Silver Clusters of Photographic Interest VIII: Electron Microscopic Observation and Analysis of Ag Clusters Formed on AgBr Grains by Light and Reduction

Tomoki Tasaka, Masako Murofushi, and Tadaaki Tani▲*

Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., Minami-Ashigara, Kanagawa, Japan

An electron microscopic method was applied to the quantitative analysis of silver clusters formed on fine cubic AgBr grains by light and reduction. The observation of only one light cluster, i.e., one latent image center, per grain and many reduction clusters per grain indicated a difference in the mechanism of cluster formation, i.e., the presence and absence of the concentration principle, respectively. We concluded that the quantum yield for the photochemical formation of clusters could be unity if positive holes were prevented from reacting with growing clusters. This was consistent with reported quantum yields for print-out silver on the basis of chemical analysis, and therefore proved the applicability of the present method for the quantitative analysis. It was also found that the formation of reduction clusters on treatment of AgBr grains with DMAB occurred nearly quantitatively. The analysis of size distribution of reduction clusters gave additional support for the proposal that DMAB formed dimers of silver atoms, which were stabilized to act as reduction sensitization centers at surface kink sites, but which aggregated to form large clusters when their amount was larger than that for the saturation of the kink sites.

Journal of Imaging Science and Technology 47: 463-470 (2003)

Introduction

In photographic processes, Ag clusters play many important roles such as latent image centers, reduction sensitization centers, and fog centers.[1,2] Latent image centers are formed on silver halide grains by light as a result of the photolysis of the grains, and initiate photographic development. Reduction sensitization centers, which are composed of dimers of Ag atoms and formed on the grains by reduction, increase photographic sensitivity without initiating photographic development. It has been revealed that there are two kinds of reduction sensitization centers; a P center acting as an electron trap and an R center acting as a positive hole trap.[3-5] It is thought that a P center consists of an Ag dimer formed at a positive kink site, and that an R center is an Ag dimer formed at a neutral kink site. Fog centers are also formed on the grains by reduction, and are large enough to initiate photographic development.

On the basis of the result of the studies on latent image centers from various aspects, it was estimated that the smallest latent image center was composed of three atoms on sulfur-plus-gold-sensitized grains and 4-5 atoms on sulfur-only sensitized grains.[6-16] Although the knowledge of the size of latent image centers that were actually formed at various parts of a characteristic curve have been scarce, it is generally recognized that their sizes should be too small to be measured by an electron microscope.

Many investigators tried to measure the number of these Ag clusters by the arrested development technique.[1,2] The procedure of this technique, as applied to latent image centers, is as follows: namely, latent image centers are formed on silver halide grains by light, and enlarged by arrested development to such an extent that the enlarged centers can be observed by a transmission electron microscope. It is however uncertain if all the latent image centers can be enlarged by this technique. This technique cannot give the real size of latent image centers. Carbon replica samples are often prepared for this technique by sputtering carbon on the grains. However, the light emitted from heated carbon is intense enough to bring about the photolysis of the grains to form Ag clusters, and to make the subsequent observations uncertain.

In this article, an attempt was made to directly observe Ag clusters on AgBr grains by the following procedure. In the first place, light, i.e., photochemically generated, clusters, and reduction, i.e., chemically produced clusters, were formed on AgBr grains in an emulsion. Secondly, the gelatinate shell technique[17-20] was used to directly observe those centers in an electron microscope, and to obtain their number, size and location on the grains. Preparation of the specimen could be carried out under a safe light. Although the smallest observable cluster was around 15 Å in diameter and contained about 100 atoms, the obtained results indicated that most latent image centers actually formed at the shoulder and plateau of the characteristic curves of

Original manuscript received January 23, 2003

▲ IS&T Honorary Member

fine AgBr grains were larger than 15 Å, and provided unique and quantitative information for the formation of Ag clusters with the knowledge of their number, size, and location on the grains.

Experiments

The emulsions used were composed of cubic AgBr grains and prepared by a controlled double jet method,[21,22] according to which aqueous solutions of 1N $AgNO_3$ and 1N KBr were simultaneously poured into the reaction solution under the condition that the concentration of silver ions in the solution was kept constant. The edge length of the resulting grains was 0.2 μm on average. In order to minimize the formation of reduction sensitization centers during precipitation of the grains,[23] the pH of an initial reaction solution was adjusted to 2. After precipitation, removal of KNO_3, and addition of gelatin, the pH and pAg of the emulsion were adjusted to 6.5 and 8.8, respectively. Reduction sensitization was carried out by digesting an emulsion for 60 minutes at 60°C in the presence of dimethylamineboran (DMAB). The emulsions thus prepared were coated on a cellulose triacetate film base with 110 μg/cm^2 of AgBr and 380 μg/cm^2 of gelatin.

