclei consists only of a methine group, $=\mathrm{CH}-$ ($n = 0$), then the dye is referred to as a simple cyanine. Increasing the chain length produces carbocyanines, dicarbocyanines, tricarbocyanines, and so on for $n = 1, 2, 3\ldots$, respectively.

The length of the conjugated chain in the chromophore and the nature of the terminal nuclei are important factors in establishing the wavelengths at which a dye molecule absorbs incident radiation. In a vinyl series, a set of different dyes for which only n changes, the wavelength of maximum absorption increases with increasing n. Such a phenomenon can be viewed in terms of a simple quantum-mechanical model. The length of the chromophore can be viewed as the length of a one-dimensional box which confines a particle (ie, an electron). As the length of such a quantum box is increased, the energy levels come closer together (230) and thereby lesser light energies (longer wavelengths) are required to effect an electronic transition. Table 1 shows the wavelengths of maximum light absorption as a function of n in such a series of dye molecules. By structural variations, sensitivity to infrared radiation can be produced. For example, chain-stabilized pentacarbocyanine dyes have been prepared that impart photographic sensitivity to silver halide crystals at wavelengths beyond 1300 nm (231). Adsorption of the dye to a grain surface reduces the energy separation between the LUMO and HOMO. This reduction accordingly produces a bathochromic shift in the absorption maximum. There are, however, limitations for spectral sensitization in the infrared. Because the LUMO must be close to the bottom edge of the conduction band, the HOMO must move to higher energies for the sensitizing dye to absorb at longer wavelengths. These sensitizing dyes become increasingly susceptible to oxidation and, thereby, increasingly unstable (232). Accordingly, practical sensitization in the infrared is complicated by the fact that compromises between the electron-injecting ability and the thermodynamic stability of the dye must be considered. Further red shifts in the absorption and photographic sensitivity maxima occur when the adsorbed dye concentrations are high enough to promote formation of oriented dye aggregates (212). The resulting long-wavelength absorption bands are referred to as J-bands and are characterized by sharp, intense absorption peaks. The extinction and wavelength of maximum absorption for a J-band depend on the refractive index of the substrate (233) and on the crystallographic orientation of the substrate (47, 48, 234).

Table 1. Amidinium Ion Chromophore Series[a]



n	Wavelength of maximum absorption, $\lambda_{\max}$, nm
0	423
1	557
2	650
3	758

[a] Ref. 229.

Adsorbed spectral sensitizing dyes generally produce a photographic sensitivity proportional to the number of photons absorbed. In fact, some sensitized silver halide grains promote latent image formation with the same efficiency per absorbed photon in the spectral region of the dye as in the intrinsic region of the silver halide absorption. However, the quantum efficiency is not always so high. Because of interference of adsorbed dyes with development, relative positions of the LUMO and the bottom edge of the conduction band, and/or other competing kinetic pathways (216, 225), certain dyes (eg, pinakryptol yellow and phenosafranine) may desensitize the photographic response, in some cases by as much as two orders of magnitude. If the LUMO of an adsorbed dye molecule is below the bottom edge of the conduction band, the dye's LUMO can desensitize the intrinsic, ie, high energy photon response by competing with the latent image centers for the photoelectrons in the conduction band. In addition to development restraint and photoelectron trapping, in some situations the photohole can cause the regression and possible destruction of the latent-image silver center. This process is favored when dyes are aggregrated and can facilitate the transport of the photohole from the point of origin to the growing latent-image center. Dye photoholes have been detected and characterized by electron spin resonance (225) and reflectance spectroscopy (224, 235).

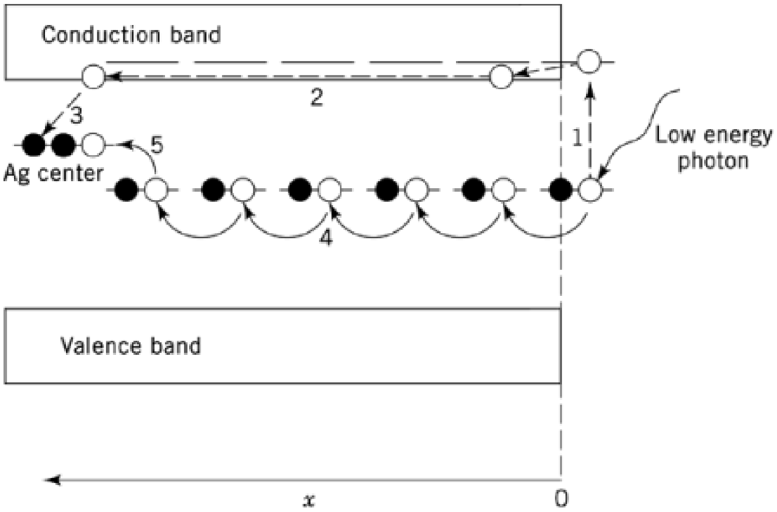


Fig. 12. A possible mechanism for the dye-induced photooxidation of a silver center. x represents the distance across a silver halide surface to which aggregated dye molecules are adsorbed. Steps 1, 4, and 5 represent the photohole (○) formation, photohole migration, and silver oxidation processes which can ultimately lead to the total regression of the silver aggregate; (●) represents an energy state occupied by an electron.

Figure 12 and equations **8**–12 depict a case in which the dye molecules are aggregated on the grain surface, a condition normally considered favorable for obtaining spectral sensitization. In this case, however, the aggregated dyes can form a pathway for transporting photoholes, whether produced by an intrinsic or a spectral exposure, to a growing latent image center. Through repeated attack, steps 4 and 5 have been postulated under certain conditions to overwhelm steps 2 and 3 (Fig. 12), oxidizing the silver aggregate and eventually leading to its total regression.

$$\mathrm{dye}_{(1)} + h\nu \longrightarrow \mathrm{dye}^{+}_{(1)} + e^{-}_{\mathrm{CB}} \qquad (8)$$

$$\mathrm{dye}^{+}_{(1)} + \mathrm{dye}_{(m)} \longrightarrow \mathrm{dye}_{(1)} + \mathrm{dye}^{+}_{(m)} \qquad (9)$$

$$\mathrm{dye}^{+}_{(m)} + \mathrm{Ag}_{n} \longrightarrow \mathrm{dye}_{(m)} + \mathrm{Ag}^{+}_{n} \qquad (10)$$

$$\mathrm{Ag}^{+}_{n} \longrightarrow \mathrm{Ag}_{n-1} + \mathrm{Ag}^{+}_{i} \qquad (11)$$

If $n-1$ photons are absorbed as in equation **8**, then the complete annihilation of the n-atom silver center can occur as shown in equations 12 and 13:

$$(n-1)\ h\nu + \mathrm{Ag}^{0}_{n} \longrightarrow (n-1)\ \mathrm{Ag}^{+}_{i} + (n-1)\ e^{-}_{\mathrm{CB}} + \mathrm{Ag}^{0} \qquad (12)$$

$$\mathrm{Ag}^0 \longrightarrow \mathrm{Ag}_i^+ + e_{\mathrm{CB}}^- \qquad (13)$$

where equation **8** is the result of photoexcitation of the dye and electron transfer into the conduction band, equation 9 represents hole migration from dye to dye, equation 10 describes the oxidation of the silver cluster, equation 11 represents the migration of an interstitial silver ion from the oxidized silver cluster, and equation 13 is the thermal regression (see eq. **7**) resulting because the highest electronic energy state for a single silver atom is within thermal energy from the bottom edge of the conduction band.

Another common loss process results from electron–hole recombination. In this process, the photoexcited electron in the LUMO falls back into the HOMO rather than transferring into the conduction band. This inefficiency can be mitigated by using supersensitizing molecules which donate an electron to the HOMO of the excited sensitizing dye, thereby precluding electron–hole recombination. In optimally sensitized commercial products, dyes and conditions which contribute to the many possible loss processes, eg, equations **8 through 13** and electron–hole recombination, must be avoided.

3. Other Emulsion Additives

In addition to chemical and spectral sensitizers, several other classes of chemical compounds are added to emulsions before coating. Additives are used to facilitate coating operations, eg, surfactants (qv) and viscosity enhancers; to reduce spontaneous development in unexposed regions, eg, tetraazaindenes and mercaptotetrazoles; and to reduce abrasion and permit high temperature processing, eg, aldehydes (qv).

For certain component compositions the viscosity and surface tension of the melted emulsion may not allow adequate emulsion spreading on the support during the coating procedures. For these situations, various surfactants that act as spreading agents are available to control the surface tension. The sulfiding reaction is a thermally activated process with an activation energy near 126 kJ/mol (30 kcal/mol). Therefore, quenching the reaction by cooling the emulsion from 60 to 25°C does not eliminate the reaction but rather reduces the rate by about two orders of magnitude. After long storage of the emulsion, continued sensitization may produce a catalytic activity in the silver halide grains and unwanted photographic fog upon development. This can be controlled partly by additions of such stabilizers as halide ions, acid, benzimidazoles, benzotriazoles, benzothiazolium salts (236, 237), and mercaptotetrazoles (238–241). Many of these compounds adsorb to silver and complex with silver ions. Specifically as a result of these interactions, phenylmercaptotetrazole (242) restrains development (243) and enhances sensitivity (244) even in freshly coated samples. Quantum-mechanical analyses coupled with photographic data suggest that the best stabilizers not only bind with silver ions but are also poor reducing agents (245). Azaindene (246–248) compounds satisfy both of these properties and are effective stabilizers and development antifoggants. Fog control for Au-sensitized emulsions can be, in part, achieved using thiocyanate (249). Gelatin cross-linking agents (hardeners) represent another class of materials that may be added before coating. These compounds render the coated emulsion layers more resistant to abrasion during handling and improve the thermal stability of the gelatin.

The desire for reduced development times required to produce an image has necessitated the use of solutions with increased activities. Temperature increases, pH increases, and increased oxidizability are all variations directed toward shortening process times. Unfortunately, high temperature processing tends to soften and dissolve the gelatin emulsions; therefore the gelatin must be hardened before development. The enhanced thermal stability and improved mechanical durability produced by hardeners result from the formation of three-dimensional bridging of various sites within the gelatin molecules (250). Both inorganic, eg, chromium salts, and organic, eg, aldehydes, compounds have been used as hardeners. Chromium appears to complex with carbonyl groups (251), whereas many of the organic hardeners seem to cross-link between the amino groups in the gelatin molecules (252).

