JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 46, Number 3, May/June 2002

Observation and Characterization of Sulfur Sensitization Centers Formed on Octahedral Silver Bromide Grains

Hiroyuki Mifune, Masafumi Mizuno, Yoshiaki Toyama, Takekimi Shiozawa, and Jun Okuda

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

We observed sulfur sensitization centers, which were formed on octahedral silver bromide grains in emulsions and decorated with silver clusters by means of an amplification treatment with a special physical developer. The concentration of the centers increased with increasing the amount of the sensitizer, and reached a plateau with the amount that gave the maximum sensitivity. The concentration of the centers, which gave the maximum sensitivity, was as many as 3200 per µm^2, and the same as the concentration of fog centers formed with excessive amount of the sensitizer. The comparison of the concentration of the observed centers with the amount of silver sulfide formed by sulfur sensitization revealed that each sulfur sensitization center contained two sulfide ions in the emulsion with the maximum sensitivity. This result supported the idea that the sulfur sensitization centers were dimers of silver sulfide, as proposed by Keevert and Gokhale,[1] Kanzaki and Tadakuma,[2] and Tani.[3]

Journal of Imaging Science and Technology 46: 262–269 (2002)

Introduction

Sulfur sensitization is indispensable for silver halide photographic materials. It was proposed that sulfur sensitization centers were aggregates of silver sulfide and formed by the processes of adsorption of a sulfur sensitizer on the surface of silver halide grains, formation of silver sulfide, and rearrangement (aggregation) of formed silver sulfide.[4] Keevert and Gokhale[1] estimated the concentration of sulfur sensitization centers on the grain surface by analyzing the rearrangement process of silver sulfide in light of Smoluchowski's aggregation equation, and proposed that sulfur sensitization centers were composed of dimers of silver sulfide, which were as many as 1000 centers per µm^2 on the surface of cubic silver chlorobromide grains. Kanzaki and Tadakuma[2] studied the formation of sulfur sensitization centers by means of luminescence-modulation spectroscopy, and proposed that sulfur sensitization centers were composed of dimers of silver sulfide. Tadakuma, Yoshida and Kanzaki[5] estimated that there were 2800 centers per µm^2 on the surface of cubic silver bromide grains. Tani[3] proposed that sulfur sensitization centers were composed of dimers of substitutional sulfide ions on the surfaces of silver halide grains, and fog centers were nanoclusters of silver sulfide.

Many investigators have tried to observe directly sulfur sensitization centers formed on the surfaces of silver halide grains by electron microscopy. For example, Aznarez[6] observed silver sulfide centers with an average size of 2 nm, and Farnell, Flint and Birch[7] observed those with average size of 3 nm. In the light of the results of the recent studies, however, we consider that the centers which they observed were fog centers composed of silver sulfide nanoclusters formed on the surfaces of silver halide grains with excessive sulfur sensitization treatment. Tani[8] observed 2400 nano-clusters per µm^2 on octahedral silver bromide grains in excessively sulfur sensitized emulsions, and ascribed them to fog centers.

We recognize that it has been very difficult to observe sulfur sensitization centers directly, insofar as they may be as small as dimers of substitutional sulfide ions on the surfaces of silver halide grains. In this study, we successfully visualize the centers by decorating them with silver clusters by means of an amplification treatment using a special physical developer.

Experimental

An emulsion containing octahedral silver bromide grains with average equivalent circular diameter of 0.2 µm was used in this study. The emulsion was prepared by a controlled double jet method with simultaneous addition of aqueous 1 M solutions of silver nitrate and potassium bromide for 60 min to an aqueous gelatin solution with pH and pAg of 2.0 and 8.3, respectively. The emulsion contained 63 g of silver bromide/kg and 70 g of gelatin/kg. The pH and pAg of the emulsion were adjusted to 6.5 and 8.9, respectively. Sulfur sensitization was carried out by digesting this emulsion in the presence of sodium thiosulfate pentahydrate as sensitizer for 60 min at 60°C.

