

PHYSICS OF THE PHOTOGRAPHIC LATENT IMAGE

The high sensitivity and efficiency of silver halide film can be traced to mesoscopic metal clusters—small groups of silver atoms subject to quantum size effects and the influence of their immediate environment.

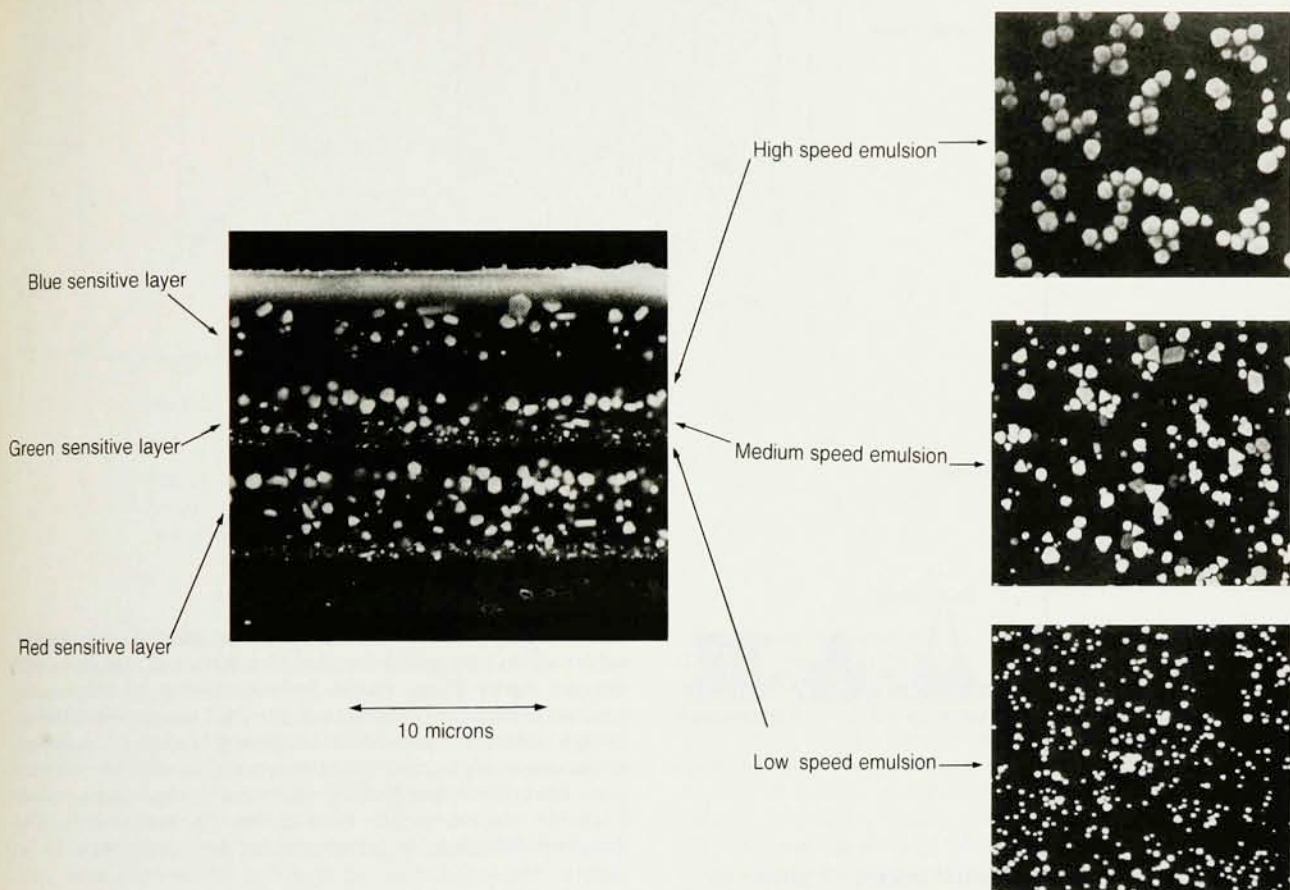
Tadaaki Tani

How does photographic film give such good images with so little exposure to light? The answer, in a word, is amplification. Light causes clusters of silver atoms to form on silver halide microcrystals in a photographic emulsion. These clusters, which may contain as few as three or four silver atoms, catalyze the reduction of *all* the silver ions in the microcrystals to which they are attached, giving a "gain" of over a billion. This is the basis for the high sensitivity and image quality of silver halide photographic film. As I will explain in this article, much is known about the physical mechanisms involved, and by using this knowledge one can improve the sensitivity and efficiency of film.