Each film strip was exposed to a Xe lamp or halogen lamp through a neutral density filter and a bandpass filter made by Schott Glas (Mainz, Germany), which transmitted light with a central wavelength of 420 nm and halfwidth of 10 nm. Exposed films were developed by use of a surface developer MAA-1[24] for 10 minutes at 20°C, fixed, washed and dried. The optical density of each developed film was measured by use of a Fuji Densitometer. Photographic sensitivity was represented by the reciprocal of the exposure which gave the optical density of 0.1 above fog. The number of photons incident to a film was measured by use of an EG&G GAMMA SCIENTIFIC Model DR-2550 radiometer/photometer. The number of silver halide grains per unit area of a film was estimated on the bases of the amount and average volume of the grains as given by X-ray fluorescence and electron microscope measurements, respectively.

Latent image centers and fog centers formed on AgBr grains were directly observed by the gelatinate shell technique as described in the literature.[17-20] Silver halide grains with a thin gelatin layer on the surface were isolated, put on a mesh for their observation by an electron microscope, and fixed for 4 seconds in a solution prepared by diluting a Super Fuji Fix 20 times with water.

Latent image centers and fog centers were observed in an electron micrograph of gelatinate shells at a magnification of 50,000x by means of a transmission electron microscope, JOEL model 2000FX with 100 keV accelerating voltage. The number of Ag atoms in a center was calculated on the assumption that each center was a spherical Ag crystal. This assumption could be supported by the fact that electron microscopically observed centers, which should be randomly oriented in gelatinate shells after the fixation of AgBr grains, looked like circles. As shown in the next section, additional support was given by the comparison of the estimated numbers of Ag atoms with those reported in the literature.

Results and Discussions

Observation of Latent Image Centers

As already shown in the former studies of this series,[3–5] photographic sensitivity increased with increasing the amount of DMAB used for reduction sensitization, and fog appeared when the amount of DMAB exceeded 7 μmol/molAg. The emulsions with DMAB of 0 and 7 μmol/mol AgBr were used as unsensitized and reduction sensitized samples, respectively. Their characteristic curves are shown in Fig. 1. Unsensitized and reduction sensitized emulsion layers were exposed to the light of 420 nm for 100 and 10 seconds, respectively. The samples for the observation of latent image centers are indicated in Fig. 1. The electron micrographs of the gelatinate shells of Samples **c** and **f** are shown in Fig. 2.

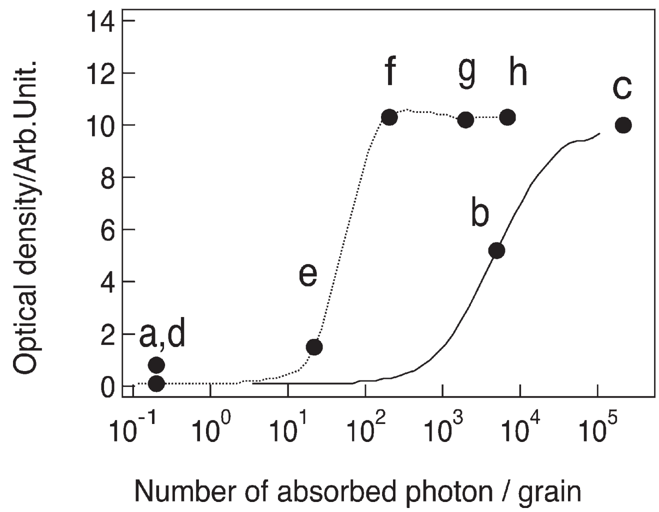

Figure 1. Characteristic curves of unsensitized and reduction sensitized emulsions are represented by those with points **a~c** and **d~h**, respectively. Each curve represents the optical density of a developed emulsion layer as a function of the number of absorbed photons per grain.

Neither unexposed grains nor exposed grains at the middle points of characteristic curves exhibited any latent image centers in the electron micrographs of their gelatinate shells. On the other hand, latent image centers formed at the shoulder and plateau of their characteristic curves were large enough to be observable by an electron microscope. Only one latent image center was observed on each grain in both unsensitized and reduction sensitized emulsions regardless of exposure intensity when they were exposed for 10 sec. This observation was in good accord with that with the arrested development technique by Spencer et al.[25] Although they could not get any quantum yield information on silver cluster formation by their technique, they found that the number of observed latent image centers per grain in a reduction sensitized AgBr emulsion increased with exposure time ranging from 1 center at 30 sec to 3 centers at 10^4 sec.

