Image and Process Specifications. Having devised working transfer processes for images both in silver and in dye, Land addressed his next experiments toward outwardly dry, one-step processes yielding silver images of neutral tone and dye images suitable for three-color subtractive photography. Whether in black and white or in color, continuous tone photographs would require images of constant hue at all densities. For use in a one-step process, a film of suitable speed and its accompanying reagent would need to be self-contained and stable in storage. The system would need to complete the single processing step rapidly and to produce pictures which would be stable without washing. New materials and new methods were required to provide one-step cameras and processes which could effectively meet these specifications.

The following pages describe and illustrate the principles involved in fulfilling the requirements of one-step camera processes. The section on *Silver Image Processes* will be devoted to the development of the initial one-step film system and of subsequent black and white products; the section on *Dye Image Processes* will cover the concurrent development of one-step color systems.

SILVER IMAGE PROCESSES

Image Formation; Color and Structure

One of the first problems to which Land directed his attention in the development of silver processes was the influence of the method of formation of the image deposit upon its structure and upon its spectral characteristics.

Images in Thick Gelatin Layers. The brown color of the transfer images formed in a gelatin receiving layer, as in Fig. 12-35b, was attributed to a distribution of small particles spread far apart.* Recent microscopy of the 1944 images in gelatin shows those deposits to comprise fine particles 10 to 30 nm in diameter formed into aggregates of a wide range of sizes, from 20 to 300 nm in diameter. The aggregates are distributed throughout a 10 to 12 μm depth, and neighboring aggregates are 1 to 6 diameters apart, as shown in Fig. 12-36a.

The gelatin matrix could evidently influence both nucleation and growth of the image aggregates. The action of gelatin as a highly protective colloid is essential in the emulsion to prevent premature decomposition of the soluble silver complex within that layer; a gelatin receiving layer would similarly inhibit formation of the positive silver aggregates. In the same gelatin layer, however, impurities could concomitantly serve as sites for nucleation—the greater the number of sites, the smaller the aggregates thus formed. The gelatin layers first used as receiving layers had been prepared by fixing and washing sheet films, so that residues might have served as nuclei.**

Formation of Compact Images. The image problem at this stage was twofold: to grow particles in an image-receiving layer directly from solution and to grow them as nearly as possible to a uniform and appropriate size. A thin image layer would provide a close-packed deposit, so that the particles could interact electromagnetically, approaching the conductive properties of a metallic layer. Ideally, the layer would be expanded just enough to be a black absorber rather than a mirror.

To demonstrate that precipitation would occur spontaneously without the protection of the gelatin and to facilitate the growth of a compact layer of large particles, Land used a nonprotective receiving layer of α-cellulose blotting paper, which is readily penetrable but insoluble. Once the silver complex left the emulsion layer it would be free to precipitate within the surface of the α-cellulose paper. When an exposed negative was pressed against a sheet of the α-cellulose blotting paper which had been prewet in a solution containing developer and hypo, a positive image outstanding for its

---

nuclei and zinc oxide; after a positive image had formed in the nucleating layer, the negative was washed off with warm water and the zinc oxide dissolved by acetic acid to leave a positive transparency.[33]

Further work by both Rott and Weyde led to successful two-sheet document copy processes, both introduced subsequent to the first Polaroid one-step camera process. Agfa's Copyrapid was first marketed in 1949 and Gevaert's Gevacopy in 1950. In Copyrapid and Gevacopy processing, an exposed low speed, high contrast negative sheet was introduced into a liquid activator bath simultaneously with a positive sheet having a gelatin receiving layer containing nuclei; the two sheets were thereafter brought into contact between pressure rollers and then stripped apart, yielding a transferred positive image. Unlike the Polaroid process, the copy processes were based on emulsions of low speed. They produced image deposits having line rather than continuous tone images, and the image hue was thus not critical. Document copy materials and processes are discussed in detail in Chapter 11 and in Ref. 30.

Earlier workers had described different image transfer phenomena in silver halide systems. The transfer of soluble silver salt images from unexposed areas of a developing silver chloride emulsion into a gelatin layer containing the developer had been reported by Liesegang in 1898.[34] Other early observations included those of Lefevre, who in 1857 transferred silver from a daguerreotype soaked in hypo to a layer of gelatin;[35] of Colson, who reported in 1898 the transfer of a negative image in terms of oxidized developer,[36] of Stenger and Herz, whose 1922 German patent claimed processes for the transfer of positive images in terms of unoxidized developer;[37] and of Stevens and Norrish, whose 1938 paper described transfer of an image from a silver halide negative to a gelatin-coated plate after wetting both with developer and subsequent physical development of the transferred image.[38]

*The 1911 data of Chapman Jones[39] had indicated the dependence of color upon size of silver particles suspended in gelatin; Jones had enlarged fine silver particles by coating them with mercury and had observed transmission colors from yellow to gray over a calculated range of diameters from 100 to 190 nm. He reported that he found no correlation between particle separation and color for particles between 1 and 10 diameters apart.

**To examine the question of nucleation by impurities, images formed in gelatin layers of this type were recently compared with images formed in coatings of refined gelatin deionized to minimize impurities. The images in the deionized gelatin comprised larger aggregates, as if indeed there were fewer points of initiation. In this purified gelatin the aggregates ranged up to 400 nm in diameter, and the image tone was bluish. Figure 12-36b shows the structure of the image in deionized gelatin, and Fig. 12-37 compares transmission spectra of images in the two gelatins.

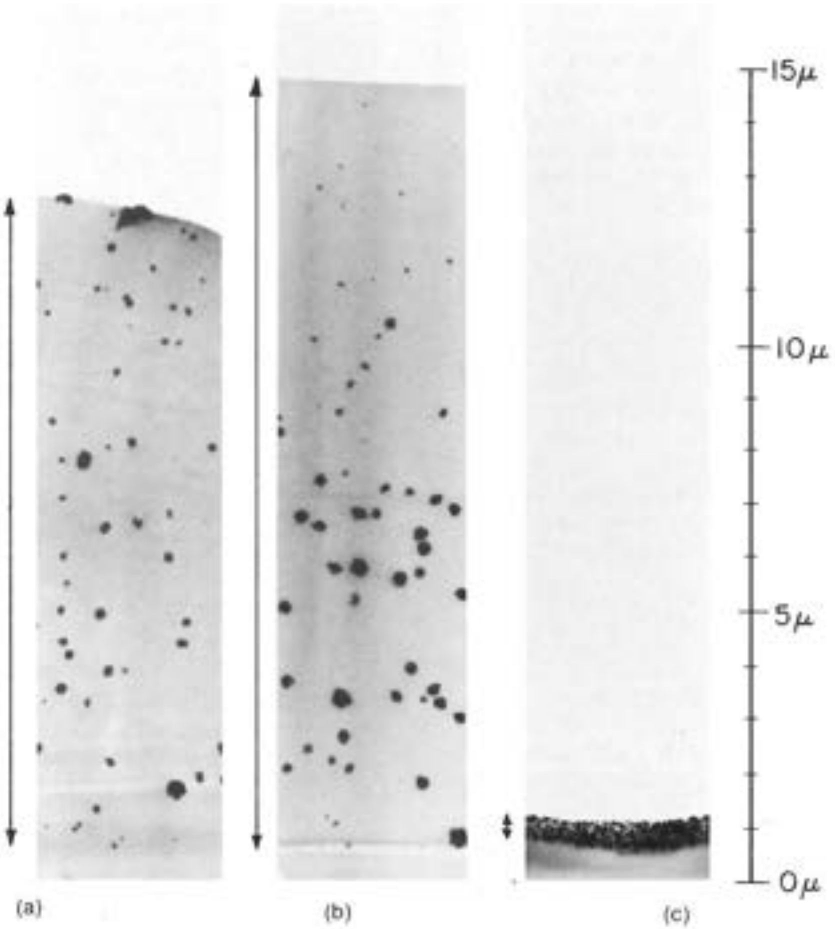


Fig. 12-36. Comparison of images deposited in impure and purified gelatin and in the pores of α-cellulose paper. Length of arrow beside each cross section shows thickness of region populated by silver particles: (a) is from a picture such as the one reproduced in Fig. 12-35(b), with the deposit in a thick layer of gelatin prepared by fixing and washing a sheet of commercial film; (b) is from a deposit in a thick layer of highly purified gelatin; and (c) is from an image formed in α-cellulose blotting paper; (c) is shown at higher magnification in Fig. 12-38. Spectra of (a) and (b) are shown in Fig. 12-37, and the spectrum of (c) in Fig. 12-39.

neutral tone was deposited in the near surface of the paper. A picture made in 1944 in this manner is reproduced in Fig. 12-35c.

Figures 12-36c and 12-38 are electron micrographs showing in cross section an image deposit recently prepared by the above procedure. The image comprises single crystalline particles rather than aggregates, the individual crystals being closely packed in a layer only 400 nm thick, less than 1/25 the thickness of the earlier image deposits in gelatin, to form a near-continuum of silver at maximum density. The single crystals in the α-cellulose paper measure 15 to 150 nm in diameter, somewhat smaller than the aggregates in gelatin. Figure 12-39 shows the strikingly uniform spectral reflectance of this compact positive image.

In succeeding experiments spectrally neutral silver images were deposited in regenerated cellulose layers prepared by the alkaline hydrolysis of cellulose acetate sheet. The image deposits comprised aggregates ranging up to 300 nm in diameter, with most of the silver in the larger aggregates in a 2–2.5 nm stratum close to the sheet surface.

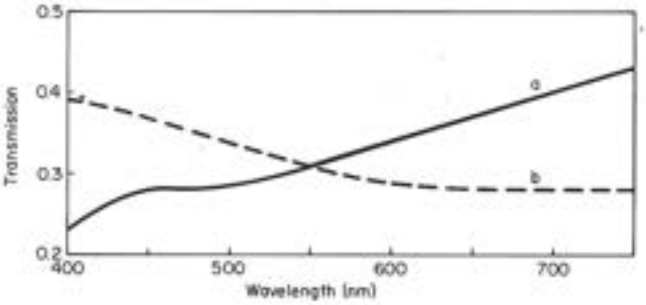


Fig. 12-37. Transmission spectra of the images in thick gelatin layers shown in Figs. 12-36(a) and (b).