The primitive and sulfur sensitized silver bromide emulsions were coated on cellulose triacetate (TAC) film base to give film samples with silver bromide of coating weight 2.1 g/m^2 and gelatin coating weight of 6 g/m^2. Each film sample was exposed for 10 sec to a tungsten lamp of color temperature 2856 K through a continuous

Original manuscript received August 20, 2001

wedge, and developed for 10 min at 20°C by use of MAA-1 surface developer. The optical density of a developed film sample was measured on a Fuji Densitometer made by Fuji Photo Film Co., Ltd., and its sensitivity was given as the reciprocal of exposure to give optical density of 0.2 above fog.

Photoconductivity with electrons as carriers in the silver bromide grains of each film sample was measured at −100°C by means of a 9 GHz microwave photoconductivity apparatus,[9] and given by the maximum signal intensity. The light source was a light pulse at 355 nm, which was the third harmonic of a pulsed Nd:YAG laser, model DCR-11 made by Spectra Physics Corporation.

Sodium thiosulfate with radioactive ^{35}S was used for the estimation of the amount of silver sulfide formed on the emulsion grains by the radio isotope method.[10] A 500 µL aliquot of the sensitized emulsion was dispensed into 10 mL of 0.1 M aqueous potassium bromide solution, which was then centrifuged to separate the emulsion grains from the liquid phase. The grains were washed three times with 10 mL of 0.1 M aqueous potassium bromide solution in order to eliminate unreacted thiosulfate ions from the grains. Then, the radioactivity of silver sulfide formed on the grains was measured busing a Tri-Carb® Liquid Scintillation Analyzer Model 1000 made by Packard Instrument Corporation.

Sulfur sensitization centers on the emulsion grains were amplified by Solutions A and B, whose formulations were as follows.

Solution A	sodium sulfite	180 g
	silver nitrate	10 g
	water	1000 mL
Solution B	sodium sulfite	20 g
	Compound-1	20 g
	water	1000 mL

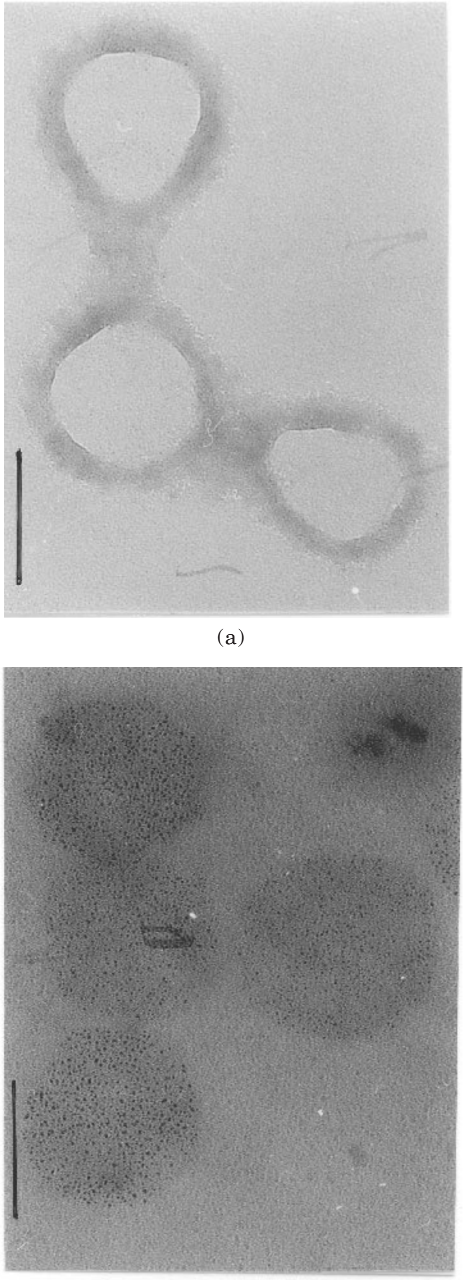
Compound-1 was 4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate, which was prepared by Wako Pure Chemical Industries, Ltd. The mixture of these solutions constituted a physical developer, similar to that prescribed by James, Vanselow and Quirk.[11] Normally, Solutions A and B were diluted 10,000-fold with water before use. An 0.1 g melted emulsion sample was added to the mixture of a diluted Solution A (25 mL) and diluted Solution B (5 mL). The mixed solution was stirred, normally for 6 hrs, at room temperature in the dark. A 5 µL sample was set on a Ni mesh, which had been covered with collodion and carbon membranes, and dried. Silver bromide grains on the mesh were fixed for 5 ~ 10 sec at room temperature by Solution C, whose formulation was as follows.