In most color photographic products, organic compounds such as couplers or redox dye releasers are added to the melted emulsions before coating. These compounds are essential to the development reactions that produce the dye molecules composing color images.

4. Coating the Emulsion

4.1. The Support

For most practical applications, the sensitized emulsions must be coated on a base or support to permit convenient handling. There are three basic classes of supports: glass, plastic, and paper. Supports are chosen on the basis of dimensional stability, low water permeability, flexibility, freedom from surface irregularities, compactness, cost, and safety. The relative importance of these requirements depends on the particular application (253). For example, dimensionally stable glass plates are one of the oldest base materials and are excellent supports for the precision photography required in astronomy, telemetry, and microelectronics. However, weight, bulkiness, and fragility make glass inappropriate and inconvenient for amateur photography. Clear plastic film supports are the most commonly used bases in modern photography. These materials are designed and selected based on safety, environmental concerns, and how they are to be used, eg, their ability to be unwound and rewound on reels and cassettes or rigidity in sheet film formats. The original plastic film supports were prepared from chemically unstable and highly flammable cellulose nitrate. Cellulose nitrate supports have been replaced by solvent-cast materials, eg, cellulose triacetate [9012-09-3], and extruded materials, eg, poly(ethylene terephthalate) [25038-59-9] (PET). These materials are not only safe but also strong and dimensionally and chemically stable. Paper supports are commonly used in products that are viewed in the reflection mode, such as color or black-and-white print materials. Before the silver halide emulsion layers are coated, some paper products are first undercoated with barium sulfate in a gelatin matrix to improve surface smoothness and visual whiteness in the highlight areas of the prints. Modern paper products are often waterproofed with impervious resin coatings of polyethylene whitened with titanium dioxide (254). Because of the water repellency of resin-coated materials, fewer chemicals are carried over from one treatment bath to another during processing. Subsequently, chemical replenishment rates can be reduced, an economical and environmental advantage (see Waterproofing and water/oil repellency).

4.2. Coating Techniques

There are rigid constraints on the technology of coating photographic materials. The emulsion coatings must be uniform in thickness and composition and free from streaks. Compounding the difficulty is the need to produce a multilayered coating often composed of more than ten separate chemical-containing layers. Furthermore, light-sensitive materials must be coated in near or total darkness. Depending on its function, an individual, coated, dried layer is generally 1–30 μm thick (40, 255–257). Most of the coating application techniques for photographic materials employ a flexible support which is transported on rollers past a coating station where the emulsion is delivered. In some systems, melted emulsion is held in troughs or trays and the emulsion is transferred to the support by bringing the moving support into contact with the surface of the liquid emulsion. As the coating rises from the trough, excess emulsion can be removed by a knife-edge or with air jets. As an alternative to trough coating, various types of coating hoppers have been developed. In the latter techniques, the liquid emulsion is delivered to the moving support by pumps or gravity flow and is spread uniformly over the support surface by variously designed hoppers (255, 257). Patent literature refers to coating rates in excess of 3 m/s (258). Once the emulsion has been spread over the support, the support is conveyed into a cooling chamber where the emulsion gels, then into a drying chamber where much of the water is removed from the coated gelatin. During drying, the emulsion thicknesses are reduced to ca 10% of the originally coated thicknesses.

4.3. Coating Structures

Light-sensitive photographic elements can be produced by coating an emulsion layer directly on the support; however such simple structures rarely have practical application. Generally, the support is electrostatically or chemically treated to improve the adhesion of the hydrophilic gelatin layer to the more hydrophobic support. Furthermore, in some products intermediate layers are coated between the emulsion and base to facilitate spreading. These intermediate layers often contain light-absorbing materials to prevent stray light from reflecting back into the emulsion layer during exposure. The stray light is reflected at the film–air interface on the back of the support because of the refractive index change at that surface. In the early days of photography the reflected light often produced photographs showing halos around small bright images, hence the use of light-absorbing materials is referred to as antihalation and the light-absorbing layers, antihalation layers. Several different light-absorbing materials have been used in antihalation layers, including finely divided carbon particles, dyes, and colloidal silver. The antihalation materials must be removed during processing as they can interfere with subsequent viewing. Colloidal silver dispersions are occasionally used in color products and can be removed during the silver bleaching and fixing stages. When carbon suspensions are used, the carbon is coated on the back side of the transparent film opposite the emulsion and removed by mechanical scrubbing.

In addition to intermediate layers and antihalation layers, most films also are overcoated with a gelatin layer that protects sensitive emulsion layers from the image-degrading effects of pressure and abrasion. Protective overcoat layers are generally only 1–3 μm thick. Because uv radiation is strongly absorbed by gelatin, an intervening gelatin layer would seriously reduce the effective response of the silver halide grains in materials designed for ultraviolet sensitivity (259), therefore some specialized products used in astronomy and vacuum spectroscopy do not have protective overcoat layers.

Virtually every photographic product has its own unique coating structure in order to optimize the sensitometric responses required for a particular application. To record an original scene accurately, photographic emulsions often must respond differentially to an exposure intensity range of 1 to 1000 times from the darkest to the brightest object in the scene. The exposure range over which an emulsion can respond differentially is called the latitude. Because most individual emulsions have exposure latitudes of only 1 to 100 times, two or more separate emulsions often are coated on the same support. Depending on the particular application, the two emulsions may be blended before coating and then coated in a single layer, or the emulsions may be coated in separate layers, one directly above the other (260). For color products, multiple emulsions must be coated for each of the three color-sensing regions, ie, blue, green, and red. For reflection print materials, there is often no need for long latitude response, but rather there is a need for high contrast and short latitude; therefore, emulsion blending and multiple-emulsion coating are not generally required. X-ray products have a unique coating structure with high coated levels of silver halide crystals to produce the desired x-ray sensitivity. Emulsions are coated on both sides of x-ray film, thereby providing the necessary high silver halide concentrations without severely reducing the accessibility of some emulsion grains to the processing solutions.

5. Exposure and Latent-Image Formation

For photographic materials in which the image is produced with uv, visible, or ir radiation, optical lens systems are required. The lens system focuses the image of a scene on the emulsion layers of the photosensitive coating. The degree of magnification is, therefore, a function of the effective focal length of the optical lens system. Furthermore, the quality of the image as recorded within the coating depends not only on the optical and chemical properties of the coated light-sensitive material, but also on the lens optics. Accordingly, lens flare, astigmatism, and chromatic and spherical aberration all must be considered in designing a photographic system. Certain photographic systems do not use lenses during imaging, eg, x-ray and laser-scanning systems. In medical radiography, x-ray images are recorded by placing the photosensitive coating next to an x-ray-absorbing screen. The phosphors of the screen are electronically excited upon x-ray absorption and emit visible light during subsequent de-excitation. The original x-ray pattern is recorded as the photographic grains absorb the photons emitted from the screen.

Scene images are recorded in the emulsion layers by the action of the photoholes and photoelectrons produced in the grains by the absorption of photons. In unexposed regions of negative-working materials, there are no photoholes and no photoelectrons. Accordingly, no latent images and no catalytic silver clusters are produced and little amplification occurs in these regions during development. However, in the exposed regions, the photoelectrons react with silver ions to form clusters of silver metal. These clusters of silver function as catalytic centers for amplification during subsequent development.

Discussions and experiments regarding the theory of latent-image formation requiring analysis of events involving one, two, or three atoms generally have been based on indirect evidence (130, 142, 156–167). However, all of the theories begin with the same latent-image formation process, ie, photon absorption by the crystals (or the adsorbed sensitizing dyes) to produce electron–hole pairs, and all of the theoretical processes end the same, ie, with a sufficiently large cluster of localized silver atoms. Furthermore, all theories describe the formation of silver atoms as the result of electrochemical reduction of silver ions by the photoelectrons. The differences among the various theories are in the descriptions of the mechanistic steps which occur between photon absorption and final formation of a stable silver cluster, ie, latent image. In the earliest mechanistic models, the growth of the latent image was viewed to consist of an alternating sequence of coulombically driven steps beginning with the formation of an electron–hole pair and the trapping of the electron at a chemical sensitization center or a kink site yielding a localized negative charge, t_e^-:

$$h\nu \longrightarrow h_{\mathrm{VB}}^+ + e_{\mathrm{CB}}^-$$

$$e_{\mathrm{CB}}^- + t \longrightarrow t_e^-$$

where h_{VB}^+ represents a mobile valence band photohole and t is an electron trap. The trap is reset and able to attract a mobile interstitial silver ion, thus initiating an alternating sequence ultimately yielding a stable and developable cluster of silver atoms, $\mathrm{Ag^0}_{\mathrm{n}}$.

$$t_e^- + \mathrm{Ag}_i^+ \longrightarrow \mathrm{Ag}^0 \xrightarrow{e_{\mathrm{CB}}^-} \mathrm{Ag}^- \xrightarrow{\mathrm{Ag}_i^+} \mathrm{Ag}_2^0 \xrightarrow{e_{\mathrm{CB}}^-} \mathrm{Ag}_2^-$$

$$\mathrm{Ag}_2^- \xrightarrow{\mathrm{Ag}_i^+} \mathrm{Ag}_3^0 \xrightarrow{e_{\mathrm{CB}}^-} \mathrm{Ag}_4^- \xrightarrow{\mathrm{Ag}_i^+} \mathrm{Ag}_5^0 \longrightarrow \quad \longrightarrow \mathrm{Ag}_n^0$$

Other models consider the steps up to and including Ag formation to be rapid in both the forward and reverse directions, thereby setting up an equilibrium condition involving h_{VB}^+, e_{CB}^-, t_e^-, t_h^+, Ag^0, and Br^0, where t_h^+ is a trapped hole and Br^0 is the result of Br^- neutralization by t_h^+. In establishing this equilibrium condition, recombination processes are also considered, ie, $t_e^- + h_{\mathrm{VB}}^+ \longrightarrow 0$ and $e_{\mathrm{CB}}^- + t_h^+ \longrightarrow 0$. In the nucleation and growth model from this collection of species, nucleation eventually occurs when the silver atom traps an electron and an interstitial silver ion to become a stable, $\mathrm{Ag^0}_2$ nucleus. The $\mathrm{Ag^0}_2$ center continues to grow by alternately trapping e_{CB}^- and $\mathrm{Ag^+}_{\mathrm{i}}$. Other models suggest that the process starts when a $\mathrm{Ag_2S}$ center traps h_{VB}^+, becomes positively charged, releases $\mathrm{Ag^+}_{\mathrm{i}}$, and becomes AgS. Subsequent trapping of e_{CB}^- and $\mathrm{Ag^+}_{\mathrm{i}}$ by another $\mathrm{Ag_2S}$

yields Ag^0. Latent-image centers can form either by diffusion and aggregation of the silver atoms or by collection of e_{CB}^- and $Ag^+{}_i$ at the silver atom. By whatever mechanistic process, a negative silver scale is produced (see Fig. 4) through the imagewise formation of latent-image centers and the treatment with a latent-image sensitive development solution. Negative dye-scale images can also be produced if the developer molecules, oxidized during latent-image amplification, are used in subsequent chemical reactions to form yellow, magenta, and cyan dyes.