Role of the latent image

When silver halide microcrystals embedded in an emulsion layer (figure 1) are exposed to light, stable latent image centers form on their surfaces. Photographic developer reduces the silver ions in the microcrystals attached to these centers, forming a visible silver image. A photographic emulsion layer is thus a compact imaging system that senses, stores and displays an image. In an electronic imaging system, by contrast, each of these functions is performed by a separate device—a solid-state array for sensing the image, a magnetic recorder for storing it and a video screen or hard-copy printer for displaying it.

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Scanning electron micrograph of the cross section of a color negative film. Its 19-micron thickness consists of 14 layers with different functions, containing a total of 1.2×10^7 well-designed silver halide microcrystals and more than 100 kinds of organic functional compounds. **Figure 1**

The growth sequence leading to a stable image involves several steps. The first is the formation of a pre-image center consisting of a single silver atom; this center is neither stable nor developable. The next step is the formation of a subimage center, presumably Ag_2 ; this center is stable but not developable. Finally, a latent image center forms consisting of a cluster of four or more silver atoms; this center is both stable and developable.¹ The formation of an Ag_2 subimage center is the threshold for the formation of a latent image and is the basis for the combination of high sensitivity and high stability in silver halide systems. Any stimulation that is not strong enough to cause the formation of a subimage center does not produce fog in an emulsion layer, even if repeated many times.

A single $1\text{-}\mu\text{m}$ photographic grain contains about 20 billion silver ions. If a stable latent image center consisting of a cluster of four metal atoms catalyzes the reduction of the silver ions in the microcrystal during development, then the amplification gain is 5 billion.

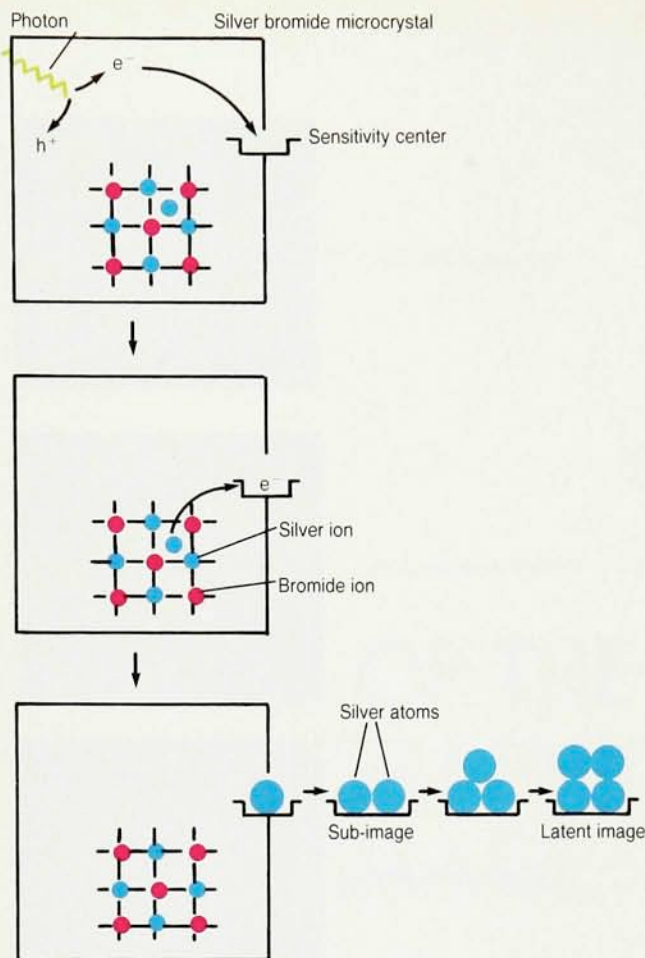
Formation of latent images

Our present understanding of the mechanism of latent image formation is based on a theory advanced in 1938 by Ronald W. Gurney and Nevill F. Mott.² According to the Gurney-Mott theory, light absorption in silver halide produces a photoelectron and a positive hole. The

photoelectron is captured by an electron trap, such as a sensitivity center composed of silver sulfide. The trapped electron combines with a mobile interstitial silver ion to form a silver atom. When the electronic and ionic processes occur repeatedly at the same place, a latent image center forms. Figure 2 illustrates this process schematically.