Solution C	0.25 M lithium thiosulfate (aq.)	125 mL
	sodium sulfite	0.3 g
	glacial acetic acid	0.5 mL
	potassium alum	0.6 g

Gelatinate shells of the silver bromide grains were then observed in a transmission electron microscope model JEM-1200 made by JEOL Ltd., Tokyo.

Results

Amplification Treatment with a Special Physical Developer to Observe Sulfur Sensitization Centers


(a)

(b)

Figure 1. Electron micrographs of gelatinate shells of octahedral silver bromide grains in the emulsion, which was sulfur sensitized with 16 µmol/molAgBr sodium thiosulfate, and treated without (a) and with (b) the amplification treatment. For Fig. 1(b) the emulsion was mixed for 6 hrs with Solutions A and B, which had been diluted 10,000-fold with water. The length of the bars in this figure indicate 0.2 µm.

Figure 1(a) shows an electron micrograph of gelatinate shells of octahedral silver bromide grains in an emulsion without any amplification treatment. The emulsion was sulfur sensitized with 16 µmol/molAgBr sodium thiosulfate. No center was observed in any gelatinate shell. Figure 1(b) shows an electron micrograph of gelatinate shells of the same grains, that were subjected to the amplification treatment by the procedure using Solutions A and B as described above. Many fine centers were observed in each gelatinate shell.

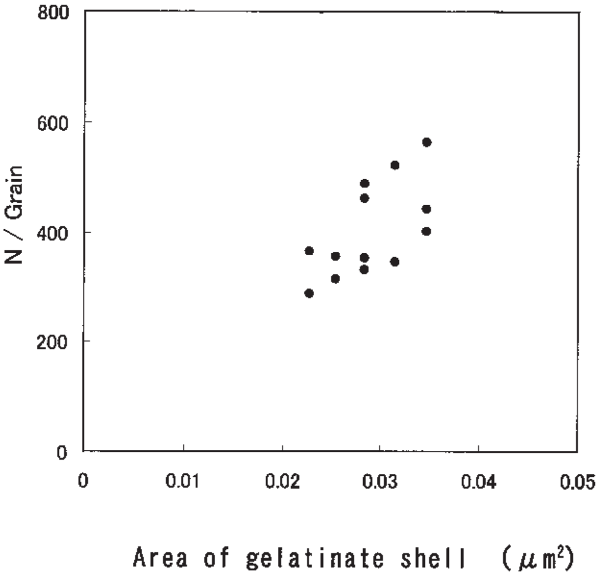


Figure 2. The number (N) of observed centers per grain as a function of area of gelatinate shell for the grains shown in Fig. 1(b).