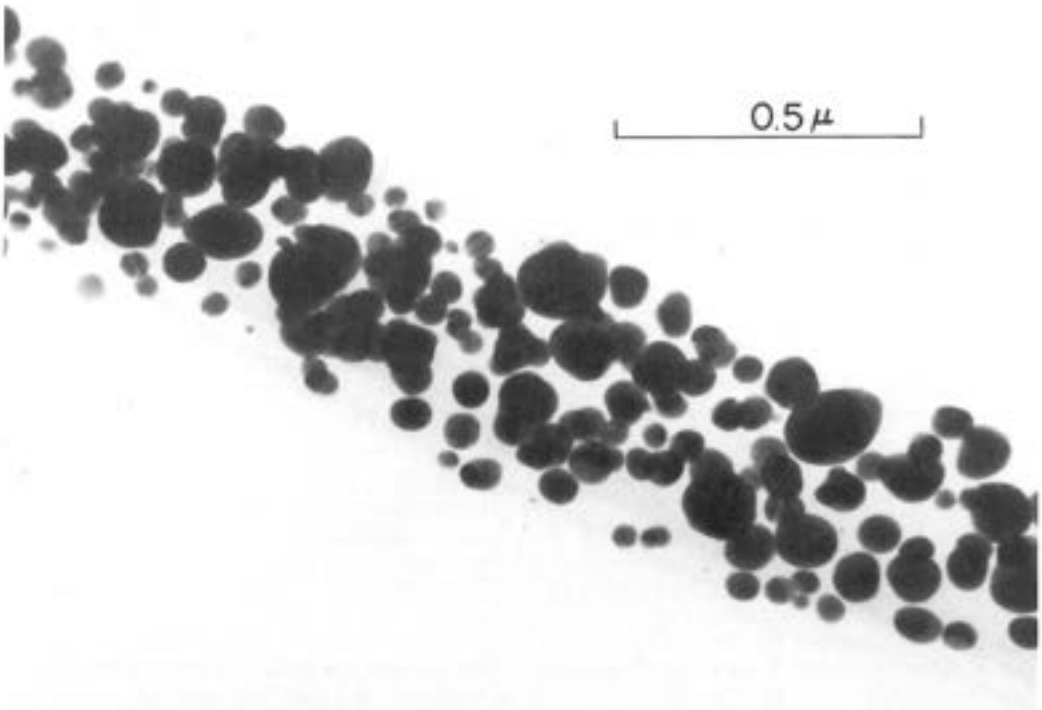


Fig. 12-38. Cross section of neutral image in α-cellulose blotting paper. Note that the deposit of crystals is compact but not solid, an ideal condition for blackness. Reflectance spectrum is shown in Fig. 12-39.

In both the pure α-cellulose blotting paper receiving layer and the regenerated cellulose receiving layer the deposition process, characterized by Land as "concentration and condensation," depends on the local concentration of soluble silver complex becoming sufficiently high to initiate precipitation. As no nucleating materials are added, the soluble silver is presumably nucleated—much as raindrops are—by sites accidentally present in low concentration in the capillaries of the blotting paper or within the regenerated cellulose layer. These are powerful examples of receiving systems not seeded with nuclei and not inhibited by a protective colloid.

Processing with Viscous Reagent. The compact silver layers in α-cellulose blotting paper and in regenerated cellulose had been identified as structures suitable for neutral, continuous tone images, but the procedures which were used to form them did not lead directly to a one-step camera process. The next step toward the camera process was to produce such an image using a viscous reagent which could be sealed in pods and incorporated in the self-contained film units described earlier.

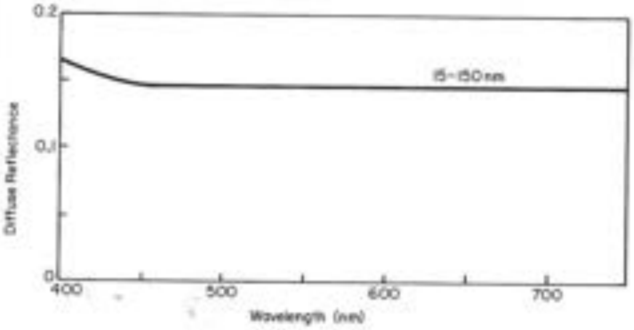


Fig. 12-39. Spectral reflectance of image deposit in α-cellulose blotting paper, shown in cross section in Figs. 12-36(c) and 12-38.

An important consequence of using a reagent made viscous with a polymeric thickener is that the polymer retards precipitation of silver from the soluble complex. In order to achieve reduction and precipitation in an image-receiving layer, it is necessary to overcome this retardation.

Approaches proposed by Land to induce the release of silver from its hypo complex in the presence of a retarding polymer include: (a) precipitation of thiosulfate ion,[40] (b) precipitation of a hypo-insoluble, readily reducible silver salt,[41] and (c) nucleation by a colloidal heavy or noble metal.[42] These reactions could be used alone or in combination. Figure 12-40 outlines reactions of types (a) and (b), and processes based on these principles are discussed below.

Precipitation of Thiosulfate. To remove thiosulfate ion, a soluble salt of a metal which forms an insoluble thiosulfate could be added to an image-receiving sheet. Reaction with the soluble silver complex would precipitate the metal thiosulfate salt and free silver ion, which is readily reducible.

A process of this type[40] used as the receiving sheet baryta-coated paper which had been impregnated with lead acetate and dried. When the lead-treated receiving sheet and an exposed negative were passed together

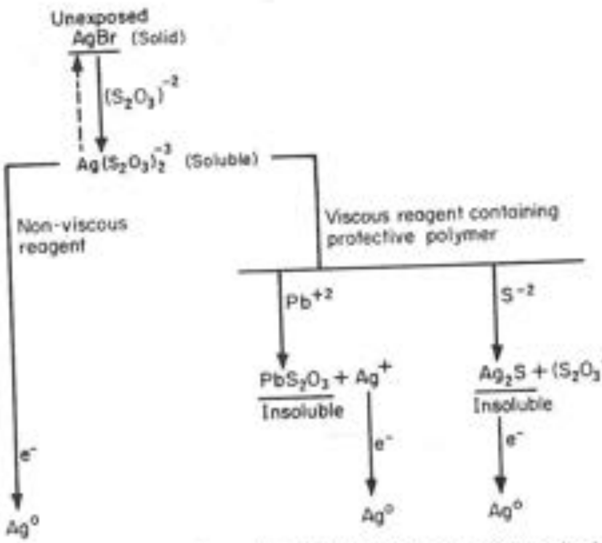


Fig. 12-40. Schematic outline of transfer and reduction of soluble silver complex images. With a nonviscous reagent, reduction and deposition of silver proceed rapidly. In reagents made viscous by the addition of a polymer, reduction and deposition of silver from the thiosulfate complex are retarded. This retardation may be overcome through the addition of ions which destroy the complex by precipitating either silver or thiosulfate.

between pressure rollers, spreading between them a viscous reagent containing developer and hypo, an image of neutral tone and excellent pictorial quality resulted. This process is another example of "concentration and condensation" deposition, as no nucleating materials are added.

Figure 12-35d is a recent reproduction of a print made in 1945 with the lead acetate receiving sheet. Figure 12-41 shows the structure of an image deposit of this type, and Fig. 12-42 shows its nearly uniform reflectance spectrum. The image silver comprises aggregates 20 to 300 nm in diameter, similar in individual appearance to those formed in the gelatin layers of Fig. 12-30. Unlike the aggregates in the thick layers of gelatin, these aggregates are arranged compactly. They are confined within the 2 μm layer of crosslinked polymer formed by reaction of lead ion with the viscous reagent; the aggregates thus comprise a nearly continuous image deposit at high densities. The fine crystals in this deposit form dense aggregates of about the same size as the large, single crystals in α-cellulose blotting paper, as described above, and, like them, behave optically as black absorbers. The lead acetate receiving sheet used with viscous reagent yielded images with a full range of densities when a fine-grained chloride, bromide or chlorobromide emulsion of low or moderate speed was used as the negative component. The higher speed silver iodobromide negative emulsions transferred considerably less silver.

Precipitation of Silver. Sulfides or selenides could be used in the receiving layer to precipitate silver from the soluble hypo complex, forming reducible silver sulfide or silver selenide. Such removal of silver ion from the thiosulfate complex frees thiosulfate for further extraction of silver ion from the remaining silver halide.

When soluble sulfides were added to the receiving system, deposition of positive silver from the complex was indeed increased, but a new gamut of problems, described as follows in Ref. 2, resulted:

> (1) Sulphide (sic) ions in solution provide so many points of initiation that an enormous number of

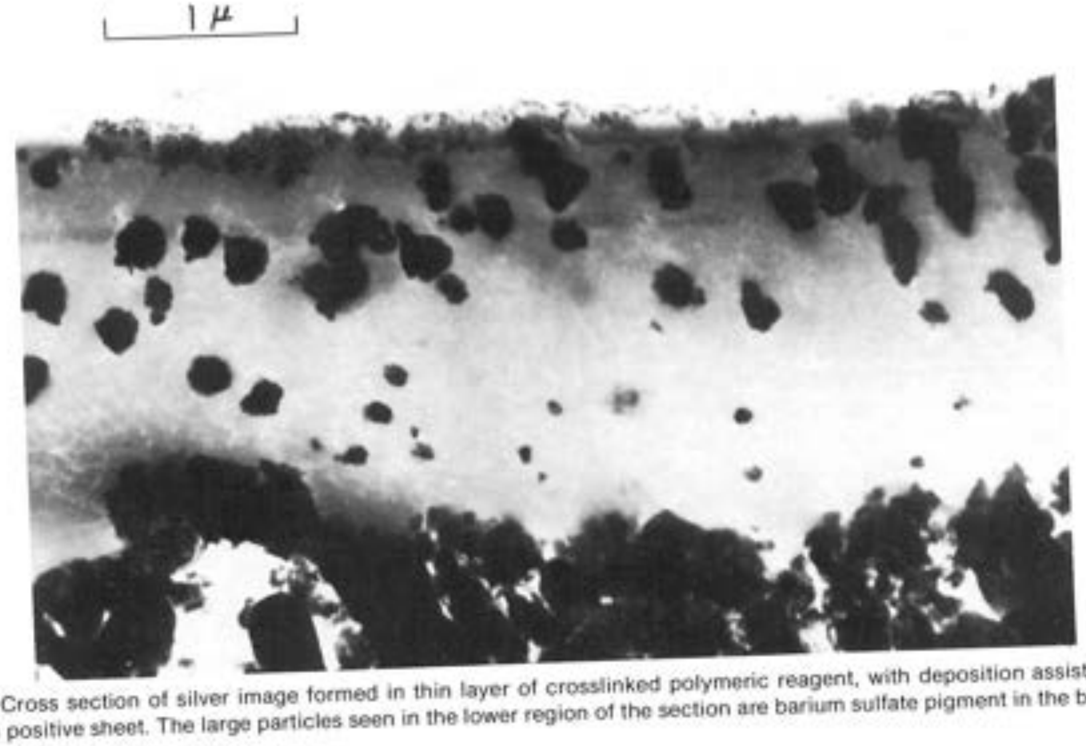


Fig. 12-41. Cross section of silver image formed in thin layer of crosslinked polymeric reagent, with deposition assisted by soluble lead ions in positive sheet. The large particles seen in the lower region of the section are barium sulfate pigment in the baryta coating.