The size distribution of observed latent image centers is shown in Fig. 3. The average number of absorbed photons per grain, fraction of grains bearing latent image centers and average number of Ag atoms per latent image center are summarized in Table I. The smallest latent image center, which could be observed in the present study, was 15 Å in diameter and was therefore composed of about 100 Ag atoms. It is generally accepted that the smallest latent image center, which can be detected by development, is composed of 4 – 5 Ag atoms. Although latent image centers observed in this study were much larger than the smallest latent image cen-

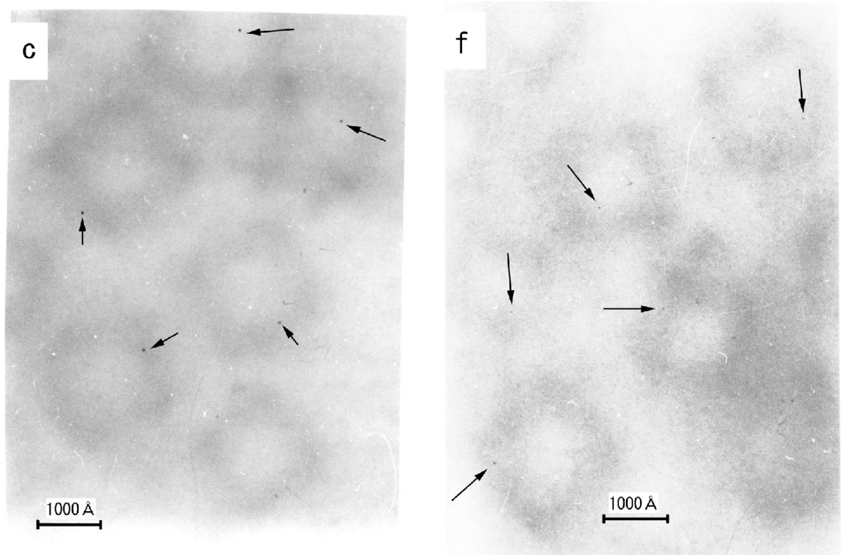

Figure 2. Electron micrographs of gelatinate shells of the grains in Sample **c** of an unsensitized emulsion and in Sample **f** of a reduction sensitized one. Latent image centers in gelatinate shells are indicated by arrows.

ter as detectable by development, it should be stressed that they were actually formed on AgBr grains at the shoulder and plateau.

Figure 4 shows the average number of Ag atoms in a latent image center on a grain as a function of the average number of absorbed photons per grain. A straight line in this figure indicates the condition that the average number of Ag atoms in a latent image center is equal to the average number of absorbed photons per grain, i.e., the condition where the quantum yield for the formation of latent image centers is unity. As seen in this figure, the quantum yield of the formation of latent image centers in an unsensitized emulsion was very low. On the other hand, it was judged that the quantum yield of the formation of latent image centers in terms of the ratio of the observed number of Ag atoms per grain to the number of absorbed photons per grain could be unity under the condition that positive holes and photolytic bromine were effectively eliminated. It is known that the quantum yield of the formation of print-out silver could be unity under the condition that photolytic halogen was eliminated.[2] Thus, we might expect that the ratio of observed number of Ag atoms per grain to number of absorbed photons might approach unity if positive holes and photolytic bromine were effectively eliminated. These results and considerations indicate that the method proposed in this study is suitable for quantitative analysis of electron microscopically observable Ag clusters on AgBr grains.

Analysis of Size of Latent Image Centers

The result described in the previous section indicated that latent image centers formed at the shoulders of the characteristic curves of unsensitized and reduction sensitized emulsions were much larger than the smallest latent image center. Accordingly, it should be effective to analyze the quantum yield of the formation of latent image centers by dividing its process into two primary processes; nucleation, i.e. the formation of the smallest latent image center, and growth.

In the first place, the quantum yield of the formation of the smallest latent image center (η_N) in unsensitized and reduction sensitized emulsions were previously measured as 0.0009 and 0.032, respectively, according to a conventional method.[3–5] Then, the actual size of latent image centers was measured and compared with those estimated under the assumptions that the quantum yield of the growth process (η_G) was equal to η_N, and that η_G was equal to unity.

TABLE I. Average Number of Absorbed Photons ($N_{h\nu}$) per Grain, Fraction of Grains on which Latent Image Centers were Observed (η), and Average Number of Ag Atoms (N_{Ag}) per Grain.

Sample	$N_{h\nu}$/ grain	η/grain	N_{Ag} / grain
C	220000	0.83	1600
E	210	0.69	520
F	2000	0.99	1800
G	6900	0.99	1100

The result for Sample **c** of an unsensitized emulsion in Fig. 1 is shown in Fig. 5. The observed size of latent image centers was much smaller than the size estimated under the assumption that η_G was equal to unity, while the observed size was larger than the size estimated under the assumption that η_G was equal to η_N. The results for Samples **f**, **g**, and **h** in a reduction sensitized emulsion in Fig. 1 are also shown with in Fig. 5. The observed size of latent image centers was nearly equal to the size estimated under the assumption that η_G was equal to unity in Sample **f** and in Sample **g**, whose exposure was 10 times larger than that of Sample **f**. In Sample **h**, whose exposure was 33 times larger than that of Sample **f**, the observed size of latent image centers was smaller than that of the centers in Sample **g**, and was between the sizes estimated under the assumption that the values of η_G were equal to η_N and unity, respectively.