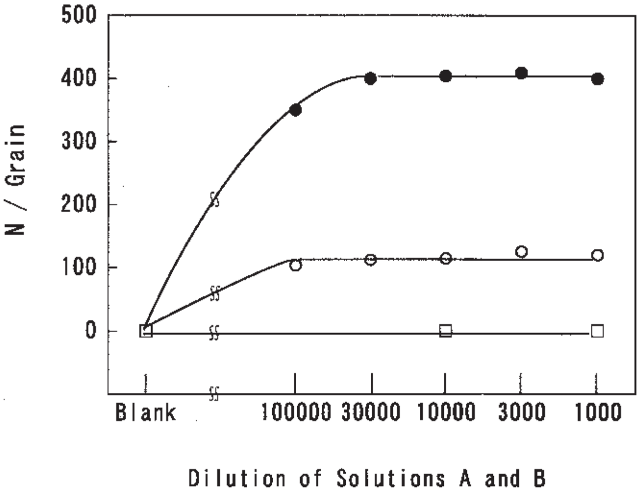


Figure 3. The average number (N) of the observed centers per grain as a function of the degree of the dilution of Solutions A and B with water, for the grains in emulsions sensitized with 0 (□), 2 (○) and 16 (●) μmol/molAgBr sodium thiosulfate, respectively. Each emulsion was stirred with the diluted solution for 6 hrs.

Figure 2 shows the proportionality of the number of the observed centers per grain to the projective area of the gelatinate shell for the grains shown in Fig. 1(b). On the assumption that the projective area of a gelatinate shell of a grain was equivalent to that of the grain itself, the result indicated that the number of the observed centers per grain was proportional to the surface area of the grain. On the average, 409 centers per grain were observed.

Figure 3 shows the number of the observed centers per grain in the emulsions sensitized with 0, 2 and 16 μmol/molAgBr sodium thiosulfate as a function of the degree of the dilution of Solutions A and B used for the amplification treatment. It was difficult to observe the centers on the sensitized grains clearly when they were treated with the solutions of dilution of more than 100,000-fold. It was also difficult to reproducibly observe the centers on the grains, which were treated with solutions with dilution less than 1000-fold, since many dirty spots appeared unavoidably, even in the gelatinate shells of primitive grains. On the other hand, we could clearly observe the centers on the sensitized grains that were treated with solutions of dilutions of 30,000, 10,000, 3,000 and 1,000-fold, while we could not observe any center on the primitive grains. The average number of the observed centers per grain was the same among these dilutions.

Figure 4 shows the number of the centers per grain observed in the sensitized emulsion in Fig. 1(b) as a function of the reaction time between the grains and the solutions with the dilution of 10,000 fold. The number of the observed centers per grain was the same among the emulsions digested for 4, 6 and 8 hrs. In this study, the emulsions were normally treated for 6 hrs by Solutions A and B with 10,000 fold dilution. The reproducibility of the observation of the centers relied upon the silver bromide fixation process, insofar as those centers were composed of minute silver clusters which were liable to be dissolved upon prolonged fixation. It was found that reproducibility was satisfactory with Solution C however.

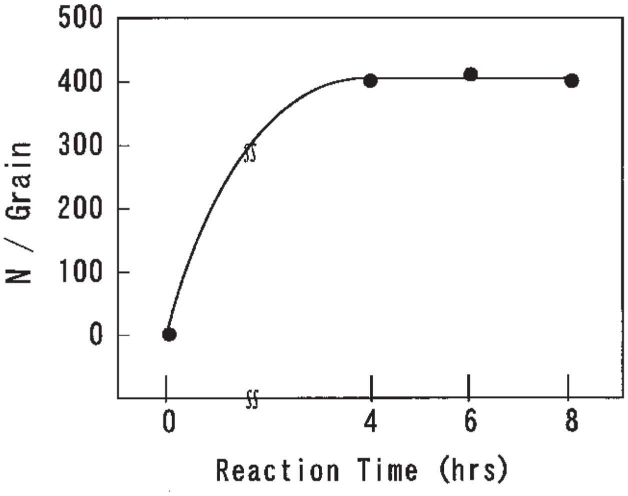


Figure 4. The average number (N) of the observed centers per grain as a function of the reaction time of the amplification treatment for the grains shown in Fig. 1(b). Solutions A and B were diluted 10,000-fold with water.