Positive imaging can be accomplished by several different techniques. In positive imaging, the density produced by developed silver or dye molecules decreases with increasing exposure. If an original negative is on a transparent film base, a 1:1 positive copy can be produced by contact printing on a negative print material, or an optically magnified positive copy can be prepared by using an enlarger. In addition to such negative–positive approaches to producing positive images, positive or reversal imaging in the originally exposed coating is also possible. One way to generate reversal images in color films is to use specially designed processing sequences. If black-and-white development is used to develop all of the exposed grains, then a positive dye image can be produced by first chemically activating the remaining silver halide and then developing the activated grains with color developers. In the latter approach the silver halide grains are of the same negative-working type as those used in negative–positive materials. Negative-working silver halide grains are also used to produce the positive images provided by instant photography products (28). After exposure in instant photography systems, the film is passed between a pair of rollers which rupture a reagent-containing pod. The reagents include development initiating chemicals that are released from the pod and uniformly spread within the film structure. Upon reaching the silver halide-containing layers, the reagents chemically promote the imagewise diffusion of silver ions in the case of black-and-white products or dyes in color products. The diffusing species are ultimately trapped in a receiving layer for subsequent viewing (see Color photography, instant).

There are other reversal imaging materials, some of which make use of specially designed reversal emulsion grains (29, 64, 261–263). Reversal grains are conveniently divided into two classes: photobleach reversal grains and internal image grains. Photobleach grains are chemically treated to have surface catalytic activity before exposure. During exposure, the photoholes migrate to and oxidize the centers of catalytic activity. Because the oxidized centers in the exposed regions have reduced catalytic activity, development yields positive silver imaging. In internal image forming grains, exposure forms an internal latent image and deactivates the surface for subsequent nucleation treatment which produces catalytic nuclei only on surfaces of unexposed grains (29). Subsequent amplification produces a positive image in silver.

For both negative–positive and reversal materials, the optical properties of the coated silver halide layers significantly influence the quality and sensitivity of the photographic response. Once the photons enter the gelatin coating, they move on a straight path until they encounter a microcrystalline grain. At this point either the photon is absorbed by the grain and produces an electron–hole pair within the crystal, or the photon is scattered through some angle and continues its journey through the gelatin. The relative probabilities of these two events determine the vertical and lateral distribution of light within the emulsion layers (264). Accordingly, these relative probabilities also partly establish the sensitivity, sharpness, and resolving power of the photographic film. The photoholes and photoelectrons produced in the grains by the absorbed photons are mobile and free to move through the crystal; the locations at which these mobile charge carriers are trapped determines the efficiency of the photographic response. If the charge carriers are trapped so that the electrons and holes recombine, they annihilate one another and the photographic efficiency is reduced. The probability of such annihilation is markedly reduced in practical photographic films by the use of chemical sensitization and skillful crystal design.

Optimized photographic grains may require fewer than 10 absorbed photons to produce a catalytic center; clusters containing only two or three silver atoms may catalyze development. The practical sensitivity or speed of such light-detection materials often is monitored in terms of the exposure required to produce a given photographic response. The exposures can be recorded on either log scales or arithmetic scales. The DIN

(Germany) speeds are logarithmic, so that doubling the sensitivity of a film corresponds to a constant additive increase in the speed. The ASA (United States) and GOST (Russia) speeds are arithmetic, so that doubling the sensitivity corresponds to doubling the speed. In determining the photographic response at which the exposure is monitored, the various systems again differ. In the DIN and GOST systems, the speed corresponds to the exposure required to produce a given optical density above fog (0.10 for DIN, 0.20 for GOST). The ASA system also considers the contrast of the response in the calculation of speed because the contrast is important in determining the quality of the recorded image. In the early 1970s an international standard (ISO) was adopted by the United States, Great Britain, and Germany (265) for black-and-white negative photographic materials. The ISO standard is an arithmetic rating which includes contrast considerations.

The developed image produced in a given photographic film is not uniquely determined by the exposure. Exposure is a measure of the total incident light energy and is therefore equal to the mathematical product of the light irradiance, I, and the exposure time, t. The developed image usually depends on the individual values of I and t; ie, a low irradiance exposure for a long time may not yield the same photographic response as a higher irradiance exposure for a short time even though the exposure, It, may be the same. Materials that behave in this fashion are said to suffer from reciprocity law failure. For low irradiance exposures, the time between photon absorption events is relatively long. Thus, a primary cause of low irradiance reciprocity failure may be thermal instability of a single atom of silver in a silver halide lattice. Chemical sensitization often reduces reciprocity law failure. In particular, gold is thought to stabilize isolated atoms of silver against thermal regression and thereby reduce low irradiance reciprocity law failure. Because different photographic emulsions have different reciprocity properties, the color balance of a reproduction with a multilayer coating may be altered if recommended exposure times are not used.

6. Special Exposure Effects

Solarization, the photobleach effect, the Herschel effect, and the Clayden effect (266) are all exposure-related phenomena that produce positive photographic images without the need for special development solutions or processing sequences. For negative-working emulsions that are conventionally processed, the developed density increases and then becomes constant with increasing exposure. For even higher exposures, the optical density and the developed silver may begin to decrease (see Fig. 4). This decrease in density is called solarization and results, at least in part, from the trapping and mobility properties of the photoholes and photoelectrons produced by high irradiance exposures. The photographic speed of positive-working films that use the solarization effect is rather low, and the phenomenon, therefore, has limited practical utility. It is generally believed that solarization results from photoholes bleaching surface latent-image centers formed earlier in the exposure. A latent-image center, Ag^0, can be completely photobleached by repetition of the following process.

$$h^+_{\mathrm{VB}} + \mathrm{Ag}^0_n \longrightarrow \mathrm{Ag}^+_n$$

$$\mathrm{Ag}^+_n \longrightarrow \mathrm{Ag}^0_{n-1} + \mathrm{Ag}^+_i$$

Several experiments seem to confirm the photobleach mechanism. In particular, the use of hole acceptors, eg, sodium nitrite and acetone semicarbazone, during exposure can reduce and eventually eliminate solarization. Furthermore, amplification with developing solutions that enhance the solubility of the silver halide grains also reduces or removes solarization. These results suggest that the latent images are not permanently destroyed by bleaching but merely that the topography of the centers within the grain is altered. Electron microscopy has been used to show that large, crystallized, undevelopable silver centers are found on the surface of grains in solarization regions (267), suggesting that a variety of mechanisms may operate during solarization.

The use of photoholes to bleach prefogged emulsion grains is applied commercially in the production of direct-positive images for micrographic, radiographic, and graphic arts applications. In these photobleach materials, catalytic centers are added to the grain surfaces before exposure. Subsequent exposure destroys the catalytic activity of the centers, so that positive imaging results upon conventional processing. The preexposure formation of surface catalytic centers has been accomplished by reduction sensitization and by uniform light flashes. The degree of catalytic activity imparted to the surface must be regulated carefully so that photoholes can destroy the centers during exposure. The photoelectrons, which also are produced during exposure, must be removed; otherwise electron–hole recombination or even amplification of the surface–center activity may result. The unwanted photoelectrons can be removed at the grain surface by electron trapping or desensitizing dyes, or by internal trapping sites provided by such dopants as rhodium (268) or iridium (269, 270).

Ag^0_n centers can be destroyed by the direct absorption of long-wavelength light, as well as by exposure-generated holes. If the light has enough energy, electrons can be ejected from the electronic orbitals associated with the silver centers into the manifold of electronic energy states comprising the conduction band of the silver halide microcrystal (182, 271). That is,

$$\mathrm{Ag}_n^0 \xrightarrow{h\nu} \mathrm{Ag}_n^+ + e^-_{\mathrm{CB}}$$

$$\mathrm{Ag}_n^+ \longrightarrow \mathrm{Ag}_{n-1}^0 + \mathrm{Ag}_i^+$$

or

$$\mathrm{Ag}_n^+ \xrightarrow{V_{\mathrm{Ag}^+}} \mathrm{Ag}_{n-1}^0$$

where V^+_{Ag} represents a vacant silver lattice position near the Ag^+_n center. Even though the cross section for light absorption by the small silver center, Ag^0, is small, iteration of these steps eventually can destroy a given silver center. This phenomenon is known as the Herschel effect. With prefogged silver halide grains, the Herschel effect can produce positive imaging. In such materials the exposure of the image is carried out with red or ir radiation (266).

The Clayden effect is another exposure phenomenon that produces a positive image. This effect is produced by two sequential exposures, the first of high irradiance and the second of lower irradiance. For certain emulsion coatings, high irradiance exposures desensitize the emulsion grains, thus a second exposure produces less catalytic activity than would have been produced without the preexposure. One of the most striking examples of this desensitization was first observed in 1899 by Clayden, when he photographed lightning flashes. The short lightning flashes desensitized the grains of the negative film, and further exposure, while the camera shutter remained open, induced catalytic activity in the grains that had not been desensitized. In this manner, white images of the lightning were produced in the negative, and “black lightning” images were produced in the positive print.