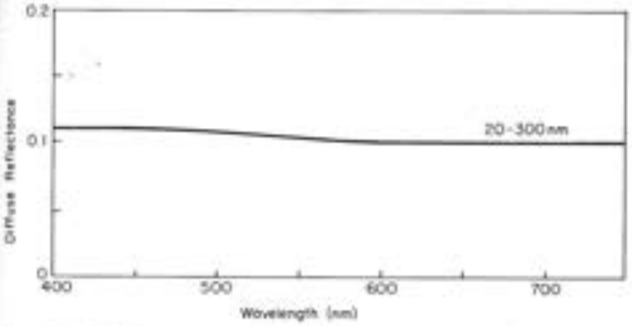


Fig. 12-42. Reflectance spectrum of the silver image of Fig. 12-41. The image comprises aggregates 20-300 nm in diameter.

grains start growing. If these become large the whole picture will be too dense. If they remain small, the picture will be bright yellow (you will recall that the colour of silver colloids depends on the particular size).

(2) There is a tendency for the grains in the shadows, opposite the unexposed portions of the negative, where much silver is available, to grow larger than the grains in the medium tones, where the available silver concentration is low, producing an unpleasant combination of blue shadows and yellow highlights.

(3) Some of the sulphide ions migrate into the negative, dropping the concentration in the positive and fogging the negative.

Thus, having determined how to extract silver ions from the appropriate part of the negative, and how to reduce them to silver atoms, we are still confronted with the problem of how to build these atoms into arrays of the correct diameter for absorbing visible light.

Greater control of the size and number of image deposit sites was achieved by incorporating in the receiving layer a small amount of a finely divided crystalline metal sulfide of low solubility.[41] Sulfide ions would remain localized until complex silver ions from the negative reached them and could thus initiate precipitation of small clusters of silver sulfide particles. The clusters would serve as loci for the deposition of silver in masses appreciably larger than those obtained with the uniformly distributed soluble sulfides.

Silica-based Metal Sulfides. A significant advance in the control of image deposition was the precipitation of the insoluble metal sulfide in a colloidal suspension of very finely divided silica.[43a] The silica, being insoluble and nonswelling, limited the volume within the layer available for precipitation of the sulfide as well as for deposition of silver. Sulfides precipitated in this matrix readily formed fine aggregates or galaxies,[43b] comprising a positively controlled population of active sites.

The sulfide ions were essentially bound in place until they reacted with the soluble silver complex to form silver sulfide. As an additional measure to avoid the release of soluble sulfide ions upon reduction of silver sulfide, an excess of soluble metal ions capable of forming sulfides more soluble than silver sulfide, but still not appreciably soluble in the developer, was included in the receiving sheet.[44] Sulfide ion freed at its original site could thus be at once reprecipitated *in situ* and the diameter of the cluster maintained. The silver image deposits produced in this system were of well-controlled size and distribution and brown or brown-black throughout their entire density range.

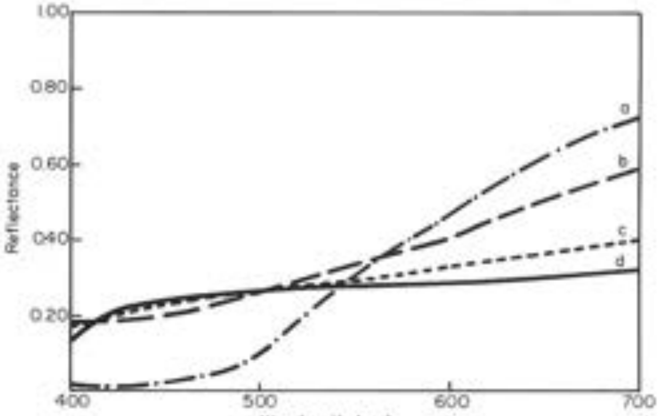


Fig. 12-43. Reflectance spectra of images transferred by viscous reagent to silica-sulfide receiving sheets, comparing the images formed when the receiving layer contains (a) soluble sulfides, (b) uniformly distributed fine crystals of a metal sulfide of low solubility, and (c) and (d) *galaxies* or clusters of very small crystals of a metal sulfide precipitated in a colloidal suspension of silica.

At this point, sulfides had been used to produce image colors from yellow to brown to nearly neutral, as the sulfides were added (a) in solution, (b) as fine crystals uniformly distributed and (c) as galaxies of microcrystals formed in the presence of silica. Figure 12-43, taken from Ref. 1, shows reflectance spectra of such a series of images. It is evident that image color was predetermined by the nature of the sulfide used and that the preferred near-neutral sepia image could best be formed when metal sulfides were precipitated in silica.

The siliceous metal sulfide receiving layer was a fundamental component of the sepia film system first put into production, and newer silica-based receiving layers continue to have a vital role in contemporary black and white systems.[45]

The Sepia Process. The sepia one-step process, publicly demonstrated in 1947,* produced pictures outstanding in pictorial quality at exposure levels equivalent to ASA

---

*The demonstration used an 8 x 10 in. view camera equipped with motorized processing rollers and a dark chamber (Fig. 12-44). The film assembly for each picture comprised a silver halide emulsion, a positive image-receiving sheet and, affixed to the positive sheet, a sealed pod filled with viscous reagent. Processing involved simply passing this assembly through the motorized rollers into the dark chamber. The roller pressure ruptured the pod, releasing and spreading the processing reagent between the two sheets, which formed negative and positive images on their respective surfaces. Pictures were taken, and each photograph was displayed 1 min after exposure, its one-step process having thus taken place automatically inside the camera. Figure 12-45 shows a picture of this type being stripped apart after processing through demonstration rollers outside the camera.

Fig. 12-48. The Model 95, first of the Polaroid Land cameras (1948).

speed 100. These untreated and uncoated images are remarkably stable, as evidenced by Figs. 12-46 and 47, which are 1976 reproductions of prints made and exhibited in 1946 and 1947. Type 40, the sepia roll-film product, was introduced along with the first one-step camera, the Model 95, in late 1948. (Fig. 12-48).

Black and White Processes. The transition from sepia to black and white reflection prints was accomplished by Land and Morse between 1948 and 1950, when Type 41 film was introduced. They precipitated metal sulfides in a silica hydrosol and coated the resulting suspension in a thin layer over baryta paper bearing a waterproof layer of polyvinyl butyral. Image deposition was restricted to the interstices of the silica-based receiving layer, and the image silver formed aggregates measuring 100 to 160 nm in diameter, each comprising many fine particles 10 to 30 nm in diameter. The aggregates were large in comparison with the Type 40 image particles, which measured 25 to 125 nm. The electron micrographs of Figs. 12-49 and 50 show the fine structure of the respective sepia and black and white images, and Fig. 12-51 compares their reflectance spectra.

Subsequent silica-metallic sulfide receiving layers have formed still larger image aggregates. Figures 12-52a and b are electron micrographs of image deposits of high and intermediate optical densities in a current receiving layer of this class (Type 107), showing in cross section the configuration of image silver aggregates in their silica matrix. Figure 12-53a shows a maximum density area as viewed through the layer, and Fig. 12-53b

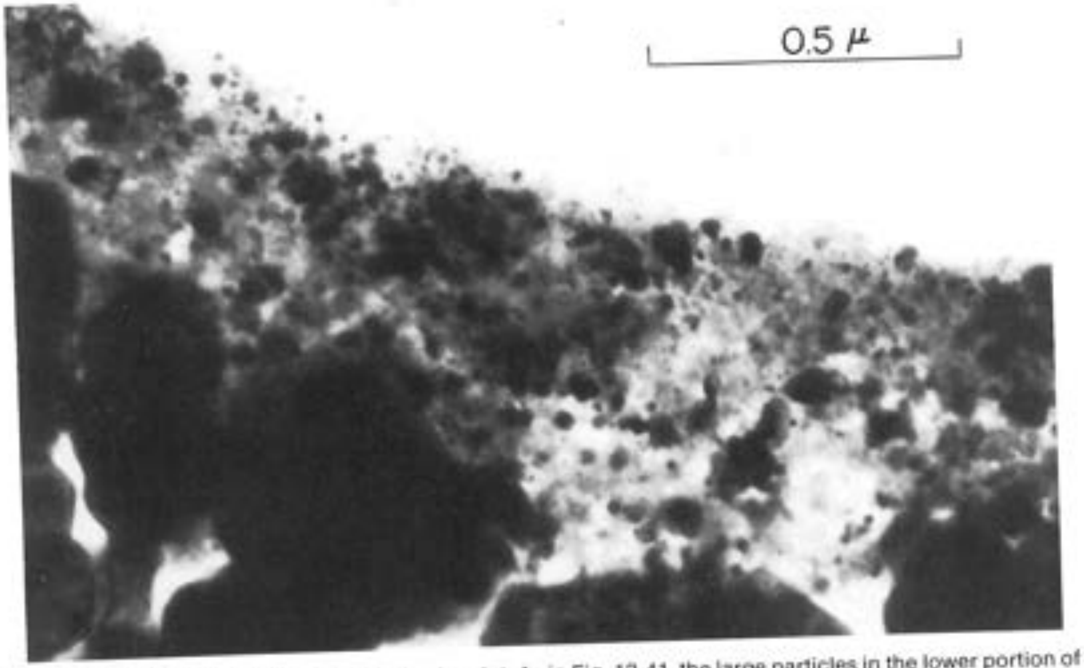


Fig. 12-49. Cross section of image layer of Type 40 sepia print. As in Fig. 12-41, the large particles in the lower portion of the section are barium sulfate pigment in the baryta coating; above the baryta is the deposit of silver in silica.