Sulfur Sensitization Centers Formed on Octahedral Silver Bromide Grains

Figure 5(a) shows photographic sensitivity and fog density of octahedral silver bromide grains as a function of the amount of sodium thiosulfate used as a sensitizer. The sensitivity increased with increasing the amount of the sensitizer and reached its maximum with the sensitizer of about 16 μmol/molAgBr. Fog appeared with the sensitizer of more than 2 mmol/molAgBr.

Figure 5(b) shows photoconductivity of the grains as expressed by the peak height of their microwave photoconductivity signals. The decrease in photoconductivity and the increase in sensitivity took place in a parallel

TABLE I. Photographic Sensitivity, Fog Density, Number of Observed Centers and Sulfide Ions per Center With and Without the Amplification Treatment

			With amplification treatment			Without amplification treatment		
$Na_2S_2O_3{\bullet}5H_2O$ (μmol/molAgBr)	Photographic Sensitivity Δlog S	Fog Density	Observed Centers (μm^2)	Observed Centers (grain)	Sulfide Ions per Center	Observed Centers (μm^2)	Observed Centers (grain)	Sulfide Ions per Center
0	0	0.02	0	0	0	0	0	0
0.25	0	0.02	0	0	0			
1	0.1	0.02	420 ± 120	53	1.4			
2	0.2	0.02	910 ± 160	114	1.3			
4	0.3	0.02	1300 ± 300	163	1.7			
8	0.6	0.02	1700 ± 500	215	2.6			
16	0.95	0.02	3300 ± 700	409	2.7	0	0	0
32	1.0	0.02	3200 ± 400	398	5.6			
64	1.0	0.02	3000 ± 600	376	12			
130	1.0	0.02	3200 ± 400	400	23	0	0	0
260	0.95	0.02				0	0	0
510	0.9	0.02	3000 ± 300	374	95			
1000	0.6	0.02						
2000	0.7	0.06	3100 ± 500	388	370	3400 ± 700	420	340
4100	0.5	1.4				3100 ± 300	393	740
8200	—	2.4	3000 ± 300	374	1500	3200 ± 400	402	1400

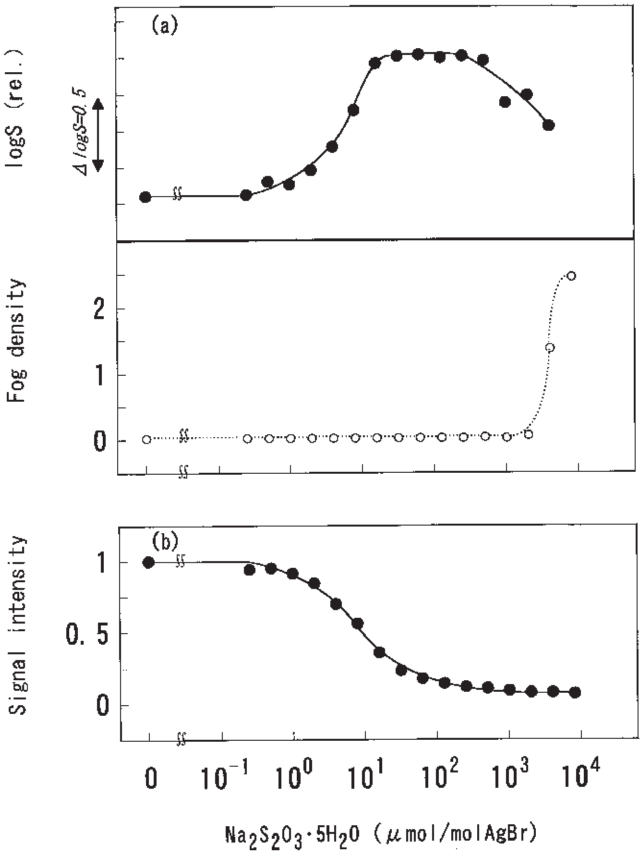


Figure 5. Photographic sensitivity (S), fog density (a), and photoconductivity (b) of octahedral silver bromide emulsions as a function of the amount of sodium thiosulfate used for sulfur sensitization.

fashion on increasing the amount of sensitizer, indicating formation of sulfur sensitization centers which capture photoelectrons to enhance latent image formation.