Knowledge of the physical properties of large silver halide crystals is essential for understanding the mechanism of latent image formation.¹ John W. Mitchell has argued against the Gurney-Mott theory on the basis of these properties, and several important points of Mitchell's theory are included in our present understanding of latent image formation.³ One of these points is the crucial role of crystal defects. Mitchell made a beautiful observation of photolytic silver specks that formed preferentially along dislocation lines. He also pointed out the importance of the mobility of the positive holes, which is high enough to promote recombination with photoelectrons and thus competes with latent image formation. He characterized sensitivity centers as shallow electron traps based on the physical properties of silver sulfide and on the observation that photographic systems do not fog readily.

The framework of the Gurney-Mott theory has been accepted by John F. Hamilton of Eastman Kodak and by other photographic researchers, based on the known



Formation of latent images. A photon (at top) absorbed in silver halide liberates an electron-hole pair. The photoelectron is then captured by a sensitivity center. Finally the trapped electron combines with an interstitial silver ion to form an atom of metallic silver. The accumulation of silver atoms forms the latent image. **Figure 2**

physical properties of silver halide microcrystals.¹ These properties are quite different from those of large crystals, and the differences are essential for the mechanism of latent image formation. One of the most striking demonstrations of the difference between large and small crystals was reported by Hamilton and Lee E. Brady in 1959.⁴ They observed that the concentration of interstitial silver ions in microcrystals is about 100 times higher than it is in large crystals, high enough for the ionic process to compete with the recombination of trapped electrons and positive holes. The analysis of microcrystals has revealed that interstitial silver ions are formed from surface "kink sites"—places where a silver ion is surrounded by only three halide ions, bearing charge $+1/2$ —demonstrating the important role of surface sites for latent image formation.

Although no analytic method has yet succeeded in directly measuring the size of latent image centers, several studies indicate that the smallest latent image center is composed of three or four metal atoms. The most efficient formation of latent images may involve small AgBr microcrystals sensitized with sulfur and gold, and hypersensitized with hydrogen,⁵ which appear to absorb fewer

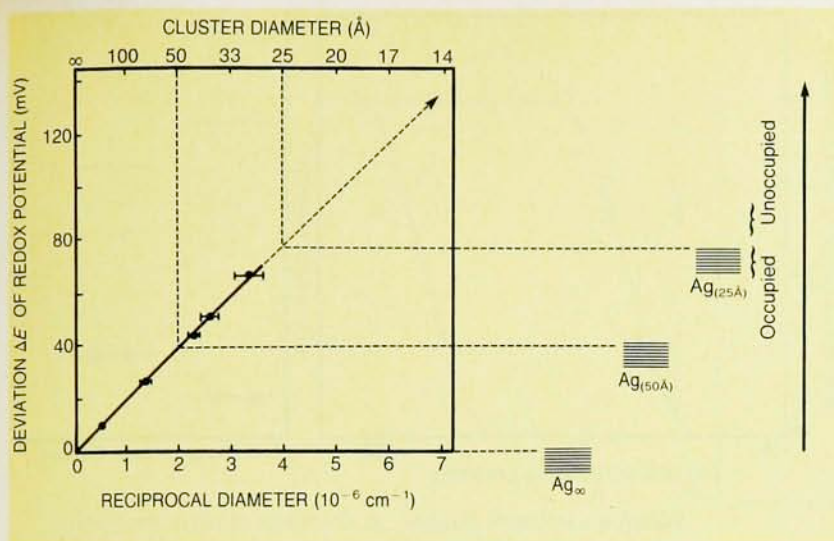
than three photons per grain.⁵ Estimates of the number of silver atoms required for the formation of stable latent images have been made by simulating photographic characteristic curves, and indicate that the smallest latent image center is composed of three metal atoms.⁶ A recent experiment measured the developability of silver cluster ions that were selected by size and deposited on silver bromide microcrystals in a mass spectrometer.⁷ The smallest developable silver cluster ion was found to be Ag_4^+ .