The results of all the experiments indicated that η_G was larger than η_N. We infer that a latent image center, once it is formed, acts as a strong concentration center, effectively collecting photoelectrons and an interstitial

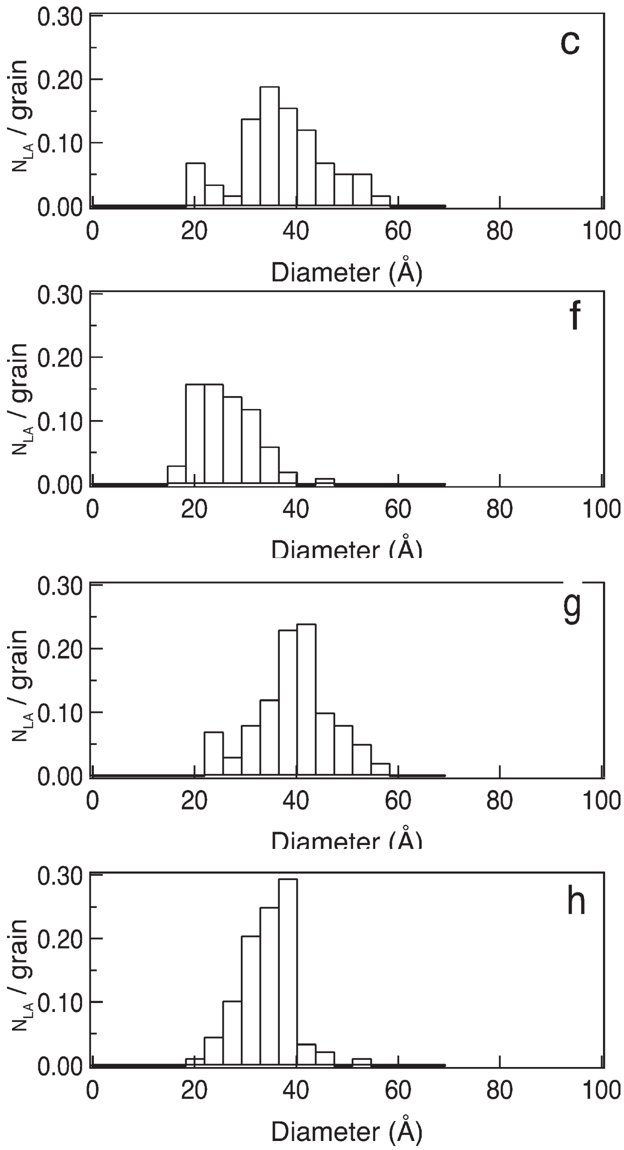

Figure 3. Size distribution of latent image centers in Samples **c**, **f**, **g**, and **h** in terms of number of latent image centers (N_{LA}) per grain as a function of their size.

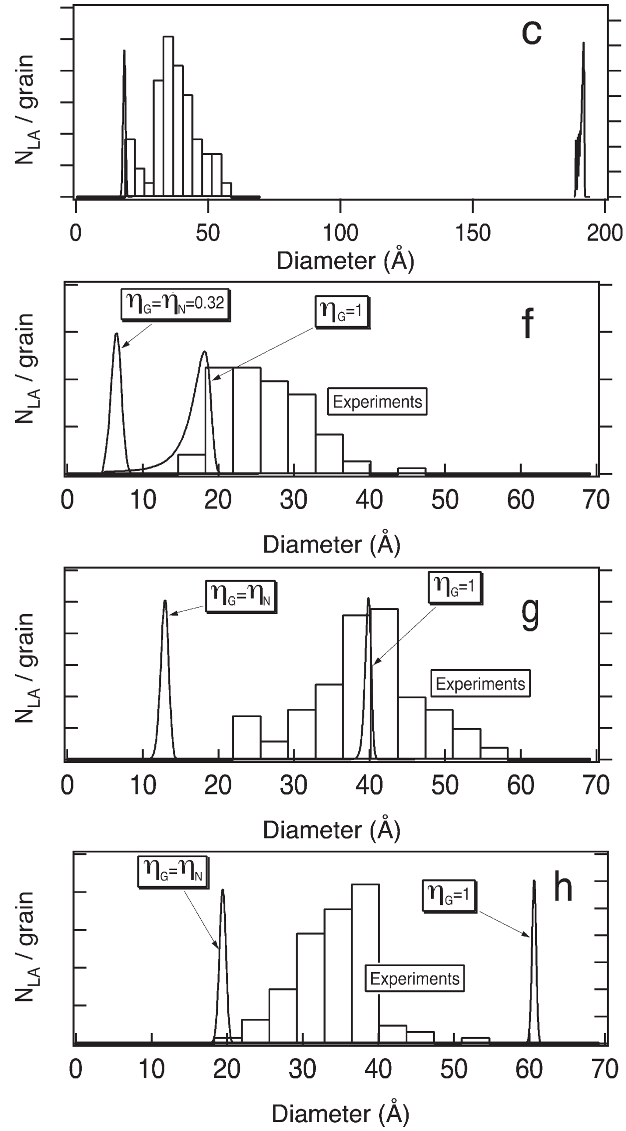

Figure 5. Comparison of simulated size distribution of latent image centers with observations in Samples **c**, **f**, **g**, and **h** of Fig. 1. Observed distributions were reproduced from Fig. 3. Simulations were made under the conditions: (a) that the quantum yield of the growth (η_G) was equal to the quantum yield of the nucleation (η_N); and (b) that η_G was equal to unity.