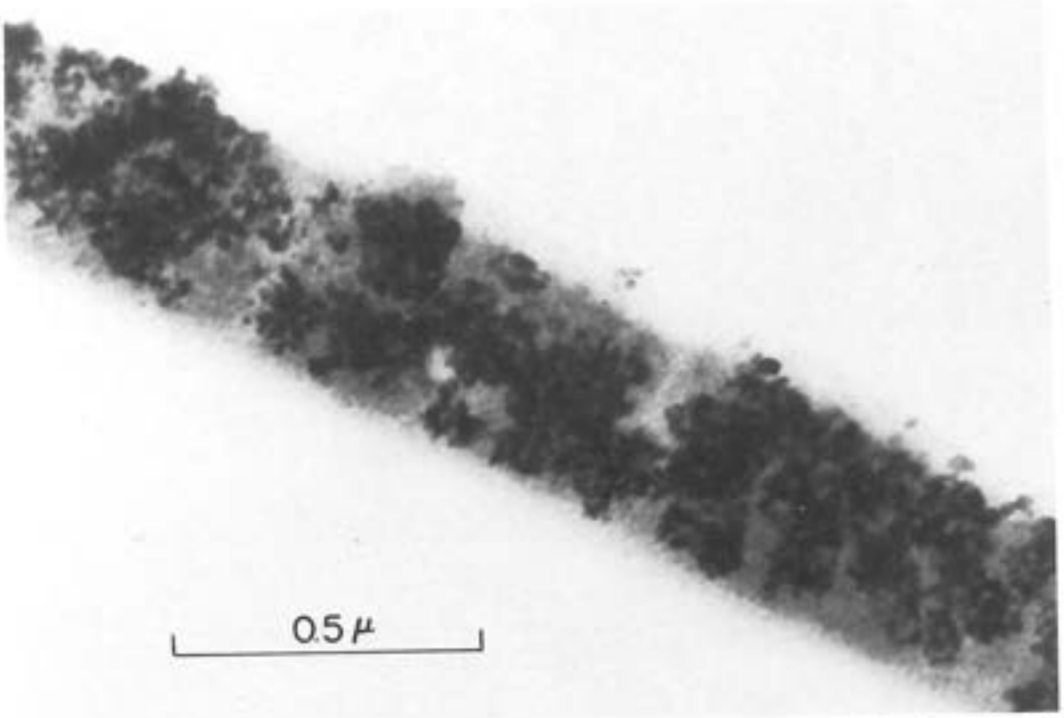


Fig. 12-50. Cross section of Type 41 image, showing silver aggregates restricted to thin layer of silica. Type 41 was the first Polaroid black and white film (1950).

shows a flake of silver aggregates separated from the silica matrix, demonstrating the continuous nature of a high density image deposit; Fig. 12-54 shows a single aggregate at higher magnification. The aggregates average 150 to 300 nm in diameter; each comprises about 40 closely associated particles 15 to 20 nm in diameter. Figure 12-55 shows the consistent neutral reflectance spectra of a Type 107 image over its full density range.

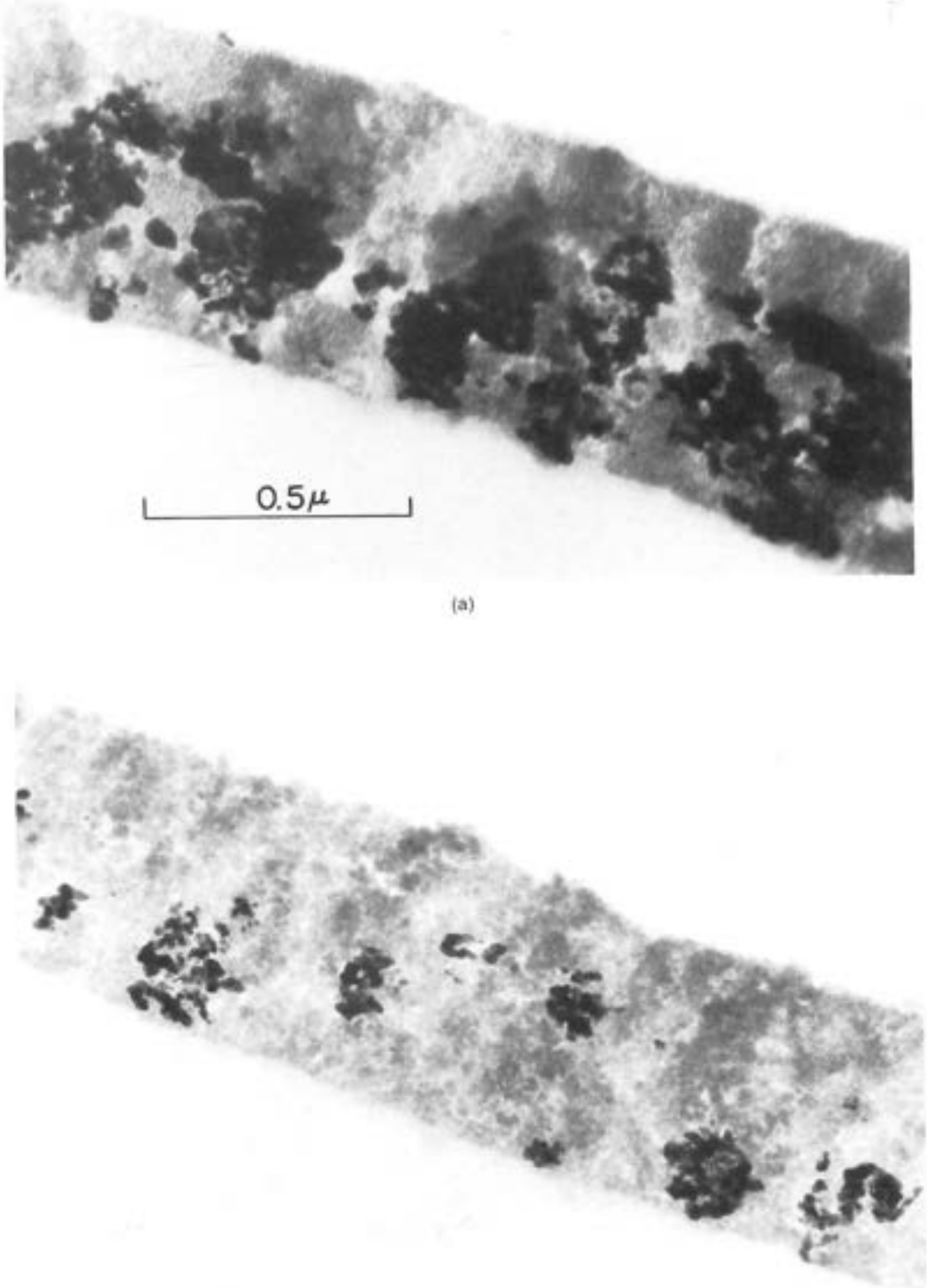
Fig. 12-51. Reflectance spectra of Type 40 sepia image (dotted line) and Type 41 black image (solid line). Numbers printed over curves indicate range of image aggregate diameters.

Nucleating Sites in Regenerated Cellulose. As noted earlier, regenerated cellulose was one of the first materials found suitable as a matrix for neutral silver image deposition. Using nonviscous reagents, nucleation and growth of silver took place readily in the absence of added nuclei.

Nuclei found suitable for incorporation into regenerated cellulose layers for use with viscous reagent systems include colloidal metals and colloidal metal sulfides and selenides. Image-receiving layers of regenerated cellulose having nuclei of well-controlled size and distribution are obtained by hydrolyzing a cellulose acetate layer containing the desired nuclei.[45] With sheets of this type image silver is deposited beneath the surface of the regenerated cellulose layer, and the resulting print is glossy and durable without the later application of a protective coating.

Regenerated cellulose receiving layers of this type are used in Polaroid "coaterless" black and white systems.* Figure 12-56 shows in cross section a high density area of a reflection print image formed in such a layer (Type 87), with palladium sulfide particles the active sites. Most of the silver image lies within a stratum 0.04 to 0.4 μm beneath the surface. The image depth corresponds approximately with the depth to which the layer had been hydrolyzed prior to image formation. The image silver includes both large aggregates of fine crystals and large single crystals, with deposits of each type ranging up to 200 nm in diameter.

*"Coaterless" systems are those yielding positive prints which are stable without coating or other aftertreatment. Further discussion is included in the section "Stabilization of Transferred Images," p. 318.



(a)

(b)

Fig. 12-52. Type 107 image silver, (a) cross section of a maximum density area (1.65) and (b) cross section of a density 1.14 area. The aggregates are embedded in silica; the dark regions are silver, the light gray silica.