Mesoscopic metal clusters

The oxidation and reduction potentials of silver metal clusters depend on the energy levels of their bonding orbitals, that is, on the highest occupied molecular orbital and the lowest unoccupied molecular orbital. These energy levels have been measured for clusters ranging in size from 25 Å to 200 Å by determining the electrochemical potential that reduces clusters that are larger than a given size while oxidizing clusters smaller than that size.⁸ Such measurements (figure 3) indicate that the energy levels are continuous, and thus the energies of a cluster's highest occupied molecular orbital and lowest unoccupied molecular orbital are nearly the same, differing from the values for bulk silver metal according to their size. This variation with size is known as the Gibbs-Thomson effect.

We should note, however, that image centers are much smaller than the clusters described above. One can use simple models to determine the properties of metal clusters that are as small as image centers.⁹ From consideration of the molecular orbitals of silver clusters (figure 4), one would expect the properties and behavior of image centers to be mesoscopic, and thus quite different from those of the macroscopic metal clusters. The differences include the following:

- ▷ Mesoscopic clusters are not directly observable and detectable by any analytic method.
- ▷ Mesoscopic clusters have discrete electronic energy levels, resembling those of molecules.
- ▷ The energies of the highest occupied molecular orbitals of mesoscopic clusters with an even number of metal atoms increase with cluster size.
- ▷ Mesoscopic clusters show an "even-odd" alternation in



Deviation ΔE of redox potential of silver clusters from that of bulk silver metal, as a function of cluster size. Figure 3

which the energies of a cluster's highest occupied molecular orbital and lowest unoccupied molecular orbital take turns changing as the number of metal atoms in the cluster increases by one, with the energy difference between these two orbitals increasing with cluster size.

▷ Mesoscopic clusters are small enough for their properties and behavior to be influenced by the environments at the sites where they are formed.

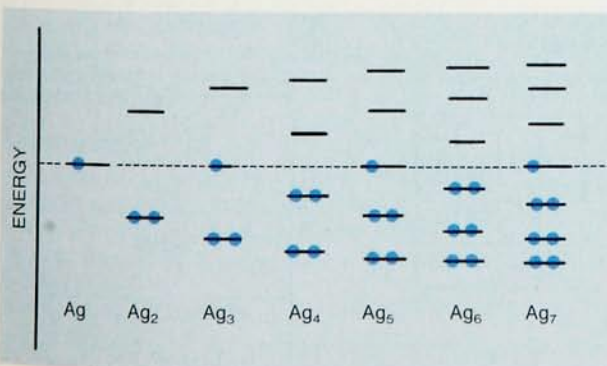
Latent image centers can be reduced electrochemically by a solution whose redox potential is less negative than that of subimage centers. The redox potential of a solution that can reduce image centers is also much more negative than that of a solution that oxidizes image centers. Furthermore, as figure 5a shows, the oxidation potential of subimage centers is less negative than that of latent image centers.¹⁰ As figure 5b shows schematically, experiments indicate that the electronic energy levels of image centers are discrete. The lowest unoccupied molecular orbital of a subimage center is higher than that of a latent image center, and the highest occupied molecular orbital of a subimage center is lower than that of a latent image center. Thus the electronic structure of image centers is mesoscopic and corresponds not to that of clusters described by the Gibbs-Thomson effect (figure 3) but to that of clusters showing a quantum size effect (figure 4).

Among the recent advances in our understanding of

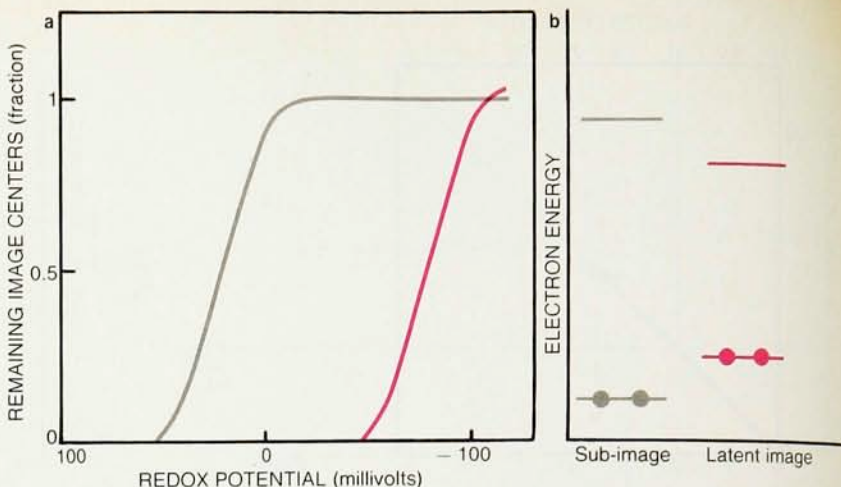
latent image centers is the clarification of the peculiar site dependences of the behavior of Ag_2 dimer clusters. At one type of site, known as a P center, a photolytically formed Ag_2 subimage center can capture a photoelectron to grow to a latent image center during exposure to light. At another type of site, known as an R center, an Ag_2 dimer cluster is formed by reduction sensitization (the weak reduction of silver halide microcrystals) and destroyed by reaction with a positive hole during exposure to light.¹¹ The existence of these two configurations of dimers was detected by measurement of the photoconductivity and photographic sensitivity of silver halide microcrystals.¹²