Figure 6 shows electron micrographs of gelatinate shells of the grains, which were sensitized with sodium thiosulfate levels of 0, 16, 130, 2000 and 8200 μmol/molAgBr, and were not subjected to any amplification treatment. While we could not observe any center in the gelatinate shells of the grains in emulsions sensitized with sodium thiosulfate levels of 0, 16, and 130 μmol/molAgBr, we could observe 400 and 380 centers per grain in the emulsions sensitized with sodium thiosulfate levels of 2000 and 8200 μmol/molAgBr, respectively, and ascribed them to fog centers.

Figure 7 shows the electron micrographs of the gelatinate shells of the grains in emulsions, which were sensitized with sodium thiosulfate levels of 0, 2, 4, 16, 32, 130, and 2000 μmol/molAgBr and subjected to the amplification treatment. The average numbers of the observed centers per grain were 0, 114, 163, 409, 398, 400 and 388, respectively.

Figure 8 summarizes the effect of the amplification treatment on the relation between the average number of centers per μm^2 and the amount of the sulfur sensitizer. The average concentration of the centers observed by means of the amplification treatment increased with increasing amount of sensitizer, and reached a plateau with 3200 centers per μm^2 at the amount of sensitizer which gave maximum sensitivity. The average concentration of centers at the plateau was the same as the average concentration of the fog centers formed with excessive amount of the sensitizer. These results are also shown in Table I. We obtained the same results as those shown in Fig. 8 and Table I, regardless of the degree of the dilution of Solutions A and B and the processing time of the amplification treatment. As seen in Figs. 6 and 7, both the centers observed with and without the amplification treatment were uniformly distributed on the surface of octahedral silver bromide grains.

As shown in Fig. 9, we found from the study using the radioisotope method[10] that 80% of the sodium thiosulfate was decomposed to form silver sulfide in emulsions when they were digested for 60 min at 60°C. On the