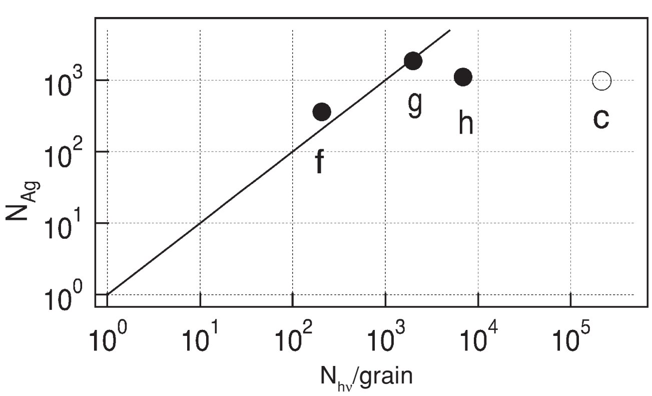

Figure 4. Relation between number of observed Ag atoms (N_{Ag}) and number of absorbed photons ($N_{h\nu}$) per grain in Samples **c**, **f**, **g**, and **h** of Fig. 3. On the solid line, N_{Ag} and $N_{h\nu}$were the same, corresponding to the condition that the quantum yield of the latent image formation was unity.

silver ions by turns to grow. In the unsensitized emulsion, η_G was lower than unity owing to the recombination of photoelectrons with positive holes and to the rehalogenation of formed latent image centers. In the reduction sensitized emulsion, a latent image center acting as a strong concentration center could grow under the condition that the recombination and rehalogenation was prevented by reduction sensitization centers, and began to suffer from the recombination and rehalogenation when reduction sensitization centers were exhausted. This idea was supported by the following observation. Namely, the number of reduction sensitization centers on a grain is 1500 – 1600, calculated on the assumption that each DMAB molecule provided six electrons[26,27] to form three Ag_2 reduction sensitization centers. It was confirmed that the average numbers of absorbed photons per grain in Samples

TABLE II. Sites where Fog Centers were Formed, Average Number of Fog Centers (N_{fog}) per Grain, Observed Numbers of Ag Atoms (N_{Ag}) in a Fog Center and in an Emulsion Grain, and N_{Ag} in an Emulsion as Calculated from Added Amount of DMAB.

	Sites	N_{fog}/grain	N_{Ag}/fog center	Observed N_{Ag}/grain	Calculated N_{Ag}/grain
C	Corners	9	1200	11000	7200
D	Corners and edges	31	600	19000	29000
E	Corners and edges	80	1300	100000	120000
F	Corners and edges	170	3300	550000	460000