7. Development

7.1. Composition of Developer Solutions

In most practical photographic materials, exposure of the silver halide grains does not produce visible images. In fact, the cluster of silver atoms composing the latent image is usually too small to be resolved with an optical or electron microscope. The growth of the small clusters of silver atoms into silver centers visible to the unaided eye is achieved with developer solutions. At least three significant classes of development components are present in most practical developer solutions: reducing agents, restrainers, and preservatives. The most important component is the chemical reducing agent.

For negative films, the electrochemical reduction properties of the reducing agents must be properly positioned to provide rapid amplification of exposed grains and much slower spontaneous amplification of unexposed grains. The ability to discriminate between exposed and unexposed grains is a well-known property of chemical reducing agents that possess the Kendall structure (272), represented by

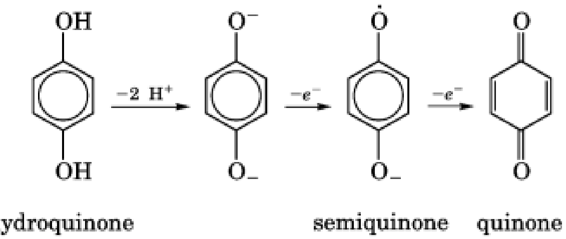
$$\mathrm{A}\!-\!\!\left(\mathrm{CH}\!=\!\mathrm{CH}\right)_{n}\!\!-\!\mathrm{B},$$

where *n* may have either zero or integral values and where A and B may be hydroxyl, amine, or substituted amino groups. Most of the useful chemical reducing agents are benzene derivatives having Kendall structures. Examples of effective compounds that have Kendall structures include hydroquinones (1,4-dihydroxybenzene), catechols (1,2-dihydroxybenzene), *p*-aminophenols, *p*-phenylenediamines, and ascorbic acid [50-81-7]. If the hydrogen of the hydroxyl group in these compounds is replaced with a hydrocarbon group, the development activity of the compound is generally destroyed. This, however, is not the case for similar hydrogen replacements on the amino groups. In fact, substitutions of the latter type enhance development activity in some cases. To be a photographically effective chemical reducing agent it is not always necessary for a compound to have the Kendall structure. In particular, phenidone [92-43-3] developing agents and certain thiadiazoles discriminately reduce silver ions (273).

The attainment of appropriate electrochemical potentials and amplification activity in development solutions is a function not only of the chemical structure of the reducing agents but also of the other chemical components of the solution. In general, the activity of development solutions is dependent on hydrogen ion and halide ion concentrations. The pH dependence is particularly noticeable in reducing agents with hydroxyl or amino functionality. The hydrogen ion concentration often regulates the concentration of the active form of the reducing agent. Therefore, maintaining stable development activity requires pH buffering, usually on the alkaline side. During the development of silver halide grains, silver ions are converted to elemental silver and halide ions are released into the solution. The presence of released halide ions near development centers restrains amplification. Consequently, the activity of a development solution tends to decrease with increasing time of amplification. To minimize the effect of increasing halide ion concentration, development formulations usually include alkali halide salts which minimize the percentage change in the halide ion concentration during development.

Hydroquinone [123-31-9] represents a class of commercially important black-and-white chemical reducing agents (see Hydroquinone, resorcinol, and catechol). The following scheme for silver halide development with hydroquinone shows the quantitative importance of hydrogen ion and halide ion concentrations on the two half-cell reactions that describe the silver–hydroquinone redox system:

Oxidation



Reduction $\mathrm{AgBr} \xrightarrow{+e^-} \mathrm{Ag}^0 + \mathrm{Br}^-$

The presence of bromide ions in the development solution restrains the conversion of Ag^+ to Ag^0 by the effect of its concentration on the electrochemical overpotential for the overall redox couple. At appropriate concentrations, bromide ions restrain the rate of fog formation more than the rate of development in image areas. Such restraint selectivity usually improves picture quality, and restrainers of this type are called development antifoggants. The activity of a development solution containing hydroquinone can also be adjusted by chemical substitutions on the hydroquinone molecule. Substitution of the hydrogen atoms on the benzene nucleus with either methyl, methoxy, hydroxide, or amino groups increases the rate of development. On the other hand, the development activity is reduced by substitution with electron-withdrawing groups, eg, nitro, sulfo, cyano, carboxy, and formyl groups.

In addition to reducing agents and restrainers, preservatives are also required in practical development formulations. Unintentional oxidation of the chemical reducing agent by oxygen dissolved in the developer solution may not only alter development kinetics but may also give colored by-products that can produce unattractive stains in the developed material. It is important, therefore, to add to the development solutions chemicals that rapidly remove oxidation by-products. Sodium sulfite [7757-83-7] is an effective scavenger for such oxidation products. Sodium sulfite also decreases the rate of atmospheric oxidation of hydroquinone (274). In addition to having preservative and stain-prevention properties, sulfite has a solvent action on the grains that promotes crystal dissolution. Such solvent action influences the rate and mechanism of development.

7.2. Chemistry and Mechanism of Development

Development has been successfully viewed as an electrochemical redox reaction (275–280), for which the overall reaction can be expressed as follows:

$$n\,\mathrm{AgBr} + \mathrm{D} \rightleftarrows \mathrm{D}_{\mathrm{ox}}^{(n-m)+} + n\,\mathrm{Ag}^0 + n\,\mathrm{Br}^- + m\,\mathrm{H}^+$$

where D and $\mathrm{D}_{\mathrm{ox}}^{(n-m)+}$, respectively, correspond to the reduced and oxidized forms of the chemical reducing agent. The electrochemical potential of the silver half-cell is given by the Nernst equation:

$$E_{\mathrm{Ag}} = E_{\mathrm{Ag}}^0 + (RT/F)\ \ln\left[a\left(\mathrm{Ag}^+\right)/a\left(\mathrm{Ag}^0\right)\right]$$

$$= E_{\mathrm{Ag}}^0 + (RT/F)\ln[K_{sp}] - (RT/F)\ln[a(\mathrm{Ag}^0)a(\mathrm{Br}^-)] \qquad (14)$$

where E_{Ag}^0 is the standard potential in volts, ie, the value of the potential at unit activity of Ag^+ and Ag^0; $a(\mathrm{Ag}^+)$, $a(\mathrm{Ag}^0)$, and $a(\mathrm{Br}^-)$ are the activities of Ag^+, Ag^0, and Br^-, respectively; K_{sp} is the solubility product of silver bromide; R is the gas constant (8.314J/(K·mol)); T is the absolute temperature; and F is the Faraday constant (9.6485×10^4 C/mol). The corresponding electrochemical potential for the developer half-cell reaction

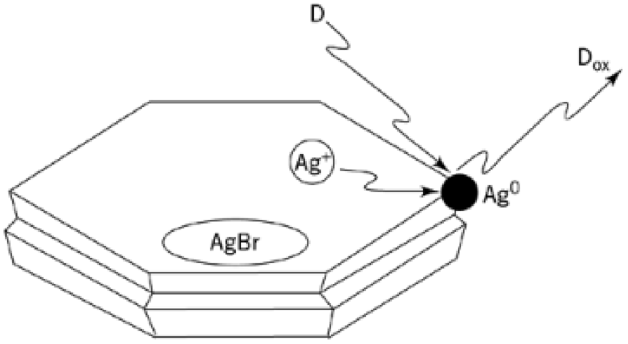


Fig. 13. A speck of developing silver on the surface of a silver halide crystal. The silver acts as an electrode for the electrochemical reduction of silver ions. The developer molecule, D, delivers an electron to the developing speck, and in turn the electron is neutralized by an approaching silver ion which, in the process, is converted to elemental silver.

is given by a similar expression:

$$E_{\text{Dev}} = E^0_{\text{Dev}} + (RT/nF)\ \ln[a(\text{D}_{\text{ox}}^{(n-m)+})a(\text{H}^+)^m/a\,(\text{D})] \qquad (15)$$

The difference, ΔE, between the two electrochemical potentials is expressed in equation 16:

$$\Delta E = E_{\text{Ag}} - E_{\text{Dev}} = \Delta E^0 + (RT/F)\ \ln\left[a\left(\text{Ag}^+\right)\right] - (RT/F)\ \ln\left[a\left(\text{Ag}^0\right)\right] \qquad (16)$$
$$-(RT/nF)\ln[a(\text{D}_{\text{ox}})] - (mRT/nF)\ln[a(\text{H}^+)] + (RT/nF)\ln[a(D)]$$

This difference is a measure of the free-energy driving force for the development reaction. If the development mechanism is treated as an electrode reaction such that the developing silver center functions as an electrode, then the electron-transfer step is first order in the concentration of D and first order in the surface area of the developing silver center (280) (Fig. 13). Phenomenologically, the rate of formation of metallic silver is given in equation 17,

$$d\left(\text{Ag}^0\right)/dt = k_f\,(A)\left[\text{D}\right] - k_r\,(A)\left[\text{D}_{\text{ox}}\right] \qquad (17)$$

where k = potential- and temperature-dependent specific rate constants, (A) is the surface area of the developing silver center, [D] is the concentration of the reduced form of the chemical reducing agent, and [D_{ox}] is the oxidized developer concentration. By using the Butler-Volmer equation, one can obtain an expression for k in terms of the overpotential, ΔE, and the temperature (281). Specifically,

$$k_f = k_f^0 \exp\{\alpha nF\Delta E/RT\} \qquad (18)$$

and

$$k_r = k_r^0 \exp\{(\alpha - 1)\,nF\Delta E/RT\} \qquad (19)$$

where $k^0{}_f$ and $k^0{}_r$ are the specific rate constants when $\Delta E = 0$ and α is the potential symmetry factor. Combining equations 16–19 generates an expression that predicts the dependence of development rates on halide ion, hydroxide ion, and reducing agent concentrations. Most analyses using the electrochemical model use additional semiempirical parameters. The temperature dependence of development is not deduced readily from the above equations. In most cases, empirical analyses have revealed that the development rate increases with increasing temperature. The observed temperature dependence and the corresponding activation energies suggest that the processes are diffusion controlled, particularly for rapid developers (282). Because processing rates are enhanced at high temperature, many modern systems have been designed for high temperature processing. The use of high temperatures has necessitated specially hardened coatings to avoid remelting of the gelatin during processing.