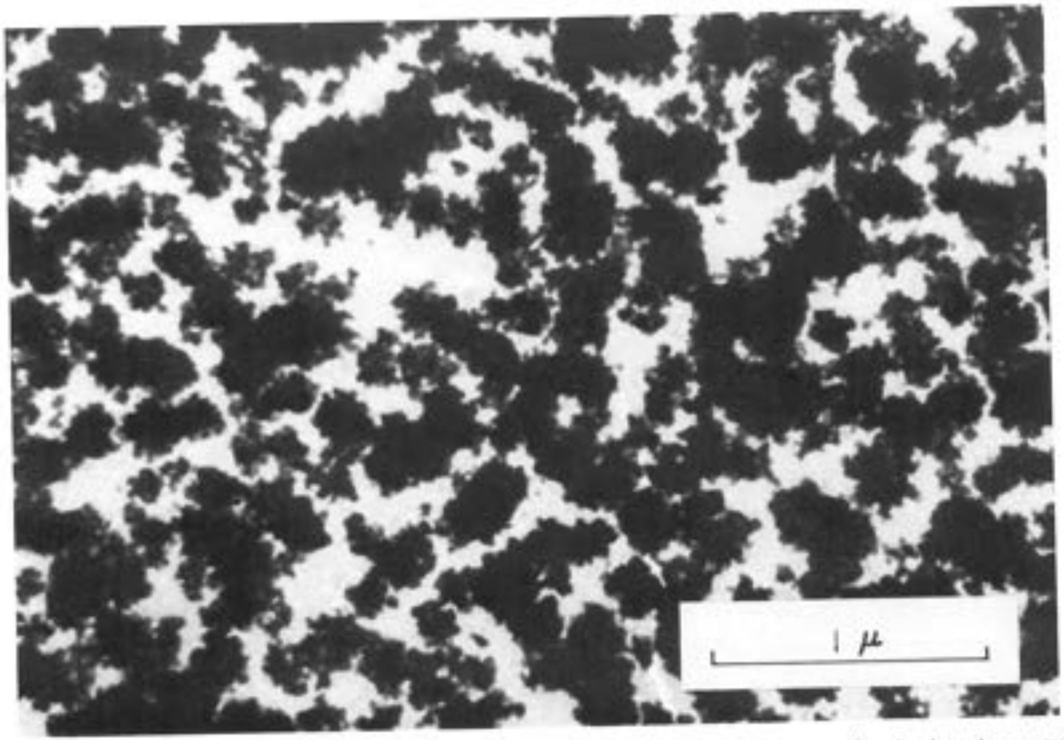


Fig. 12-53a. Type 107 image silver in maximum density area, as viewed through the layer. The magnification here is somewhat lower than in the cross section of Figs. 12-52(a) and (b) to provide a more extensive field of view.

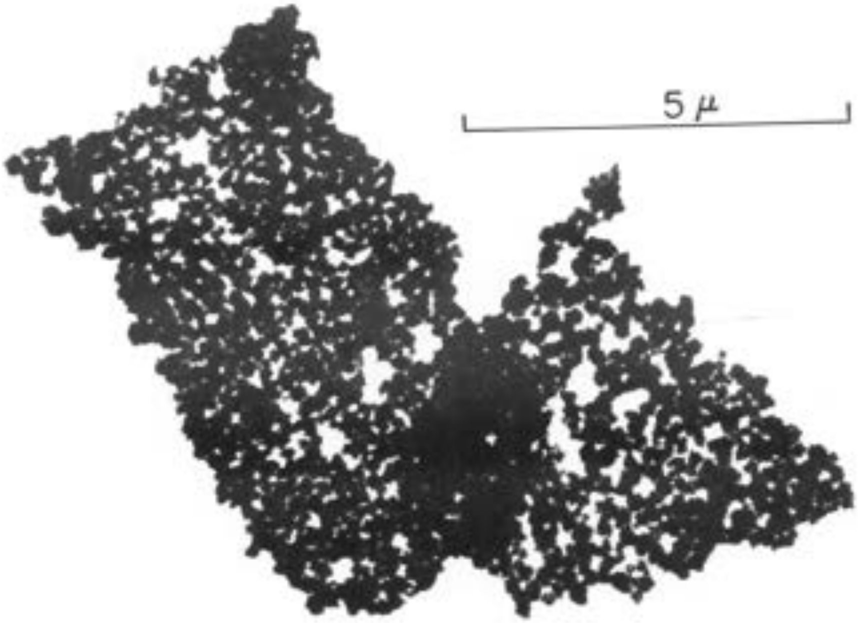


Fig. 12-53b. Type 107 positive image silver removed from a maximum density region and treated with hydrofluoric acid to remove silica from the interstices; the aggregates are sufficiently interconnected to remain in "flakes." This figure illustrates the concept of the metallic network that leads to the neutrality of Type 107 images at all densities.

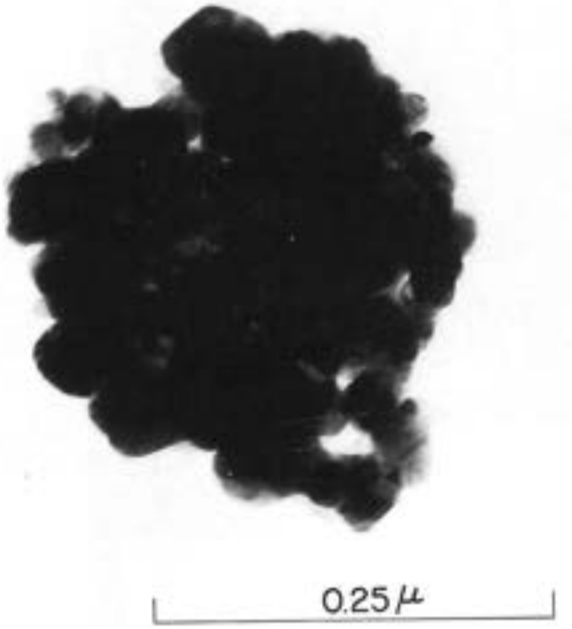


Fig. 12-54. A single Type 107 image aggregate at high magnification. Aggregates average 150 to 300 nm in diameter, and each comprises about 40 closely associated fine particles, which are individual crystals of silver.

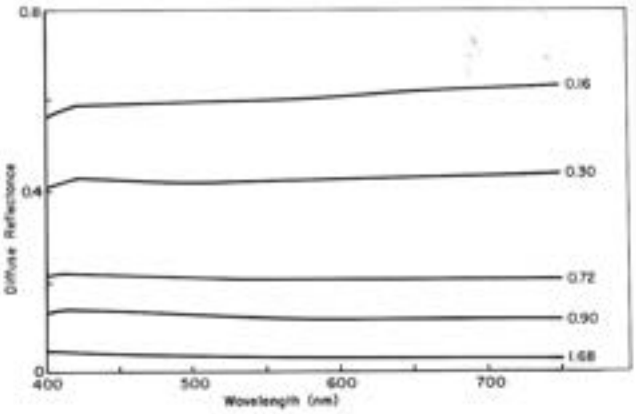


Fig. 12-55. Reflectance spectra of Type 107 images over a wide density range. The neutrality of all densities, as shown by these curves, was a terminal product of research from 1944 to 1950; the system has been in use in the basic black and white product from then to the present (1976). Since the curves are flat over the visual range, each can be characterized by a single reading of diffuse reflection density. These densities are shown to the right of the curves.

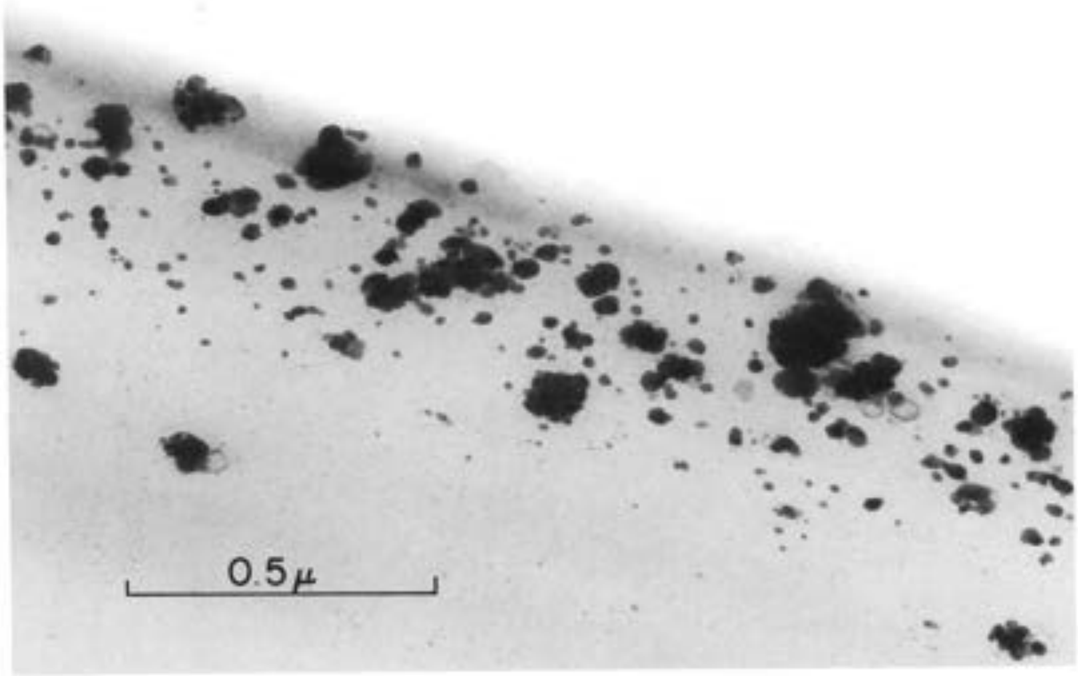
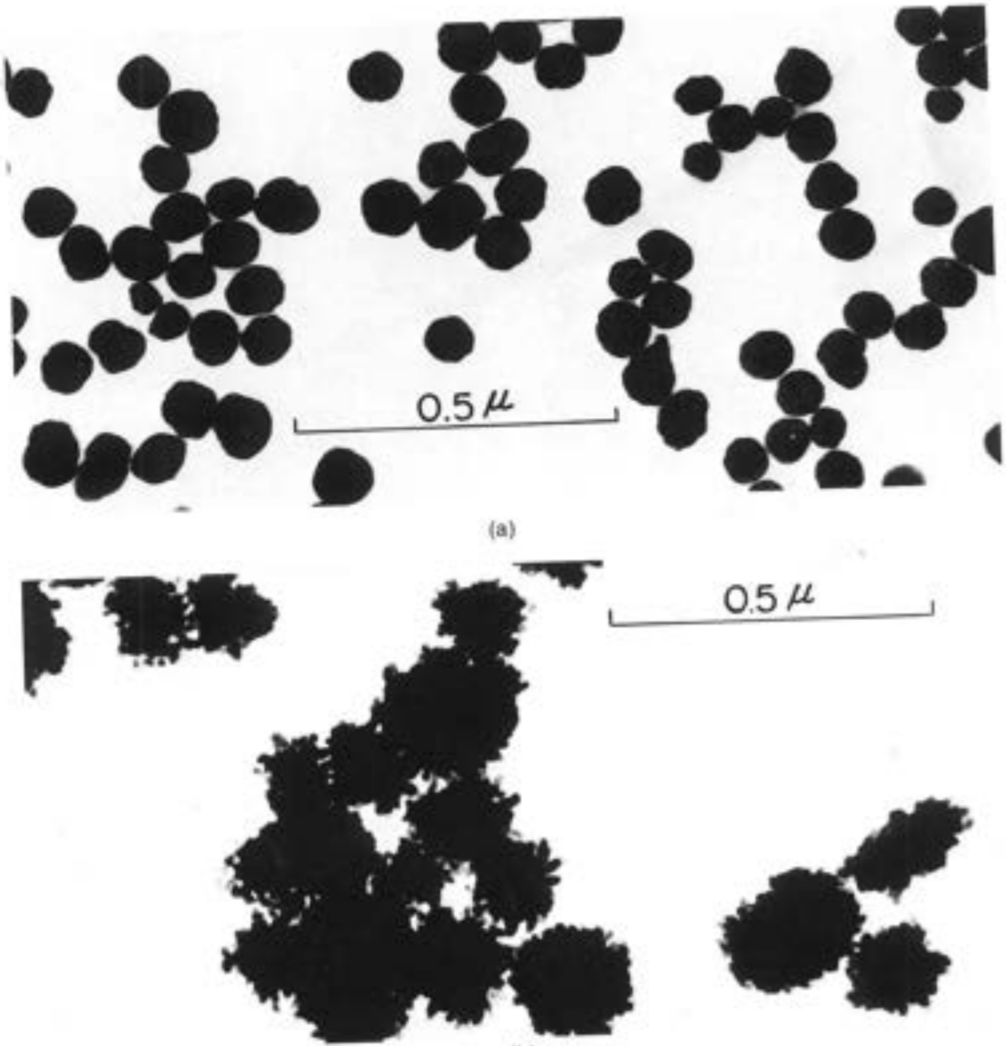