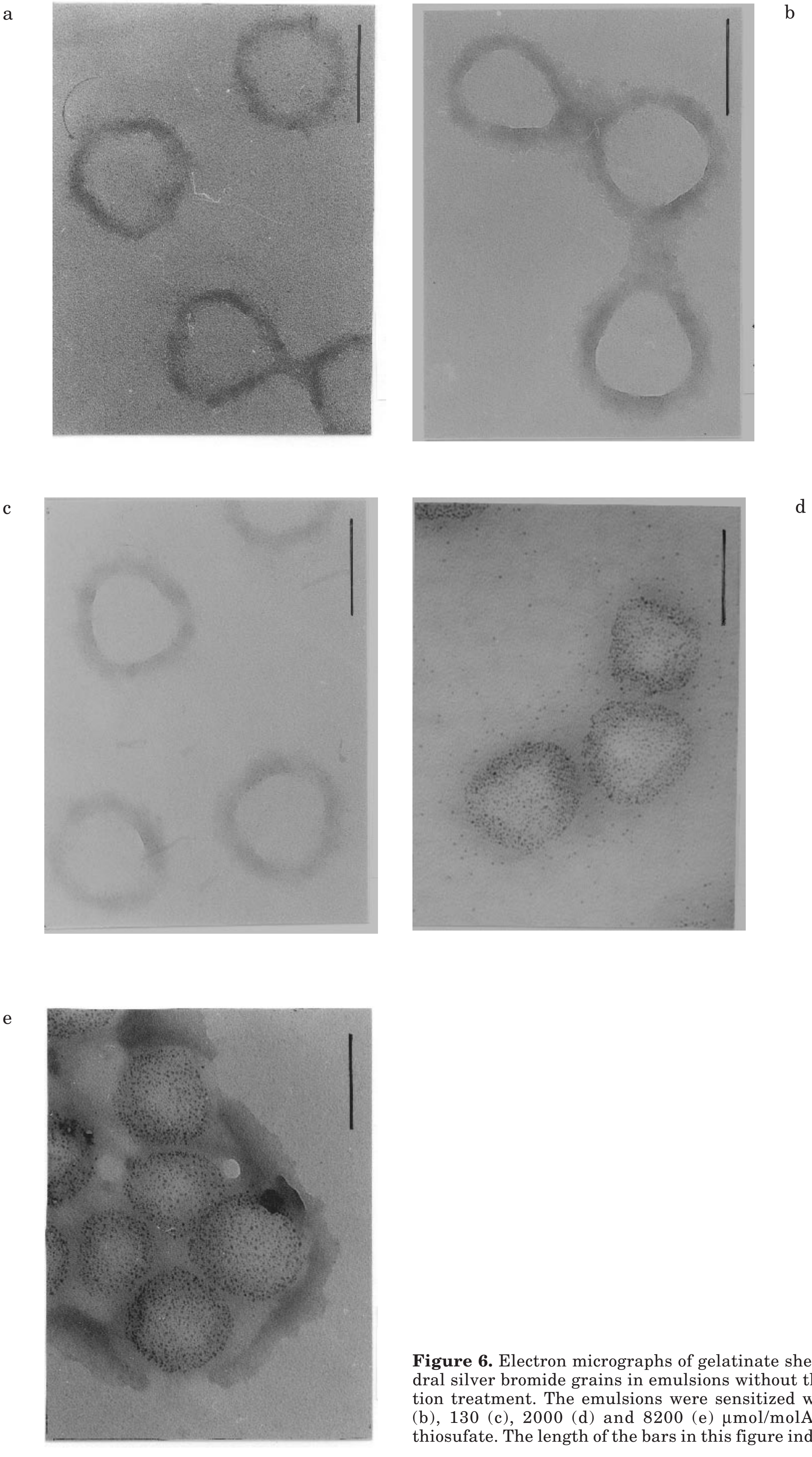


Figure 6. Electron micrographs of gelatinate shells of octahedral silver bromide grains in emulsions without the amplification treatment. The emulsions were sensitized with 0 (a), 16 (b), 130 (c), 2000 (d) and 8200 (e) μmol/molAgBr sodium thiosufate. The length of the bars in this figure indicate 0.2 μm.