Initiation of development also depends on the diffusion rates of the developer components through the gelatin to the silver halide grain surfaces where the catalytic silver centers are located. It has been suggested that such diffusion processes are rate limiting (283, 284). Once a chemical reducing agent has diffused to a grain surface, nucleation and growth of an elemental silver phase can be initiated in unexposed regions. In the exposed regions, the Ag^0 nuclei, ie, latent-image centers, that were photochemically produced continue their growth via chemical amplification. If the activity of the silver in the developing center, $a(Ag^0)$, is assumed to be unity, the calculated ΔE values for the initiation of development frequently are greater than those required to sustain development, once started. The silver specks constituting the latent image appear to have activities greater than unity, in accord with the Gibbs-Thomson equation (285, 286). Such effects may explain the requirement for larger ΔE values during nucleation and early growth. Furthermore, the ability of a developer to discriminate between exposed and unexposed grains has been attributed to this inverse relationship between silver center activity, $a(Ag^0)$, and silver center size (286–288); ie, as the size of the silver center increases, ΔE, the specific rate constant, and the rate of development increase (see eqs. 16–19). As development proceeds, oxidation by-products, eg, D_{ox} and Br^-, build up. These components decrease the overpotential, ΔE, and thereby reduce the rate of development. Thus, maintaining high development rates requires diffusion of oxidation products away from development centers. Under development conditions for which diffusion processes become important, effective agitation of the development solution is required. In general, agitation improves the uniformity of development and enhances the overall development rate. Solutions can be agitated by bubbling nonreactive gases, eg, nitrogen (qv), through the developer solution by mechanical paddles that sweep back and forth near the coated surfaces, or by jets that force streams of developer across the coated surfaces.

7.3. Source of Silver Ions During Development

For rapid electrochemical reduction of silver ions throughout development, high silver ion activities must be maintained (see eq. 16). The silver ions may come from the development solution, directly from the silver halide crystals, or indirectly from the crystals after crystal dissolution. If amplification is achieved with silver ions from the development solution, the amplification process is called physical development. Most physical development solutions are thermodynamically unstable because of the simultaneous presence of silver ions and a reducing agent. In most practical photographic materials, the silver ions in the silver halide lattice serve as the source of silver ions during amplification. If the silver ions migrate directly to the developing center via solid-state diffusion, without venturing into the solution, the process is called chemical or direct development. On the other hand, if the silver ions from the silver halide pass through the solution on their journey to development centers, the process is referred to as solution physical development. Some studies suggest that silver halide dissolution before chemical reduction of the silver ions is particularly important during the early stages of development (289–291).

7.4. Adjacency Effects During Development

The presence of photographic grains at one point in a coating can influence significantly the behavior and response of neighboring grains. During exposure, such phenomena can occur because of light scattering. The

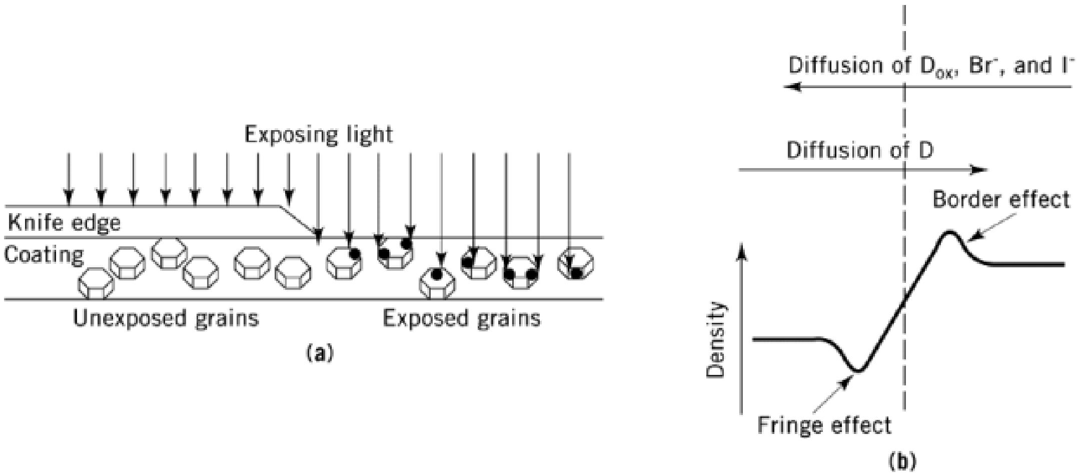


Fig. 14. Edge effects produced during development: (**a**) schematic and (**b**) a microdensitometric trace across a developed edge resulting from a knife-edge exposure which reveals the effects of diffusion processes during development. See text.

path of a photon entering a film coating is not necessarily confined to a straight line; collisions with coated silver halide grains may scatter the photon several times before it is absorbed by a grain. The lateral photon displacement, which may result from scattering events, reduces the visual sharpness of the recorded image. Interactions among the grains also occur during development. Because of the latter interactions the optical density produced upon development is a function not only of exposure but also of development characteristics. If two adjacent areas of a coated photographic film are given exposures differing significantly in magnitude, then development phenomena in one area may influence the course of development in the adjacent area. For a negative-working film, the area receiving the greatest exposure develops more rapidly, and accordingly a relatively high concentration of development by-products, eg, oxidized developer and bromide ions, is produced. As these by-products migrate into the adjacent areas that received lower exposures, development is relatively retarded and a light line or fringe is created. Similarly, the relatively high concentration of fresh developer in low exposure areas diffuses into high exposure regions and produces a dark line or border as a result of enhanced amplification rates. This edge effect phenomenon is diagrammed in Figure 14 for a knife-edge exposure. The parallel light and dark lines generated in a coating by knife-edge exposures are often called Mackie lines. Intergrain diffusion of development components and by-products is also monitored by line exposures of various widths, usually in a range from micrometers to millimeters. Line exposures are produced by either visible or x-ray radiation. Because x-rays are not scattered by silver halide grains, the adjacency effects observed for low (ca 30×10^{-16} J) energy x-ray line exposures are a result solely of development phenomena. On the other hand, the observed adjacency effects resulting from light-line exposure are a consequence of the superimposed contributions from light-scattering and developer component diffusion. Figure 15 shows microdensitometry tracings for x-ray line exposures of 10-μm and 1000-μm line widths. The enhanced density in the 10-μm line relative to the 1000-μm line is an example of the Eberhard effect, which was discovered in 1912 upon photographing bright astronomical bodies of various sizes (292). The densitometric traces of edge effects and Eberhard effects are mechanistically useful in establishing the role of diffusion during development.

For some developer formulations, partly oxidized or partly exhausted developer may be more active than fresh developer, eg, formaldehyde–hydroquinone developers. For these situations, the photographic adjacency effects are opposite to those observed in the Eberhard and Mackie line effects. In particular, grains in the neighborhood of developing grains develop more rapidly than they would otherwise. This phenomenon of development by-products sensitizing and accelerating the development of adjacent grains (infectious devel-

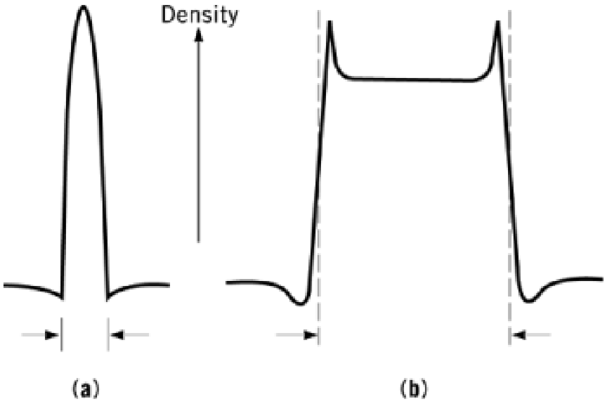


Fig. 15. Microdensitometer tracings of x-ray line exposures with line widths of (**a**) 10 and (**b**) 1000 μm.

opment) can lead to image spread and high contrast (293, 294). Compounds such as formaldehyde (qv) and hydrazine, when added to hydroquinone developer solutions, appear to promote the electrochemical reduction of the fully oxidized developer (quinone) to the semiquinone form, which is then free to migrate and act as a development initiator. Formaldehyde seems to promote semiquinone formation by buffering sulfite concentrations; hydrazines appear to promote semiquinone formation directly by electrochemically reducing quinone to semiquinone.

Development-induced adjacency effects frequently enhance edge contrast, which translates into desirable sharp and crisp photographs. Such chemical sharpness often compensates for the sharpness losses produced by light-scattering during exposure (34). The apparent sharpness of developed images is also influenced by certain gelatin-developer interactions, eg, the oxidized form of the developer pyrogallol [87-66-1] (1,2,3-trihydroxybenzene) acts like a hardening or tanning agent and shrinks the gelatin. Therefore, in regions of high exposure a considerable concentration of oxidized developer is generated and a corresponding differential shrinkage of gelatin occurs upon drying. The use of tanning developers may offer yet another approach to visual sharpness control.

7.5. Special Development Methods

In addition to the negative–positive and reversal process sequences, several photographic materials have been produced based on special development techniques including activator processing, photodevelopment, thermal development, monobath processes, and silver diffusion transfer. To reduce the chemical content and thereby improve the stability and oxidation resistance of development solutions, materials that use an activator process have been developed. The light-sensitive materials used in activator processes have developing agents incorporated in the coated layer during manufacture. Incorporation of developing agents during coating without the production of severe photographic fog is possible because the coating pH is kept low enough to inactivate the developer. After exposure, the coating is developed by immersing it in an alkaline activator solution. The initiation of development in the activator solution is more rapid than in conventional processes because the developer molecules need not diffuse into the light-sensitive layers from the processing solution. In spite of the low activity of the coated developer, some unintentional reduction sensitization may occur, which produces unwanted fog. Therefore, coating the developer in a separate layer usually is preferred. Because of simplicity, rapid access, and solution stability, incorporated developer papers have been used for office copying applications.