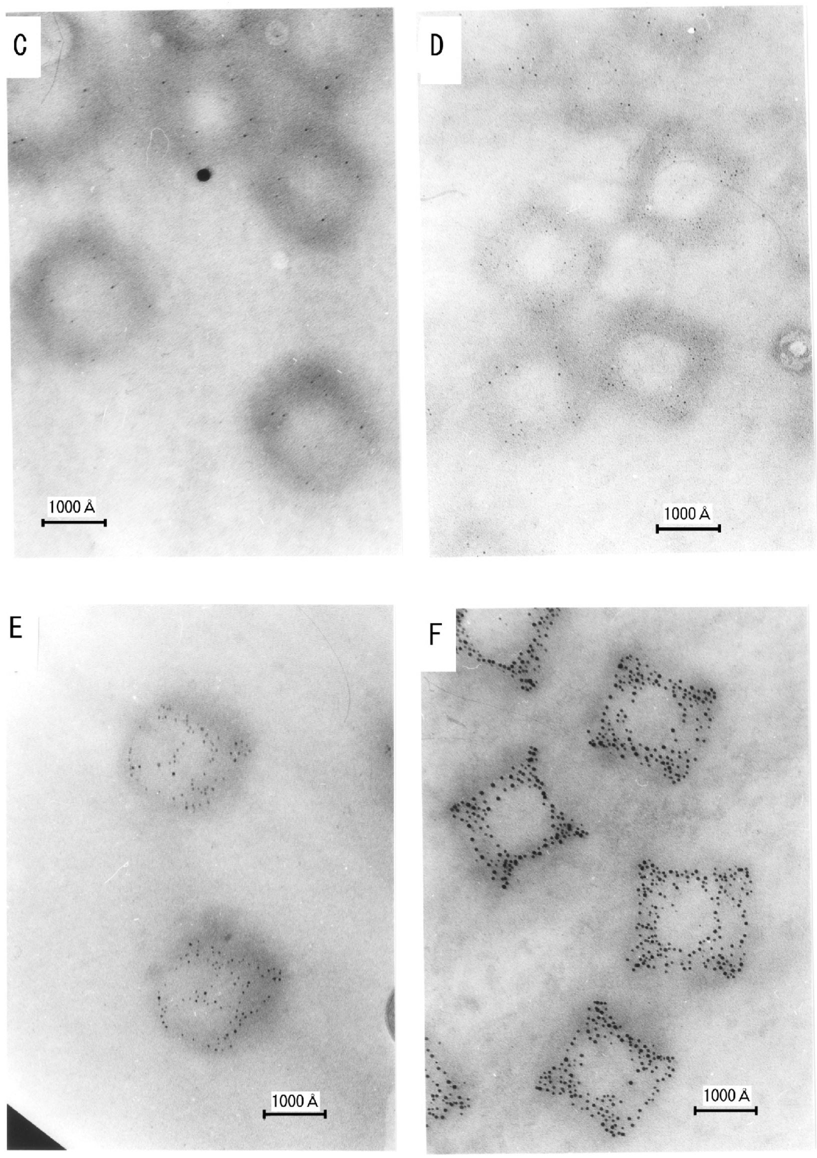

Figure 6. Electron micrographs of gelatinate shells of emulsion grains in emulsions, which were digested at 60°C for 60 min in the presence of DMAB of 41 (**C**), 166 (**D**), 663 (**E**), and 2650 μmol/mol AgBr (**F**).

f and **g**, but not Sample **h** were smaller than or compared to the estimated number of reduction sensitization centers (see Table I).

As seen in Fig. 5, the observed size distribution of latent image centers was wider than the one calculated under the assumption that the size distribution resulted solely from the distribution of absorbed photons among grains. It is however quite probable that there were other kinds of causes for the size distribution among grains. They should include the distributions of the grain size, η_N, and η_G. Especially, the condition that η_G was always larger than η_N should widen the distribution of the size of latent image centers among grains.

Observation of Fog Centers

A cubic AgBr emulsion was reduced by a reducing agent (DMAB) at concentrations of 0 (**A**), 10.5 (**B**), 41 (**C**), 166 (**D**), 663 (**E**), and 2650 μmol/mol AgBr (**F**). While Samples **A** and **B** were scarcely fogged, all the grains

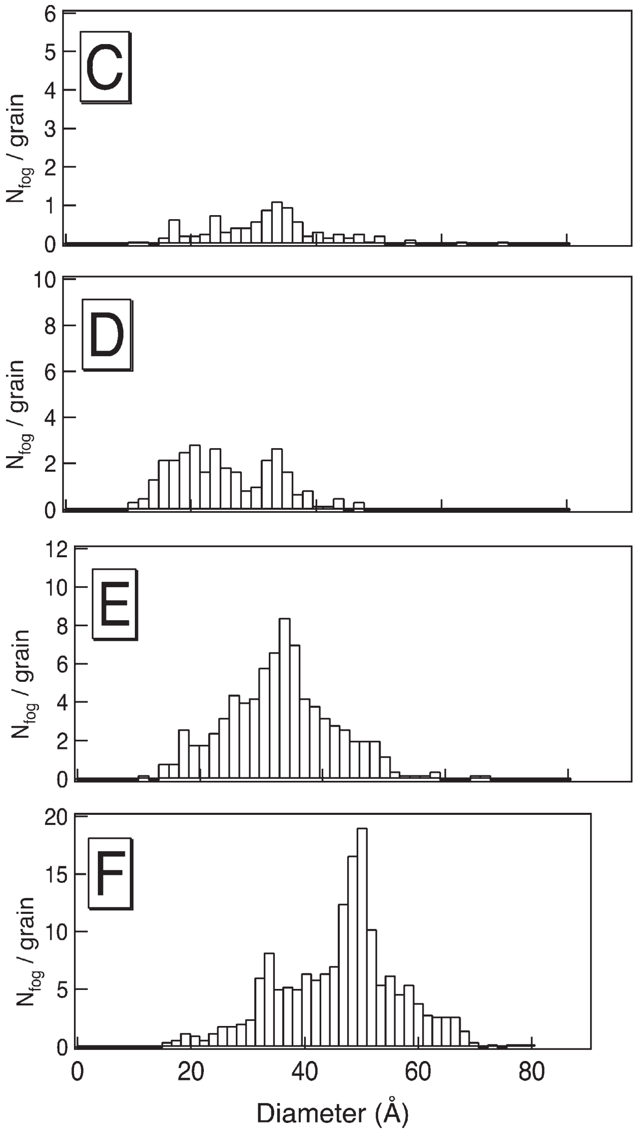

Figure 7. Size distribution of fog centers in Samples **C**, **D**, **E**, and **F** in terms of number of fog centers (N_{fog}) per grain as a function of their size.