Fig. 12-56. Cross section of an image in regenerated cellulose (Type 87). The depth of the image is approximately the depth to which the layer of cellulose has been regenerated.



(a)

(b)

Fig. 12-57. Transparency image deposits: (a) brown image formed in mercaptan-free reagent; and (b) black image formed in reagent containing cysteine.

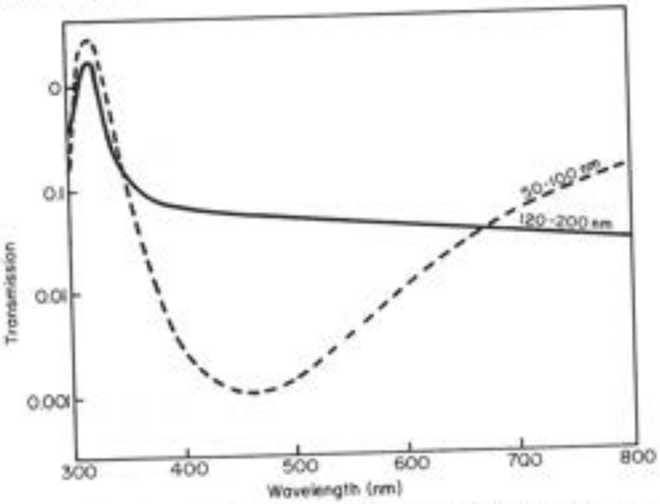
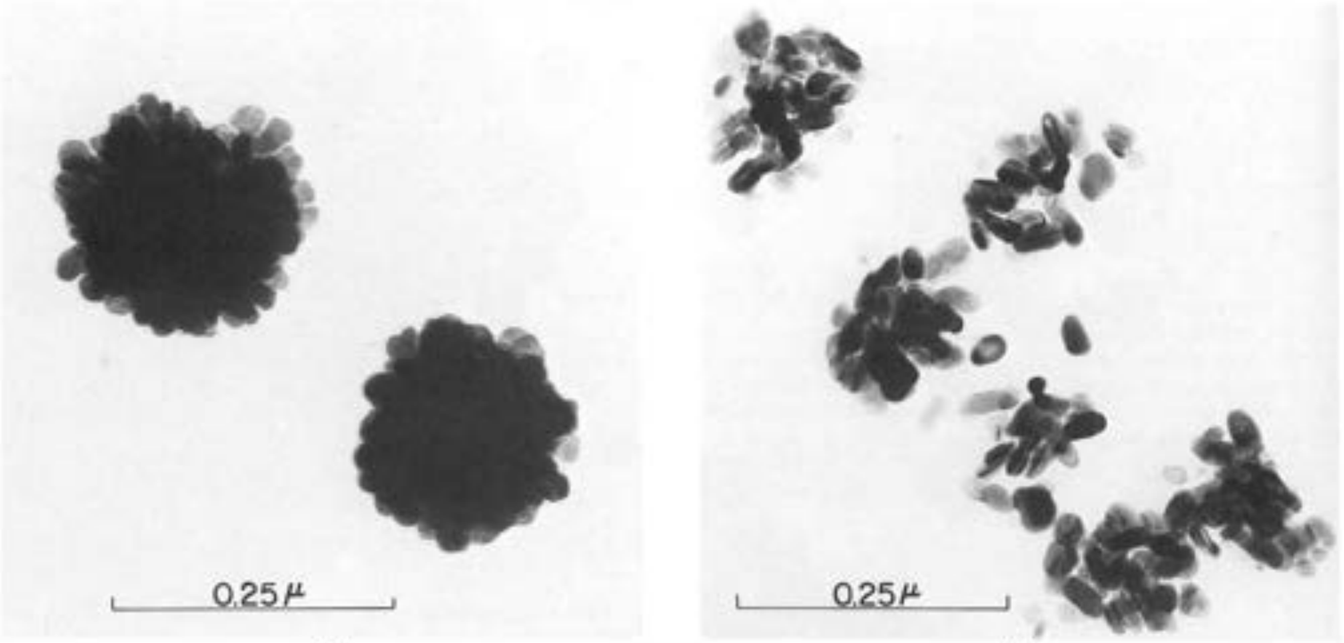


Fig. 12-58. Transmission spectra of brown image (dotted line) and black image (solid line) of Fig. 12-57. Range of diameters of particles and aggregates is indicated over each curve.

Nucleation in Viscous Reagent. The blotting paper, regenerated cellulose and siliceous networks described above all provide environments in which the large single crystals can be aggregated or the aggregates of very small single crystals can be aggregated to satisfy the requirements for blackness; and in these environments the precipitation of the image in the desired state is achieved with remarkable independence of the chemistry of precipitation. In general, the most primitive reduction of silver ion is all that is required. When these environments or their equivalent are not available—for example, when the image is to be precipitated in the viscous reagent—simple precipitation will lead to single crystals too small and too far apart to satisfy the large single crystal condition, but too large to enter into spontaneous clustering. Figure 12-57a shows such a deposit.

In the black and white transparency systems in which a viscous reagent containing nuclei becomes the matrix for growth of image aggregates[47] (Types 46L and 146L), the formation of small particles which readily form



(a) (b)

Fig. 12-59. (a) Single agregates of Type 46L image silver washed free of polymer (120 keV electron micrograph); (b) aggregates like those shown in (a) sectioned while in place in the finished image layer (200 keV electron micrograph).

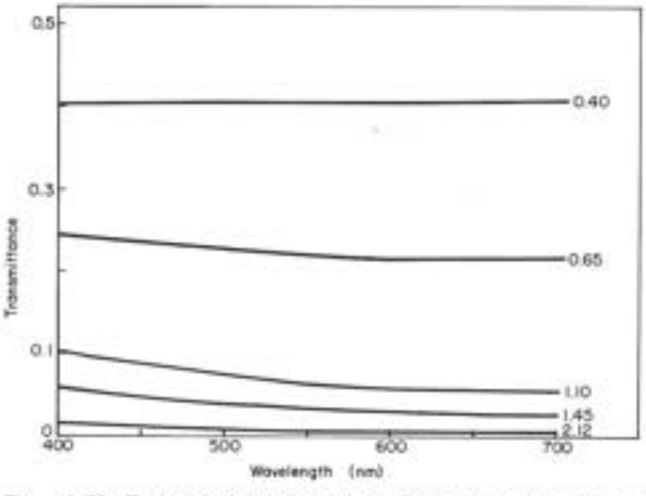
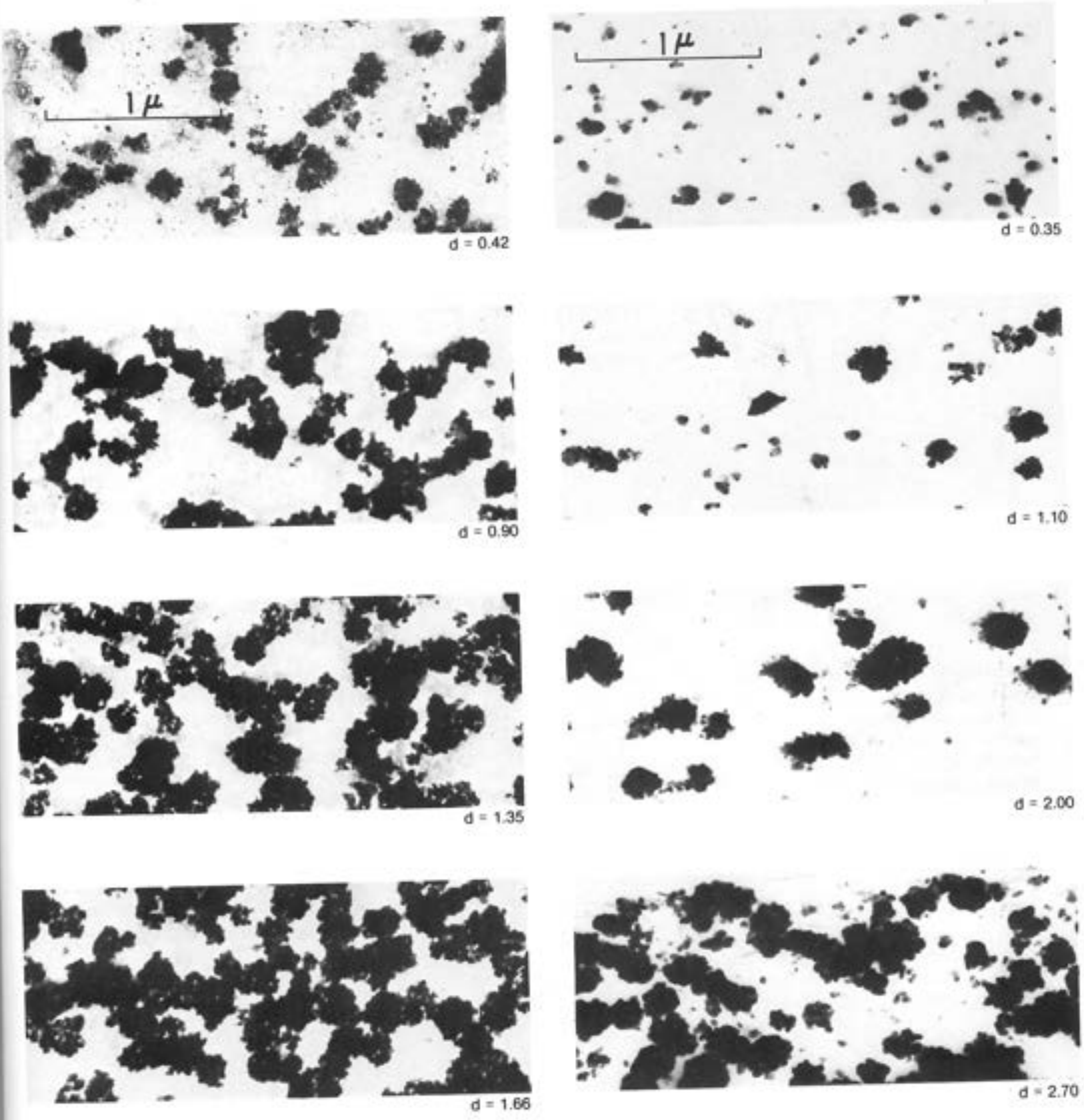