The proposed idea that a P center forms at a positively charged site, whereas an R center forms at a neutral site, has been supported by several investigations.^{13,14} The rate of reduction of R centers by negatively charged developing agents is small and increases with the adsorption of positively charged dyes by the microcrystals; the rate of reduction of P centers is large and is not influenced by the positively charged dyes.¹³ Molecular orbital calculations for model systems composed of Ag_2 dimer clusters at positively charged and neutral kink sites on the silver bromide lattice (figure 6) support this hypothesis.¹⁴

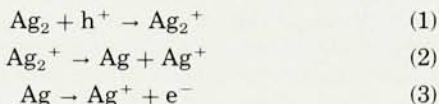
Wesley G. Lowe at Eastman Kodak proposed that the reaction of an Ag_2 R center with a positive hole (h^+) proceeds as follows, taking into account that Ag_2^+ and Ag are unstable:¹⁵



Molecular orbitals of linear silver clusters. Figure 4



Stabilities vs latent images. **a:** Stabilities of latent images (red curve) and subimages (gray) formed on sulfur-sensitized octahedral AgBr grains ($0.7 \mu\text{m}$ across) in aqueous buffer solutions, as a function of redox potential. **b:** Schematic representation of the electronic energy level of the image centers. Subimages were revealed by gold latensification prior to development. Latensification enhances the developability of imaging centers by treating them with a solution of gold (I) thiocyanate. **Figure 5**



Lowe's hypothesis suggests that one photon absorbed by a silver halide microcrystal can produce two free electrons in the presence of R centers. It was found recently that sensitizing dyes capable of trapping positive holes can delay phenomena associated with those holes, enabling the processes to be observed.¹⁶ Lowe's hypothesis has been tested by observing the increase in photographic speed due to the formation of a free electron through processes 1–3, and also by measuring the efficiency of latent image formation.¹⁷ The number of absorbed photons per grain required to render half the grains developable is the usual measure of efficiency of latent image formation. Richard K. Hailstone and his coworkers have reported values for various kinds of grains (figure 7).¹⁸ They showed that hydrogen-hypersensitized small grains can be rendered developable by less than three absorbed photons per grain, under the condition that the smallest latent image center is composed of three metal atoms. This indicates that an absorbed photon produces more than one electron, supporting Lowe's hypothesis.

The mesoscopic properties of image centers as metal clusters are the basis for the performance of the silver

halide photographic system. According to the considerations described above, the total energy E_T of the mesoscopic metal clusters is the sum of the energies contributed from the Gibbs–Thomson effect (E_{GT} ; figure 3), the quantum size effect (ΔU_Q ; figure 4) and the site effect (ΔU_S ; figure 6):

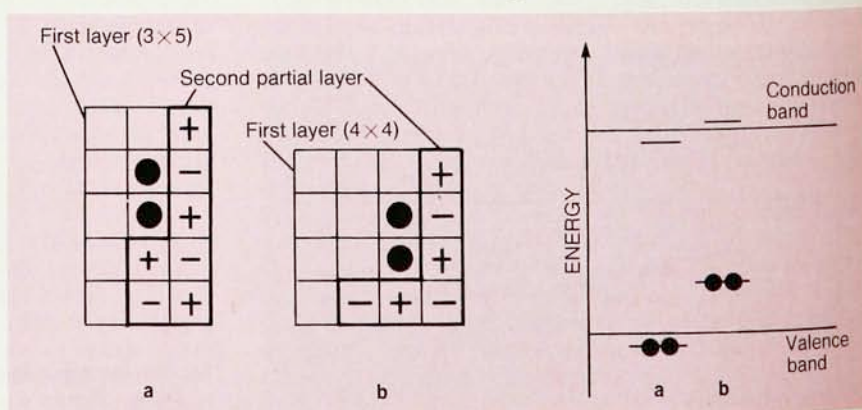
$$E_T = E_{GT} + \Delta U_Q + \Delta U_S$$