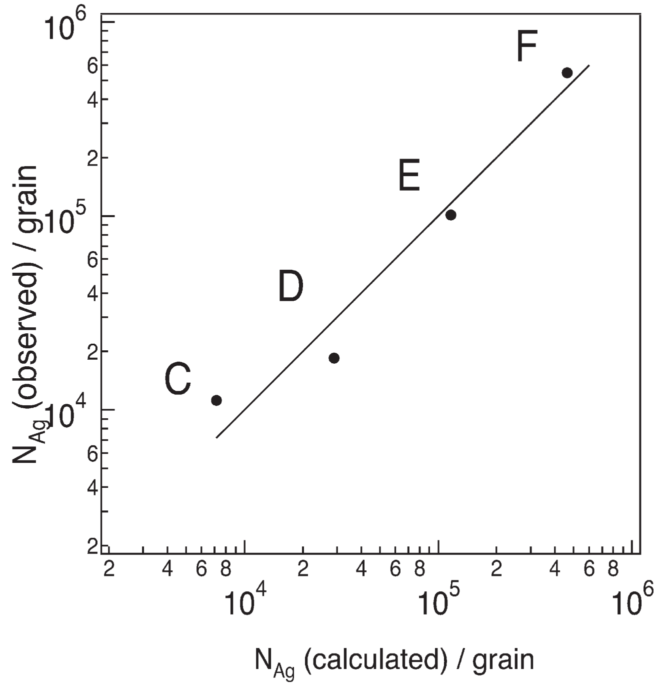

Figure 8. Relation between observed and calculated numbers of observed Ag atoms (N_{Ag}) per grain in Samples **C**, **D**, **E**, and **F** of Figs. 6 and 7. Observed N_{Ag} was estimated from the sizes of the fog centers, and the calculated value was based on the assumption that each DMAB molecule reduced six silver ions.[26,27] The solid line corresponds to the case where observed N_{Ag} was equal to the calculated value, indicating the condition that formation of fog centers was quantitative.

in Samples **C**, **D**, **E** and **F** had fog centers on the surface. Fog centers could be observed in the electron micrograph of the gelatinate shells of the grains, as shown in Fig. 6. As shown in Table II, the number and size of the fog centers increased with increasing quantity of DMAB used as the reduction sensitizer. On the other hand, reduction sensitization centers, i.e., R centers and P centers, could not be observed in the gelatinate shells. Fog centers started to appear at the corners of cubic grains and were then distributed along the edges with increasing the amount of DMAB. Few fog centers were observed on the main surfaces of the grains. The size distribution and average number of fog centers per grain are shown in Fig. 7. The number of Ag atoms in the observed fog centers on a grain was determined and compared with that theoretically determined under the assumption that each DMAB molecule reduced six silver ions[26,27] in Fig. 8. As seen in this figure, the observed numbers were nearly equal to the calculated ones. It appears that formation of reduction clusters on treatment of AgBr grains with DMAB occurred nearly quantitatively.

Simulation of Growth of Fog Centers as a Result of Aggregation of Ag Atoms

As described in the previous section, Sample **C** contained many observable Ag clusters in contrast to Sample **B**, in which hardly any observable centers were present. However, many reduction sensitization centers composed of Ag_2 should exist on the surface of the grains in Sample **B**. This abrupt change in the growth of Ag clusters was analyzed on the basis of alternative models: (a) continuous aggregation; and (b) and aggregation above a threshold.

According to model (a), DMAB brings about instantaneous formation of silver atoms, which move and collide randomly with each other to contribute to the nucleation and growth of Ag clusters. Fraction of Ag cluster of size i, C(i,τ), is represented by Smoluchowski's equation.[28,29]

$$c(i,\tau) = \frac{\tau^{i-1}}{(1+\tau)^{i+1}} \tag{1}$$

where τ characterizes the size distribution of clusters and represents (total number of Ag atoms) × (rate of aggregation) × (time). Namely, × depends solely on the added amount of DMAB, since all the emulsions were ripened at 60°C for 60 minutes, and therefore the reaction time and rate of aggregation were the same among all the emulsions.