Fig. 12-60. Transmission spectra of Type 46L transparency images at several densities. Since the curves are flat over the visual range, each can be characterized by a single reading of diffuse transmission density. This density is indicated to the right of each curve.

"large" aggregates is assisted by mercaptans included in the reagent. To demonstrate this effect, Fig. 12-57 compares the structures of image deposits formed in a viscous reagent (a) without and (b) with a mercaptan component.[48,49] The mercaptan-free reagent used as control produced a brown image comprising particles 50 to 100 nm in diameter, many of which appear to be single crystals. A reagent containing the mercaptan cysteine[50] produced a black image comprising 120 to 200 nm aggregates, each including 50 or more fine particles in close association. The spectra of these two images are compared in Fig. 12-58.

The silver aggregates which make up the Type 46L image deposit, shown at high magnification both entire and in cross-section in Figs. 12-59a and b, measure 150 to 250 nm in diameter, and each aggregate includes about 50 fine particles 10 to 25 nm in diameter. The extinction bands visible in the fine particles of the sectioned aggregate are indicative of their crystallinity. The transmission spectra of Fig. 12-60 demonstrate the near-neutrality of a Type 46L image over a wide density range.

Although they are formed in a completely different environment, the image aggregates of the transparency positive show a great structural similarity to the black



(a)

(b)

Fig. 12-61. "Step wedges" illustrating the approximation to uniformity of aggregates for (a) Type 107 and (b) Type 46L images over the full range of optical densities.

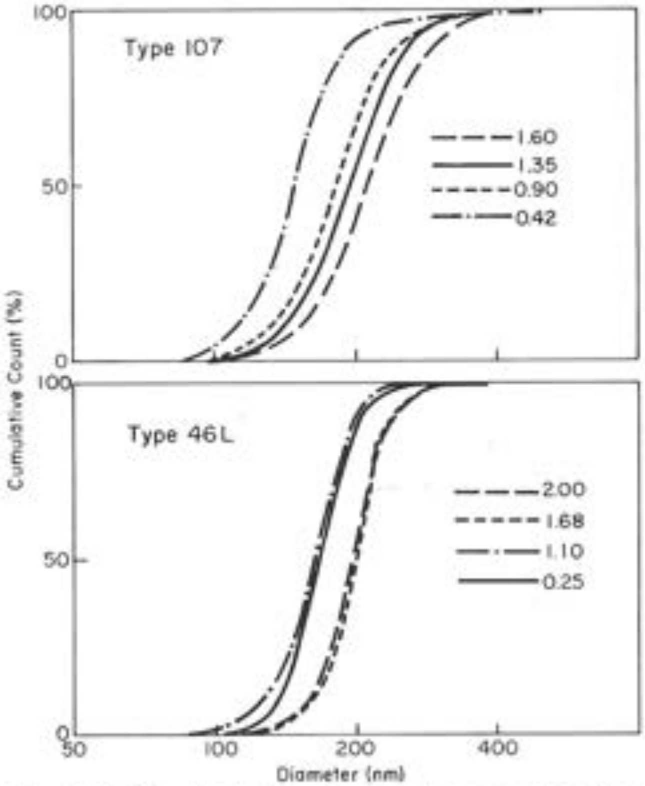


Fig. 12-62. Size distribution of aggregates comprising Type 107 and Type 46L images over a wide range of densities. For each density indicated, cumulative percentages of aggregates, sized from electron micrograph counts, are plotted against diameter (log scale) corresponding to calculated aggregate volume. In both cases most of the silver is in large aggregates.

and white Type 107 reflection print image aggregates already described. In the black and white transparency processes mercaptans, often referred to as blue-black toners, are used to induce rapid formation of small particles which readily collect into an aggregate. The resulting aggregate is similar in size and form to the aggregate which in the reflection print forms spontaneously with or without a mercaptan present.* The dramatic similarity in diameter of the total aggregates, in the structure of the aggregates, in the size and number of constituent particles and in the flatness of the absorption spectra for these two quite different systems supports the hypothesis that the ultimate role of the toner is not to alter the chemical composition within the aggregate but rather to bring into being an aggregate of appropriate size and configuration for uniform light absorption.

Neutrality of Images. In both the reflection and transparency systems the growth of compact arrays of large aggregates (100 nm or more) accounts for the spectral neutrality of the images.** Neutrality of aggregate images requires the fine particles within each large aggregate to be in contact or in close proximity, acting together as a single unit of appropriate size and conductivity; acting individually, the 10 to 30 nm particles would produce yellow or orange images.

The spectral curves and corresponding electron micrographs of the compact images described here have demonstrated a consistent size-color relationship for silver deposits formed in very different thin layer environments. In all cases, from the close-packed single crystals of the 1944 images in α-cellulose blotting paper (Fig. 12-38) to the Type 46L aggregates of 50 or more fine crystals (Fig. 12-59), the images are black when the crystals or aggregates of crystals are tightly packed together and greater than about 100 nm in diameter.*** Sepia pictures, on the other hand, comprise either considerably smaller single crystals, in the range of 50 to 100 nm, spaced at least as far apart as the crystal diameter (as in Fig. 12-57a) or loosely packed aggregates of very fine crystals (as in Fig. 12-49).

In the black and white processes consistently neutral hue at all densities is achieved by producing large particles or aggregates over the entire density range, as illustrated by the micrographs of aggregates from representative steps of Type 107 and Type 46L images presented in Figs. 12-61a and b, respectively. Figure 12-62 shows corresponding size distribution curves of the aggregates comprising images at several density steps. In both systems most of the silver at each density step is in aggregates 150 to 300 nm in diameter, large enough to produce neutral spectra in a compact layer; the small aggregates included at the lower densities account for only a very small amount of silver and do not materially affect the absorption.

The Fate of Silver During Processing

In silver transfer processes leading to positive images, the silver of both exposed and unexposed grains undergoes development concomitantly in different strata. While the exposed grains are developing in the emulsion layer, the silver of grains which have been exposed is involved in a rapid train of events: the unexposed grains dissolve, and the resulting soluble silver complex transfers to the receiving layer, where it immediately develops to form the crystals of silver which comprise the positive image.

---

*The effect of mercaptans in this process is unlike that characterized by Cassiers, who described a mercaptan-induced shift from brown to black in Gevacopy transfer images comprising silver particles of approximately 65 nm in diameter. Cassiers reported that this color shift was accompanied by changes of crystal order and surface crystalline state, with no significant change in overall dimension or distribution of silver particles.[51]

**This observation is based on the correlation of microscopic and spectrophotometric data. Calculations based on the classical Mie equation for scattering and absorption by isolated metallic spheres, often useful in characterizing the optical properties of loosely packed silver image deposits,[52] are not applicable to these compact images.

***A 1962 paper of Weyde, Klein and Metz[53] describes shifts from brown to black for silver deposited in thick gelatin layers as the packing density of silver is increased. The color shift is attributed to increasing incidence of twin- and triple-particle aggregates of particles; the illustrations show that even their most densely packed deposits are much more dilute and much less aggregated than the compact deposits discussed here.