Continued exposure to light can convert enough silver halide photolytically to metallic silver to produce a satisfactory image. This approach to photographic imaging is used for specialized applications (295). For certain emulsion grains, photolytic amplification under low irradiance produces a visual density, provided the photolytic amplification was preceded by a high irradiance exposure. In regions of the light-sensitive element that received high irradiance pre-exposures, photodevelopment produces a higher covering power (ratio of optical density to developed silver) compared with background areas. Electron micrograph examinations of the image and background areas reveal that the covering power effects result from a higher dispersity of developed specks per grain in the image areas. The discrimination between the image and the background of photodeveloped films may be a consequence of color differences resulting from the diverse shapes of the developed silver particles. The images produced by photodevelopment generally are not permanent; however, specially formulated bathing treatments have been devised to stabilize the photodeveloped images. Photodevelopment materials provide a rapid, solution-free approach for recording data from the output of oscilloscopes and other scientific instrumentation.

Heat or thermal development is another example of amplification that does not require the use of aqueous development solutions. Photothermographic materials are developed by heating the coatings after image exposure (296). In these materials, all of the required chemicals are incorporated into the coated layers during manufacturing. There are several types of heat-processed materials that are silver based; some are quite similar to conventional silver halide materials. The light-sensitive components are silver halide microcrystals and amplification is effected by the incorporation of a reducing agent that is thermally activated. Some thermally processed materials are amplified at least in part by physical development. In addition to coated silver halide and reducing agent, these materials also have an incorporated source of silver ions, usually in the form of organic silver salts. Another thermally processed material is based on silver oxalate. The oxalate material does not require an incorporated reducing agent; silver oxalate thermally decomposes to form metallic silver in a reaction catalyzed by photoproducts formed during image exposures (297, 298).

In most conventional processing, development is completed before the start of fixation, which removes the undeveloped residual silver halide. However, in monobath systems, development and fixation occur simultaneously and not sequentially. Monobath processing is a time-saving procedure in which large quantities of a silver halide solvent, eg, thiosulfate, are added to a development solution. The solvent forms a water-soluble silver complex which transfers silver from the coating to the solution. The developer component of a monobath solution must be very active to ensure that latent-image sensing and initial amplification occur before crystal dissolution. Balancing the relative concentrations of developing agent and solvent and controlling the temperature can give the desired sensitometry. Because of the pronounced adjacency effects that occur in monobath processes, images with good sharpness and high resolving power have been produced. A further extension of the monobath process allows the formation of positive images. The positive image is formed by laminating a monobath-processed coating to a receiving layer containing silver nuclei coated on a separate support. The solubilized silver ions from the original coating are thus permitted to diffuse to and grow via physical development on the nuclei in the receiving layer. Because the originally developed silver remains immobilized in the original coating, subsequent separation of the laminated layer yields not only a positive silver image in the receiving layer but also a negative image in the original layer. This process of silver diffusion transfer has been used for document copying, aerial photography, instant photography, and in graphic arts for the preparation of prepress materials (299–301).

8. Stop-Bath Treatment and Fixation

Once development has progressed to some desired extent, amplification usually is quenched by a rapid decrease in pH. In conventional photographic films, the pH is decreased by mechanically or manually transferring the coatings from the alkaline developer solution to an acidic stop bath. Quenching usually can be done by a brief treatment with a stop bath composed of a dilute solution of a weak acid, eg, 0.5% acetic acid. For both the silver diffusion-transfer films and the dye-transfer films used in instant photography, development is initiated by spreading a viscous alkaline reagent between an emulsion layer and an image-receiving layer (26–30). In the early versions of these products, development was stopped by a peel-apart step in which the processing chemicals and developing grains were physically separated from the image-receiving layer; more recent integral films rely on the timed release of an acid to quench development. In instant photography, the final image, whether dye or silver, is formed by diffusion. In this process unwanted chemicals that could potentially interfere with viewing and image permanence are left behind. On the other hand, in conventional photography the image remains where it was originally formed. Thus, the image and the by-product chemicals are in the same layer after development has been quenched. In the latter films, post-development procedures are required to remove the unwanted chemical by-products. To remove undeveloped silver halide, development and quenching are followed by fixation. Most fixing baths are composed of thiosulfate ions formed by dissolving the corresponding sodium or ammonium salt in water. The thiosulfate ions convert the remaining silver halide to water-soluble complexes such as argentodithiosulfate, $Ag(S_2O_3)^{3-}{}_2$, and argentotrithiosulfate, $Ag(S_2O_3)^{5-}{}_3$. Once bound in these complexes, the silver can be washed readily from the gelatin coating. During the dissolution of the residual silver halide grains, silver ions break away from the lattice of the crystal surface and pass into the solution in the form of complexed ions. In the absence of thiosulfate, the concentration of silver ions continues to increase; eventually the solubility product of the silver halide is reached, and accordingly dissolution ceases. However, by sequestering silver ions and forming various argentothiosulfate complexes, the use of thiosulfate-fixing solutions permits continued dissolution and eventual removal of all of the undeveloped silver halide. Efficient fixing agents must have large stability constants (302); ie, they must be ligands having a sufficiently high capacity for complexing with silver ions. The stability constants at 25°C for $Ag(SO_3)^{5-}{}_3$, $Ag(NH_3)^{+}{}_2$, $Ag(SCN)^{2-}{}_3$, $Ag(S_2O_3)^{5-}{}_3$, and $Ag(CN)^{2-}{}_3$ are ca 8×10^8, 1.6×10^7, 2×10^{10}, 8×10^{13}, and 8×10^{21}, respectively. Cyanide is an effective complexing agent because of the large stability constant, however health and safety factors prohibit its use in most situations. Thiosulfate is nontoxic, relatively inexpensive, and nonreactive with the gelatin or developed silver, in addition to having a satisfactory stability constant. For the fixation of silver chloride, silver bromide, and silver bromochloride, thiosulfate is effective. However, for the relatively insoluble silver iodide with a solubility product of ca 10^{-16}, dissolution rates with thiosulfate solutions are significantly diminished.

In black-and-white photography, fixation generally is conducted under acidic conditions. The acid environments assist in arresting continued development and in preventing stain associated with the oxidation of developer molecules carried over from the development solution. Furthermore, weak acidity is required for the hardening of gelatin by potassium alum and chrome alum, which are components that can be included in acidic fixing baths. The hardening provided by alum helps prevent physical damage, eg, scratches on the coating surfaces, during handling of the wet gelatin materials in the course of various post-development processes. The acidity can be maintained if, in addition to the salt of a strong base (eg, the sodium ion from sodium thiosulfate and sodium sulfite), a weak acid (eg, acetic acid) is present to provide a buffered solution. In alkaline thiosulfate fixing baths, alum forms an undesirable white sludge of aluminum compounds.

The primary component of a fixation bath, thiosulfate, tends to decompose in acidic environments according to the following reaction:

$$S_2O_3^{2-} + H^+ \longrightarrow HSO_3^- + S$$

Although this decomposition is not substantial at pH values greater than 4, approaches have been developed to protect the thiosulfate should more acidic conditions occur. The decomposition rate and the accompanying reduction in fixation efficacy can be retarded significantly by additions of bisulfite. Bisulfite ions disproportionate in the presence of thiosulfate (303). This disproportionation therefore balances the decomposition of thiosulfate and extends the useful lifetime of the bath. Besides silver-complex-forming agents, hardeners, bisulfite, and buffers, some fixing baths also contain boric acid, which increases the fixing bath lifetime by extending the pH range of effective hardening to higher pH values. This reduces sensitivity to the adverse effects of alkaline carryover from the development solution. Boric acid also decreases the propensity for alum hardeners to initiate sludge formation.

In climates where temperatures and humidity are high, extreme hardening of the gelatin generally is necessary to avoid surface abrasion of the processed coatings. A solution of potassium chrome alum (potassium chromium sulfate) can be used in these situations as an intermediate treatment between development and fixation. In the presence of organic acids, eg, acetic acid, chrome alum solutions do not attain their optimum hardening capacity. The required acidity for optimum hardening by chrome alum baths is achieved with sulfuric acid, which does not produce a buffered solution. Therefore, bath lifetimes are limited and frequent acid additions are required. For environmental reasons, the chromium hardeners are no longer preferred and hardening through the use of aluminum ions in fixing baths has become increasingly popular.

The rate of silver halide dissolution and of the ultimate total removal of undeveloped silver from a coating depends on the nature of the coated emulsion, the coating format, the thiosulfate ion concentration, the nature of the thiosulfate's cation, and the temperature and degree of agitation (304). Ammonium thiosulfate [7783-18-8] solutions remove silver halide faster than equivalent concentrations of sodium thiosulfate solutions; for this reason the ammonium compound is often preferred for the fixation of camera-speed emulsions, which are often composed of grains with relatively insoluble iodide-containing phases. Temperature increases enhance the rate of silver removal by increasing the rate of diffusion. Increased temperatures also increase the chemical reaction rates of crystal dissolution and complex ion formation. Dissolution rates can be increased up to an optimum value by increasing the concentration of the complexing agent. Increasing the complexing agent concentration beyond the optimum generally results in reduced fixing rates. For most practical analyses, the rate of fixation is monitored in terms of the clearing time, which is defined as the time required for the last visible opacity to disappear. Generally, the clearing time increases with increasing coated layer thicknesses and increasing sizes of the silver halide grains. Clearing times are inversely related to fixation rates. In conventional color films the developed silver is not used for the final image. In these films the developed silver is bleached, ie, oxidized with an agent such as ferric ion, before fixation and nearly all of the originally coated silver can be cleared and recovered from the coating.

9. Washing

At various stages during the post-development process, the coatings are rinsed. One of the most important reasons for rinsing is to reduce chemical carryover from one treatment bath to another, which increases solution lifetime. The most important washing occurs at the end of the processing, just before drying. The purpose of this washing is to eliminate all soluble compounds from the coated gelatin layers. Efficient removal of certain compounds is essential for good keeping properties and image permanence. Thiosulfate and argentothiosulfate complexes have particularly damaging effects on the keeping properties of the final print or film. Residual thiosulfate eventually reacts with the silver image in black-and-white products to produce silver sulfide and thereby confer a yellowish brown appearance or tone to the image. Inadequately removed silver thiosulfate complexes gradually decompose and are converted to silver sulfide with an accompanying yellow stain. For photographic materials coated on water-impermeable bases, such as glass plates and film, efficient washing can remove unwanted soluble residues almost completely. However, it is difficult to completely desorb and remove thiosulfate and argentothiosulfate complexes from the paper supports and baryta layers of reflection-print paper products. Resin-coated paper bases have made possible the manufacture of print materials having washing properties similar to those of films and plates.