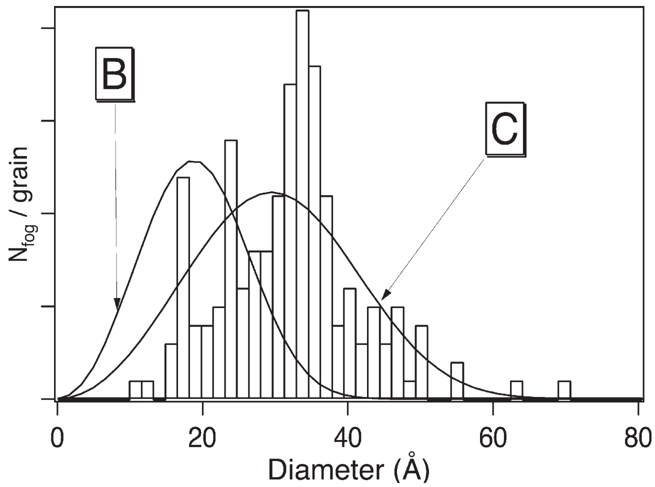

Figure 9. Comparison of simulated size distributions of fog centers with observations on Samples **B** and **C** from Figs. 6 and 7. Observed distributions are represented by histograms, reproduced from Fig. 7, while there were no observable fog centers in Sample **B**. Simulated distributions were based on Smoluchowski's Equation[28,29] with the assumption that fog centers were created by the aggregation of Ag atoms. The simulated distribution for Sample **C** was the result of the best fit of the Equation to the observed data by adjusting the parameters. The simulated distribution for Sample **B** was then obtained using the parameters adopted for Sample **C**.

The value of τ under the present experimental condition was determined by fitting equation (1) to the size distribution of Ag clusters in Sample **C**, and was then used to estimate the size distribution of Ag clusters in Sample **B**. The result is shown in Fig. 9. As seen in this figure, the result of the simulation on the basis of model (a) indicated that almost all the Ag clusters in sample **B** should be large enough to initiate development as fog centers, and that many of them should be larger than 15 Å in size and therefore observable by an electron microscope.

However, the result of the simulation carried out on model (a) was evidently different from the experimental results, insofar as fog density was fairly low, and no Ag cluster was observed in an electron micrograph of the gelatinate shell of each grain in sample **B**. This result therefore indicated that the formation of Ag clusters on AgBr grains was due, not to the model (a), but to model (b). It is known that a cluster composed of more than four Ag atoms has ability to initiate development, and that a dimer of Ag atoms has already a very stable electronic structure. It is therefore thought that a threshold exists between a dimer and larger clusters. Namely, only dimers of Ag atoms were formed and stabilized at kink sites on the surface of AgBr gains in Sample **B**, and Ag dimers aggregated to form large clusters after kink sites were saturated with Ag dimers in Sample **C**.

Discussion on the Formation of Reduction Sensitization Centers

As stated above, the analysis with electron microscopy could be quantitatively applied to the formation of Ag clusters, i.e. fog centers, by reduction. Many clusters were formed on a grain by reduction on the contrary to the fact that only one cluster, i.e., a latent image center, was formed by light on a grain owing to operation of the concentration principle.[1,2] Namely, the formation of reduction clusters does not obey the concentration principle. On cubic emulsion grains, reduction nanoclusters appeared at their corners and then along their edges with increasing quantity of a reduction sensitizer. This implies the existence of sites where Ag clusters could be stabilized. The number and size of observable reduction clusters increased with increasing quantity of a reducing agent.

The results of the simulation of the aggregation of Ag atoms (above) and former studies[3–5] revealed the existence of a threshold in the growth process of the reduction clusters of Ag atoms. According to the shell model in cluster science,[30] Ag_2 is the smallest Ag cluster with stable electronic structure although the smallest Ag cluster, which can initiate development, is Ag_4 or Ag_5. Mitchell has emphasized that Ag_2 is stable and should play important roles in the photographic process.[31,32] It was also demonstrated in a former study of this series[33] that reduction nanoclusters were diamagnetic owing to their composition of even number of Ag atoms per cluster, while many photogenerated nanoclusters were paramagnetic owing to their composition of odd number of Ag atoms per cluster. These results indicated that the reduction of AgBr grains directly formed only Ag dimers, which were stabilized at neutral and positive kink sits to act as R and P types of reduction sensitization centers, respectively, and aggregated to form reduction nanoclusters when the number of Ag dimers exceeded the number of the kink sites. This condition brought about the formation of many clusters on a single grain, which were diamagnetic. It should be noted that neither free electron nor single Ag atom take part in the formation of the reduction clusters on AgBr grains.

Proposed Method to Quantify Ag Clusters Formed on AgX Grains

The present study proposes a method to characterize Ag clusters formed on silver halide grains by electron microscopic observation and analysis of the clusters in the gelatinate shells of the grains. The method proved to be suitable for the quantitative analysis of the number of Ag atoms in clusters larger than 15 Å, and useful to obtain unique information regarding number, size, and location of latent image centers and fog centers on fine AgBr grains. Most latent image centers formed at the shoulder and plateau of the characteristic curves of the grains were larger than 15 Å. The proposed method was applied to the measurement of the numbers of light clusters and reduction ones on a grain, the determination of the quantum yield of the formation of those clusters, and the analysis of the growth process of the reduction clusters, to support the mechanism of formation of reduction sensitization centers.

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