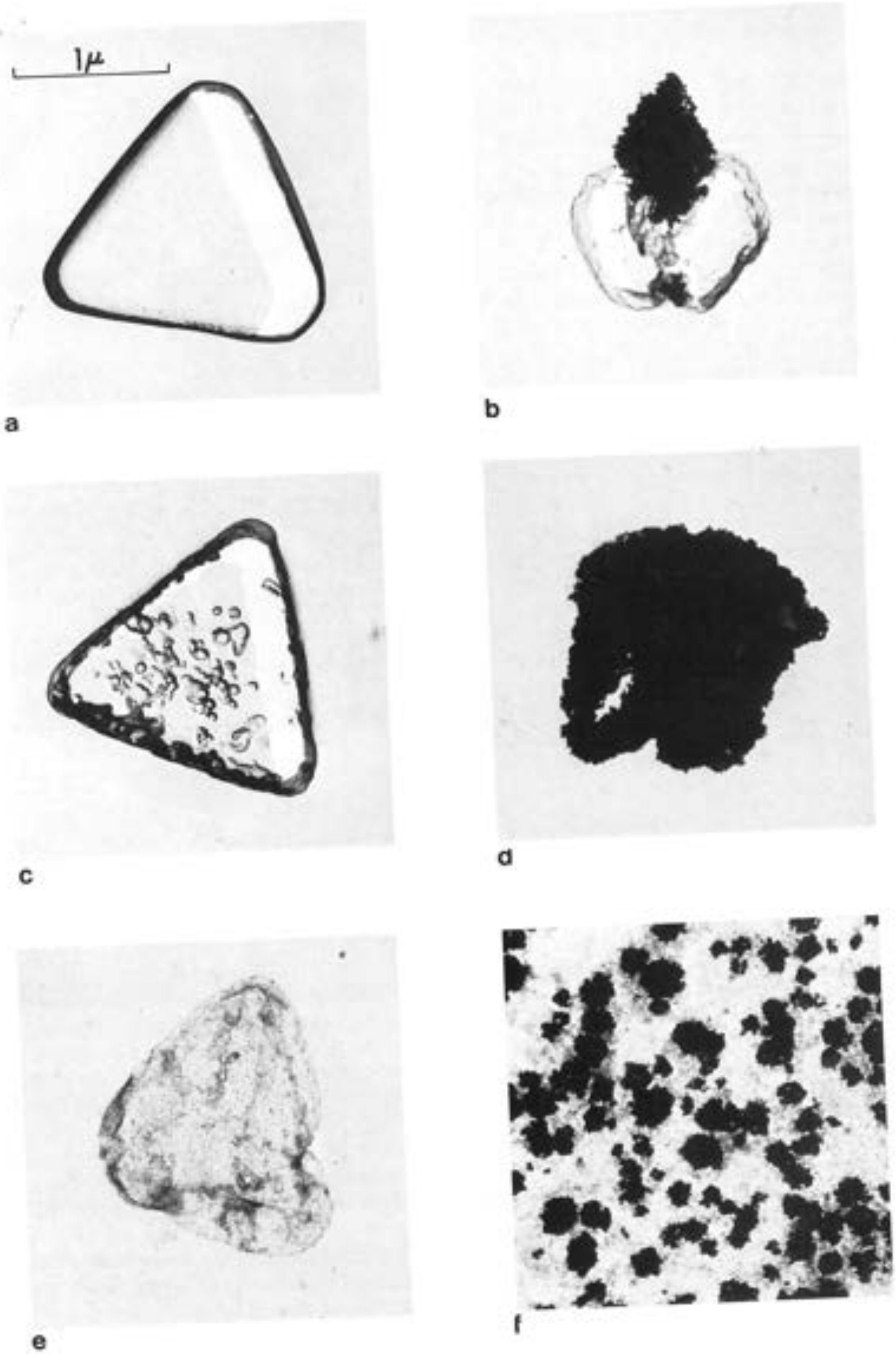


Fig. 12-63. Stages in processing of Type 107 grains: (a) is replicated from an unexposed undeveloped grain, (b) and (c) from grains processed 1/10 sec; (b), an exposed grain, is partially developed; (c), an unexposed grain, is partially dissolved; (d) is a fully developed grain; (e) the imprint of a dissolved grain as it appears after the gelatin is removed; (f) is positive image silver derived from a single grain such as (a) and transferred to an image-receiving layer, shown at the same magnification as the negative grains (a) through (e).

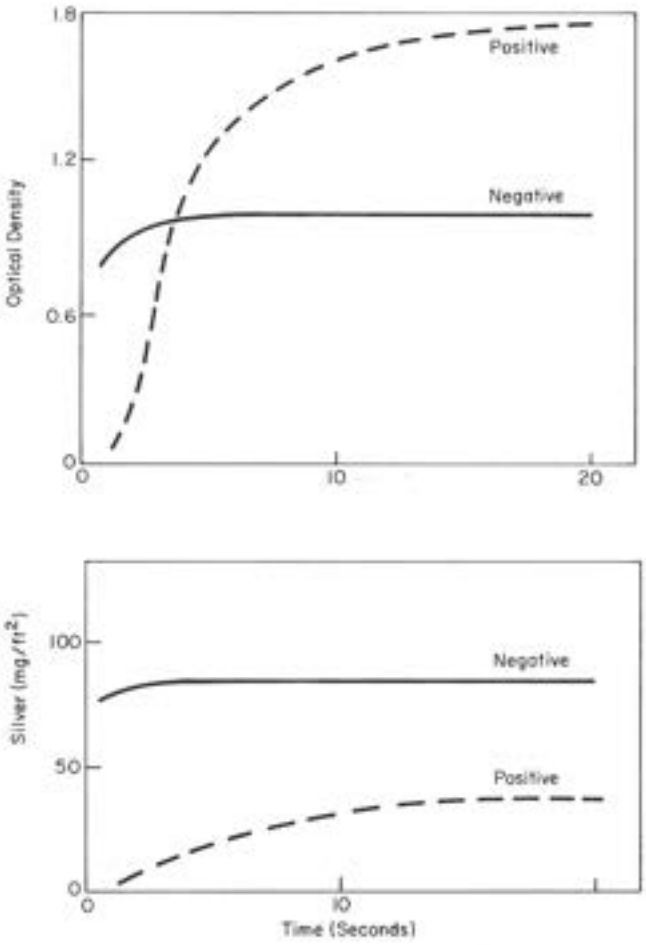


Fig. 12-64. Rates of formation of Type 107 negative and positive image deposits. The upper curves show image growth in terms of optical density, and the lower curves show growth of the same images in terms of the amount of silver developed. Comparing the two dotted lines, on the one hand, and the two solid lines, on the other, note the greater covering power of the positive silver.

Image Formation in the Type 107 Process. The electron micrographs of Fig. 12-63 illustrate the changes which take place in individual silver halide grains as they participate in the formation of negative and positive images in the Type 107 process. The exposed grains show appreciable development after only 1/10 sec and full development within 15 sec; the unexposed grains show considerable etching after 1/10 sec and leave only empty "shells" after 15 sec. The final figure of the series is a micrograph of the central portion of the deposit of positive silver derived from a single Type 107 grain. (See also Fig. 12-73c.)

The rapid deposition of Type 107 negative and positive silver is further illustrated in Fig. 12-64, which shows the rates of formation of negative and positive images of maximum density in terms of both optical density and silver coverage. Each image reaches asymptotic values within 20 sec. Figure 12-65 shows maximum density areas of the positive image at several stages during its growth.

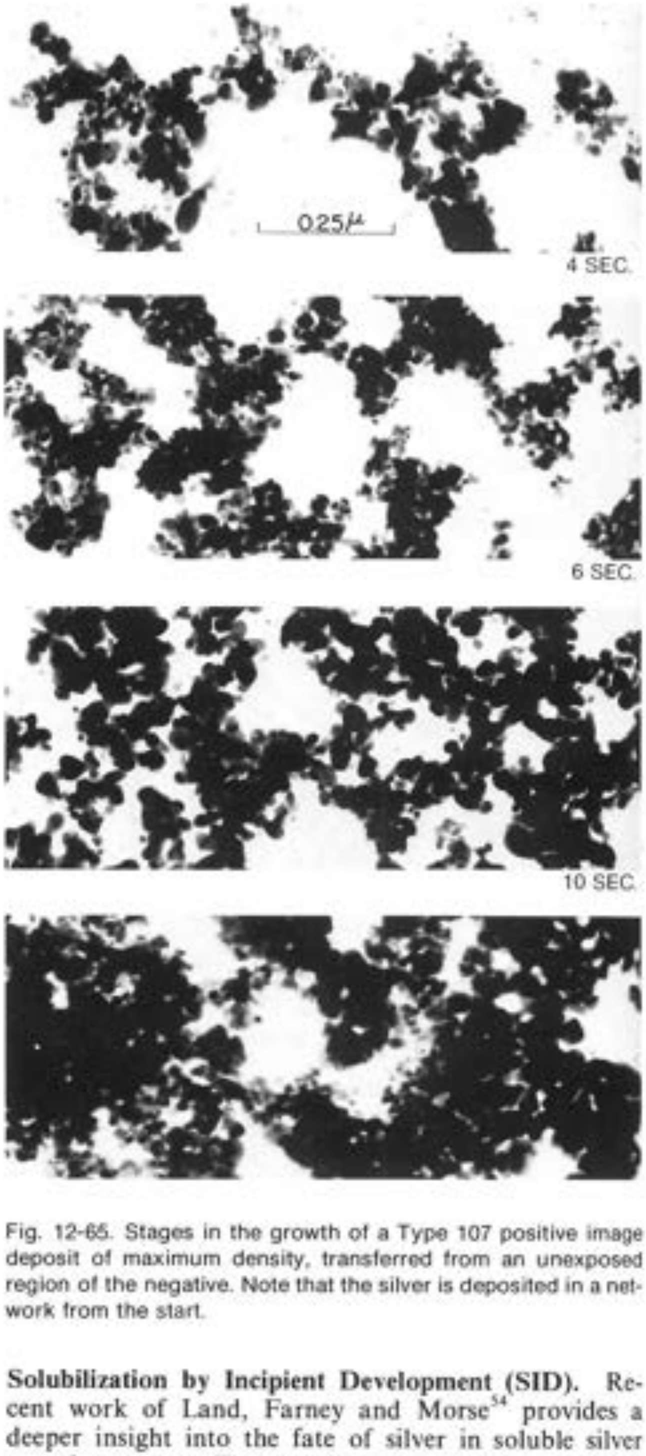


Fig. 12-65. Stages in the growth of a Type 107 positive image deposit of maximum density, transferred from an unexposed region of the negative. Note that the silver is deposited in a network from the start.

Solubilization by Incipient Development (SID). Recent work of Land, Farney and Morse[54] provides a deeper insight into the fate of silver in soluble silver complex systems. They had observed that weak negative images resulting from very low exposures often accompanied the usual positive images of the black and white transfer processes, as shown in Fig. 12-66. Land suggested that the weak negative image could form only if the slightly exposed grains were rendered preferentially soluble during early development.

The phenomenon, designated "Solubilization by Incipient Development," is enhanced by reagents which include both a high solubility (HS) ligand and a low solubility (LS) ligand for silver ion. The HS ligand is