The rate of washing primarily depends on the rates of diffusion of the water-soluble species in gelatin. Because the process is diffusion controlled, washing is accelerated by temperature increases and by maintaining a fresh layer of water at the film surface. Therefore, good agitation is necessary and jet washing is particularly effective. Reticulation of the coated gelatin occurs when the temperature of the wash water is excessive.

Because the wrinkling of reticulation remains even after drying, this effect establishes an upper limit to wash temperatures. Washing rates are also affected by pH of the wash bath, hardening that may have occurred in previous steps, and the presence of certain salts in the wash bath (305). At pHs below the isoelectric point of gelatin, the gelatin assumes an overall effective positive charge, which appears to reduce coulombically the rate of removal of various negative species, including thiosulfate and the argentothiosulfate complexes. Thiosulfate is desorbed more rapidly from gelatin that has been previously hardened with potassium chrome alum than from gelatin hardened with potassium alum. The rate of thiosulfate elimination can also be enhanced by the use of wash baths containing sodium chloride. However, a brief fresh water rinse is required to remove residual chloride, which might otherwise have adverse effects on the image silver in black-and-white films.

10. Stabilization

Stabilization is an alternative to fixation for the production of a permanent although probably not archival image. In stabilization, the undeveloped silver halide is not removed but rather is converted to a compound that is relatively insensitive to light and stable to heat, humidity, and atmospheric gases. As in fixation, stabilization is achieved by the use of complexing agents to transform silver halide into silver complexes. Because the silver complexes and the unreacted complex agents are retained in the coated gelatin layer, the stability of these compounds is critical to the utility of the stabilization process. Stabilization is used where rapid access is needed, eg, news film and oscillograph tracing. Thus the complexing agents should react rapidly and completely with the silver halide contained in the gelatin layers. Furthermore, the agents cannot be toxic and should not soften the gelatin, bleach the image silver, or form colored complexes with silver.

Table 2. Worldwide Producers of Sensitized Materials

Company	Country
Eastman Kodak Co.	U.S.
E.I. du Pont de Nemours & Co., Inc.	U.S.
Minnesota Mining and Manufacturing Co.	U.S.
Polaroid Corp.	U.S.
Fuji Photo Film Co.	Japan
Konishiroku Photo Industry, Inc.	Japan
Agfa-Gevaert, Inc.[a]	Germany/Belgium
Ilford Ltd.[b]	U.K.
Ciba-Geigy Photochemie Ltd.	Switzerland
Anitec[b]	U.S.

[a] Subsidiary of Bayer Chemical (Germany).
[b] Subsidiary of International Paper (U.S.).

Stabilizing agents can be classified into two categories: those agents that form water-soluble silver complexes and those that form insoluble complexes. The former category includes thiocyanate, thiosulfate, and thioureas. The latter category includes mercapto compounds, ie, RSH, where R represents any aliphatic, aromatic, or heterocyclic group (306) (see Thiols). The rapid-access print process generally uses specially prepared papers containing incorporated developing agents. The papers are processed by an activator–stabilizer sequence requiring only a few seconds of machine process time, and the final drying of the prints is in room air (306–308).

11. Economic Aspects

The conventional photographic industry continues to prosper. The Gross National Photo-Product (GNPP), defined as the shipment of photographic equipment and supplies by American manufacturers minus exports plus imports, is a measure of the photographic goods consumed in the United States (309). The GNPP increased from $\$4.1 \times 10^9$ in 1971 to $\$20.9 \times 10^9$ in 1991, which corresponds to an average annual increase of ca 8.5%, within one-tenth of one percent of the average annual gross national product growth rate over the same period. In 1991 in the United States, the total number of pictures taken was greater than 21×10^9 and approximately 2.1×10^6 kg (66×10^6 oz.) of silver were consumed by the photographic industry. Worldwide the number of pictures taken was about 56×10^9. The United States makes up ca 41.6% of the international photomarket. Japan, with 27.8% of the worldwide market, and Western Europe (excluding Germany), with 10.9%, consume 1.94 and 1.91×10^6 kg (61 and 60×10^6 oz.) silver, respectively. Germany (6.6%), Eastern Europe (10.3%), and others, including Africa and Asia (2.8%) make up the remaining countries in the international market. Table 2 gives a partial list of worldwide producers of sensitized photographic materials.

12. Environmental Aspects of Processing

The quality of industrial effluents discharged into public sewage systems is specified by regulatory agencies. For certain quality parameters, photographic processing effluents fall within the required range without special treatment. For example, the pH of processing wastes generally is 6.5–9.0 and thus within the usual sewer code range of 5.5–9.5. Lubrication oils and greases are not present in photographic wastes, and the concentrations of suspended solids are too low (generally <20 mg/L) to be significant. Occasionally, specific processing baths must be maintained in a range of 38–51.5°C. However, when the total effluent is mixed, the temperatures are usually below 32°C, and thermal effects are generally of little consequence. Despite these qualities of photographic waste, processing effluents that ultimately are discharged into streams almost invariably require special treatment to meet stream standards. These treatments normally include silver removal, settling, biochemical degradation, aeration, and finally chlorination. Settling removes the solid wastes, biochemical degradation and aeration reduce the biochemical oxygen demand (BOD) of the waste, and chlorination destroys any pathogenic organisms remaining after treatment.

The concentrations of chemicals found in photographic processing effluents generally are not toxic to the bacteria and other treatment plant microorganisms necessary for biological degradation (310). However, hexavalent chromium used in dichromate bleaches as an oxidizing agent to remove developed silver from color coatings can be toxic to bacteria. It must, therefore, be electrochemically reduced before discharge. When the waste bleach is mixed with waste fixation and development chemicals, electrochemical reduction of hexavalent chromium generally occurs, and the adverse bactericidal properties are eliminated. Some processing components that may have undesirable environmental effects can be recycled during photographic processing and are not discharged into waste-disposal systems. Wash water, developer, and fixing and bleach-fix solutions are often regenerated, recycled, and reused. Silver can be electrochemically removed from thiosulfate fixing solutions which can then be chemically readjusted and reused (311). Many color-processing sequences have used ferricyanide as a silver bleaching agent, however, the ferricyanides hydrolyzed in the presence of oxygen and sunlight produce iron hydroxide and soluble cyanides which are toxic to fish at levels as low as 1.0 mg/L (312). Because of adverse environmental impact, some of these solutions have been replaced by bleaches containing iron(III) ethylenediaminetetraacetic acid. For economic and environmental reasons, there has been an elevated emphasis on recycling, reuse, and recovery since the 1970s (313). Furthermore, the use of thinner and harder coated layers in photographic products has reduced the carryover from tank to tank during processing. Accordingly, solution replenishment rates and the total effluent volumes have been substantially reduced (314). Effluent codes for many areas regulate not only the concentrations of certain chemicals but also the BOD and chemical oxygen demand (COD) in effluents. Photofinishing businesses occasionally install aerated lagoons capable of reducing the oxygen demand of their waste before discharge into community sewer systems. Such lagoons must be carefully engineered to guarantee that subsurface soil and streams do not become chemically contaminated.

Compounds containing such metals as copper, barium, lead, molybdenum, and nickel generally are not used in processing solutions. However, trace quantities of certain metal dopants occasionally are used to impart desired solid-state and photographic properties to emulsion grains. Because of its toxicity to aquatic life and microorganisms, the metal of primary ecological concern in the photographic industry is silver. Silver that is not salvaged during recovery operations may be present in the waste from photographic processing. The discharged silver usually is bound in thiosulfate complexes, which are not detrimental to the essential microorganisms in sewage treatment plants. The silver thiosulfate complexes can be converted to insoluble silver sulfide and removed as a solid sludge. Optimization of silver recovery is not only an important conservation measure but is also an economic benefit to photographic processing businesses. Various techniques for silver recovery are in common use including electrolysis, metallic replacement, ion exchange (qv), and silver precipitation. Although relatively costly, electrolytic recovery does produce high purity silver plated on an electrode. Metallic replacement can be accomplished by passing the waste fixation solution through a filter cartridge containing spun steel (steel wool), iron mesh, or iron-coated fiber glass. Because iron is more electropositive than silver, it is ionized and dissolved into the solution; silver ions are reduced and precipitate as solid metallic silver sludge. Most reclaimed silver is sold to industries that manufacture photographic goods. Not all photographic processing facilities take advantage of this recycling process. Only about 50% of the silver is recovered. This percentage is expected to continue to increase because of the market value of silver and costs of noncompliance with governmental regulation.

13. The Silver Image

13.1. Stability

Image permanence and archival quality of recorded information (315) is of increasing interest. Recording information using silver, a relatively inert noble metal, is one of the most effective archival approaches available. However, after the silver image of a black-and-white processed material is produced, it is usually subjected to a variety of environmental conditions during subsequent handling and storage. In addition to the effects of residual thiosulfate and silver thiosulfate, the humidity, temperature, and chemistry of the environment can also adversely affect image permanence. The elemental silver composing the image is not completely stable and may be oxidized by the atmosphere to silver sulfide or silver oxide. Because such oxidation is initiated on the surface of the developed silver image, image degradation by air oxidation is of particular concern in photographic materials containing grains with high surface-to-volume ratios, especially if keeping properties are desired. For example, some microfilm images for which image permanence is often particularly important are susceptible to spontaneous image degradation upon normal storage (316). The gelatin binder also can influence image-keeping qualities. Because of the shielding effects afforded by gelatin vehicles, most modern photographic materials are considerably more resistant to air oxidation than were the early daguerreotype and calotype images. However, various degrees of image fading can still occur even in large grains with gelatin protection. If the silver image is exposed to oxidizing fumes from such sources as automobile exhaust, freshly painted rooms, nitric oxides, and peroxides, then the possibility of image fading is enhanced.