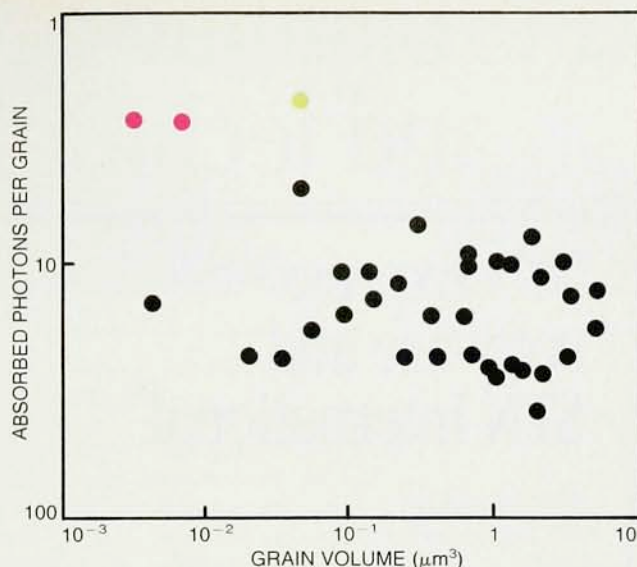
Future study

According to our present understanding of the photographic process, there remain several inefficiencies that could be reduced to achieve higher photosensitivity.¹⁹ Optical absorption is low,²⁰ and in particular, the efficiency of latent image formation is considerably lower than its ultimate limit. Hence, accurate and quantitative knowledge of the mechanism of latent image formation is indispensable in seeking ways to improve the sensitivity of the photographic process.

A key issue is the study of image centers as mesoscopic metal clusters, because the mesoscopic properties are fundamental to the photosensitivity of the silver halide system. This viewpoint is rather new, and calls for direct measurement of the sizes and properties of image centers. Use of a mass spectrometer to analyze the developability of size-selected mesoscopic cluster ions is a new approach

Models of Ag_2 dimer clusters on a positive kink site (a) and on a neutral site (b) of $(\text{AgBr})_{11}$. Corresponding energy levels are indicated at right. (Adapted from ref. 14.) **Figure 6**





Average number of absorbed photons per grain required to render half the existing grains developable for various kinds of grains, as a function of grain volume. For hydrogen-hypersensitized grains, values of less than three photons per grain were reported by Thomas A. Babcock and Thomas H. James⁵ (red) and by Richard K. Hailstone and coworkers (green). **Figure 7**

that permits study of the role of these clusters in the formation of latent images.⁷ It is reasonable to expect that the new scanning microscopy techniques such as scanning tunneling microscopy, scanning atomic force microscopy and scanning optical microscopy will allow direct observation of image centers. As to investigating the site dependence of the properties and behavior of mesoscopic clusters, one might be able to use techniques associated with molecular-beam epitaxy to construct crystal sites for the study of latent image formation on an atom-by-atom basis.

The physical properties of silver halide microcrystals need further clarification as well. Modulation spectroscopy has been used to determine the depths and numbers of sensitivity centers on microcrystalline surfaces.²¹ A microwave photoconductivity technique is being used to study the behavior of photoelectrons on a nanosecond time scale in microcrystals.²² And picosecond spectroscopy was used recently to study the transfer of electrons to microcrystals from sensitizing dyes in the excited state^{23,24}; this spectroscopy should be able to detect rapid processes associated with photoelectrons and positive holes in microcrystals.

State-of-the-art high-speed photographic film uses about one-third of the incident light²⁰ and forms latent images with a quantum efficiency of about $\frac{1}{5}$, as judged from the values for larger grains in figure 7. However, as this figure indicates, an efficiency of nearly unity has been achieved experimentally for smaller grains. Increasing film speed by a factor of 10 through improved light absorption and more efficient latent image formation in larger grains appears to be an appropriate target for the near future.

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