During aging, some microfilms develop red or yellow spots 10–150 μm in diameter. These blemishes have been associated with the disappearance of the silver filaments formerly composing the image and the ensuing formation of small spherical particles of silver. The mechanism of silver transport is likely to involve the oxidation of silver metal to silver ions, which migrate through the gelatin matrix and ultimately regather to form isolated colloidal particles of silver. The coloration of the blemish is at least in part a result of the fact that light scattering by a colloidal particle of a given size is wavelength dependent. The coloration may also be affected by a thin silver sulfide shell, which has been observed to reside on the silver in the blemish areas. Occasionally, Liesegang ring structures have been found to be associated with such blemish spots (316). To improve silver image resistance to oxidation, photographic coatings can be treated with solutions such as gold chloride-plus-thiourea solutions or with iodide either during or after the process. Adsorbed iodide appears to stabilize the silver image by reducing the surface energy of the silver filaments (317). Selenium toning of microfilm products has been shown to enhance image stability (318) (see Selenium and selenium compounds).

13.2. Image Tone

The morphology and size of developed silver depends on factors relating to the emulsion grain as well as the method of development and composition of the developer. Developed silver is often in the form of long, narrow, cylindrical filaments. The filaments are commonly 15–25 nm in diameter but may be as large as 50–80 nm with slow-acting developers such as ascorbic acid (280). Development in environments that promote solution physical development tends to enhance the filament thickness. The filament dispersity, ie, the number of filaments per grain, depends in part on the grain size. In general, increases in the silver halide grain size translate into increased filament dispersity. For sufficiently small grains, development can lead to only a single filament per grain (319). In addition to grain size increases, exposure irradiance increases also have been observed to increase filament dispersity. For large grains exposed with high irradiance, a mass of developed filaments can be produced. Under an electron microscope, such filament masses resemble steel wool. In some cases the morphology of the silver halide grain itself, as well as adsorbed chemical compounds and trace impurities, have influenced the morphology of the developed silver (320–323). At sufficiently low concentrations of developed silver within the gelatin matrix of the coating, the spectrum of the light absorption is dependent on filament size and morphology. However, when the volume concentration of silver exceeds 3%, the coatings become visually neutral and the effect of particle size lessens (324).

Once the silver is developed, changes in image tone are sometimes desired. Treatment with any of a wide variety of toning baths can alter image tone. Two types of toning baths are used: one type involves the conversion of the image silver to silver sulfide, and the other involves the substitution of silver in the image with yet another metal. Metal toning makes possible a wide range of image colors. For example, blue and red tones can be achieved using gold substitutions, yellow and green tones are obtained using vanadium substitution, and sulfide and selenide toning can produce brown tones. Sulfide toning can be accomplished directly by treatment with a heated bath containing sodium thiosulfate and alum. An alternative method of sulfiding involves two steps. The silver image is first bleached to form silver bromide, which is then converted into silver sulfide. The bleaching can be accomplished by a treatment with a solution containing potassium ferricyanide and potassium bromide. Conversion can then be effected by imbibition either in a dilute solution of an alkali sulfide or in a solution containing thiourea and sodium hydroxide.

13.3. Image Intensification and Reduction

In addition to tone changes after processing, it may also be necessary to alter the optical density or contrast of the original negative. Such alterations are rarely applied to the print. The process of increasing the image density is called intensification, whereas the process of lowering image density is called reduction. An image is intensified by adding a metal, eg, mercury, chromium, silver, or copper, to the image silver. If a given negative had sufficiently detailed information of an original scene but was underdeveloped during processing, then intensification may be useful. However, in underexposed films, the density of the original negative may not only be low but also the information may not have been recorded satisfactorily. In the latter case, intensification increases the density, but cannot provide missing details from shadow areas, ie, the toe region of the original negative (see Fig. 4). In contrast, reduction selectively removes silver from the developed image. Reduction can be used to correct overdevelopment (overexposure) or to alter the contrast of a negative. Lowering the density of a negative allows printing exposure intensities or printing exposure times to be reduced. Exposure time reduction becomes of practical importance when multiple printed copies of an original negative are required.

Intensification with mercury can be achieved by first treating the negative with a mercuric halide which oxidizes elemental silver and partly converts the silver image to a mixture of silver halide and a mercury salt. The bleached image is then darkened by a treatment with either ammonium, sodium sulfite, or a Metol-hydroquinone developer (325). During this step, both the silver and mercury ions are reduced electrochemically to their metallic forms, and thereby the image density is enhanced. An alternative single-step mercury intensification can be accomplished by using a solution containing mercuric iodide and sodium sulfite. In chromium intensification, a two-step process fundamentally equivalent to the two-step mercury process has been formulated.

Reducing treatments can be classified according to their effects on contrast. Cutting reducers reduce the density in the toe and fog regions more than in the saturation region, and therefore enhance the contrast. Reducing treatments that remove silver in proportion to the amount present at any given point in the coating are called proportional reducers. Proportional reducers lower the density of a coating with an accompanying reduction in contrast, whereas subtractive reducers decrease the density equally over the exposure scale and do not alter the contrast. In all cases, reduction involves the chemical oxidation of some of the elemental silver in the image followed by or concurrent with fixation. Ferricyanide is a commonly used oxidant, and thiosulfate can be used as the fixing agent.

13.4. Image Evaluation

The subjective quality of a developed silver image depends on the color tone of the developed silver, brightness reproduction of the original scene (35), and perceived graininess and sharpness. Certain objective measurements and analyses correlate with these subjective qualities of a developed image. For example, quantitative optical density measurements and the corresponding D-log H curve analysis are used to monitor tone and brightness reproduction. Quantitative and objective analysis techniques have also been developed for graininess and sharpness evaluation. The silver image is granular because it is composed of a random distribution of discrete specks and filamentary clumps of metallic silver. Consequently the photographic image is inherently inhomogeneous and nonuniform, which becomes increasingly apparent under increasing magnification. Such nonuniformity is referred to as graininess. If a given field of the silver image is optically scanned with a density measuring device, a microdensitometer, having a sufficiently small detection aperture, spatial variation in the light-transmitting or light-reflecting properties of the image can be recorded and statistically analyzed. Such analyses produce an objective measure of graininess called granularity. If the density of a given measurement is denoted by D_{i} and if there are a total of N measurements in some specified uniform exposure area of the image, then the root mean square (rms) granularity, ς_{D}, is given by a statistical expression for the deviation in density:

$$\sigma_D = \left\{ \sum_{i=1}^{N} (D_i - \langle D \rangle)^2 / N \right\}^{1/2} = \left\{ \langle D^2 \rangle - \langle D \rangle^2 \right\}^{1/2}$$

where $\langle D \rangle$, the average density, is given by

$$\langle D \rangle = \sum_{i=1}^{N} (D_i / N)$$

The rms granularity, σ_D, is dependent on the aperture size and decreases with increasing aperture area. However, the product $A^{1/2}\sigma_D$, where A is the area of the scanning aperture, is nearly independent of aperture size in many cases (326). Accordingly, the granularity, $G = (2A)^{1/2}\varsigma_D$, called the Selwyn granularity, is often taken as a measure of the granularity of a film. Photographic films that either require high photographic speed or are ultimately to be viewed under high magnification are usually the most sensitive to the image-degrading effects of granularity. A trade-off between photographic speed and low image granularity is intrinsic to photographic films. One way to enhance the speed of a photographic film is to increase the size of the microcrystalline grains. However, grain size increases usually enhance the granular appearance of developed images.

Throughout the history of silver halide-based photography, much research has been directed toward improving the efficiency and therefore the speed without increasing the size of the silver halide grains. These research efforts have produced several improvements. Through advances in emulsion-making and sensitizing techniques, emulsion quantum efficiency has been increased. Because these advances have rendered grains of a given size more sensitive to light, the speed–grain relationship has been improved correspondingly. Furthermore, alterations in coating formats and modifications of development chemistry also have contributed significantly to improved speed–grain positions.

The visual sharpness of a recorded image is yet another subjective measure of image quality. The impression of sharpness or crispness is achieved when the boundaries and edges of the objects composing the image are clear and well defined. When high resolution of fine detail is required in the image, then, in addition to contrast and granularity, sharpness becomes a particularly important image quality parameter. The presence of a light-scattering grain population, resulting from a given set of emulsion-making conditions, can have a pronounced effect on the photographic response and the quality of the photographic image. The light-scattering and light-absorption properties of the silver halide grains within a coated layer establish the vertical and lateral distribution of light within the layer (264, 327–330), which significantly affects the sharpness of the photographic image. In addition to the effects of the lateral scattering of light by emulsion grains, the optics of camera lens systems and the optics of enlargers also influence the path of photons and the apparent sharpness of the final photographic image. The ability of a photographic material to record fine detail is a function of development effects as well as of optical effects. The lateral diffusion of development by-products can produce adjacency effects that enhance the apparent sharpness of a recorded image.

Sharpness is evaluated by a number of methods. It is often measured as the ability of a recorder to produce an image of very narrow and closely spaced lines. In such an analysis, the resolving power of a recording film is determined by photographing a test object composed of a series of alternating black-and-white lines of increasing narrowness set in geometric patterns. The last visually distinguishable set of lines is recorded, in lines per millimeter, as the resolving power of the recorder under the particular test conditions. The resolving power of a photographic material is determined by granularity and contrast as well as by effects of image spread. The modulation transfer function (MTF) is a more objective and quantitatively interpretable measure of the quality of sharpness. For MTF analyses, the recorder is exposed with a band of light that varies sinusoidally in intensity. The frequency of the sine wave continuously increases along the length of the exposure band. This spatial frequency is 2–500 cycles/mm. The density modulation of a microdensitometric trace along the resultant image can be expressed as the percentage of input modulation at each frequency (34). The MTF is independent of the processing conditions for a linear recorder and can be translated mathematically through Fourier analysis to the spread function. The spread function represents the spatial distribution of light within a coating that results from the isotopic scattering of an infinitesimal incident point of light. Analysis of MTF data can also be used to deduce the image density distribution produced by knife-edge exposures; it is in general more reliable than direct analyses of such edge exposures.

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