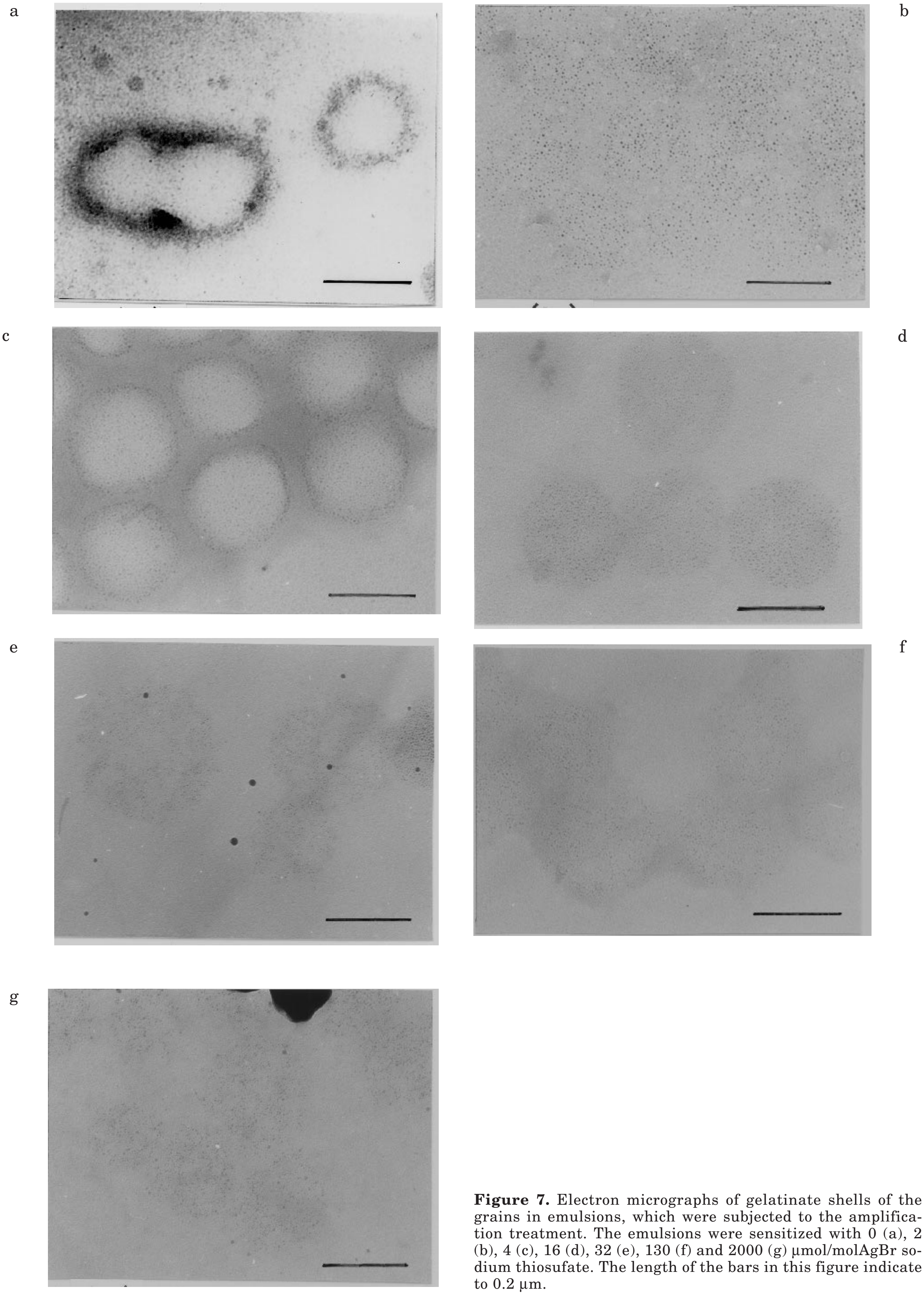


Figure 7. Electron micrographs of gelatinate shells of the grains in emulsions, which were subjected to the amplification treatment. The emulsions were sensitized with 0 (a), 2 (b), 4 (c), 16 (d), 32 (e), 130 (f) and 2000 (g) μmol/molAgBr sodium thiosufate. The length of the bars in this figure indicate to 0.2 μm.

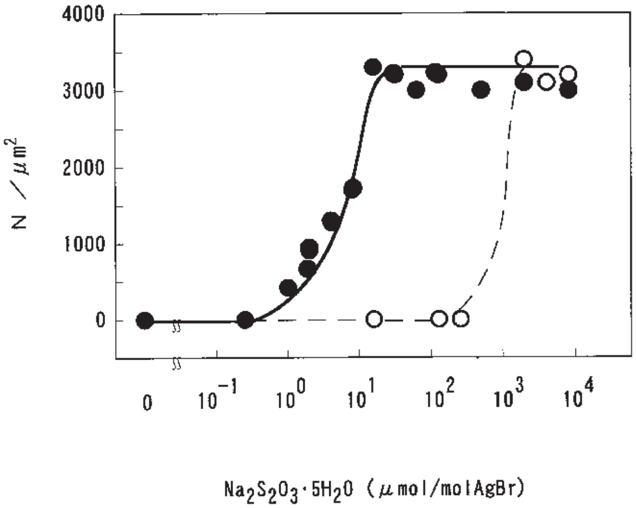


Figure 8. The average number (N) of the centers per μm² observed with (●) and without (○) the amplification treatment as a function of the amount of sodium thiosulfate.

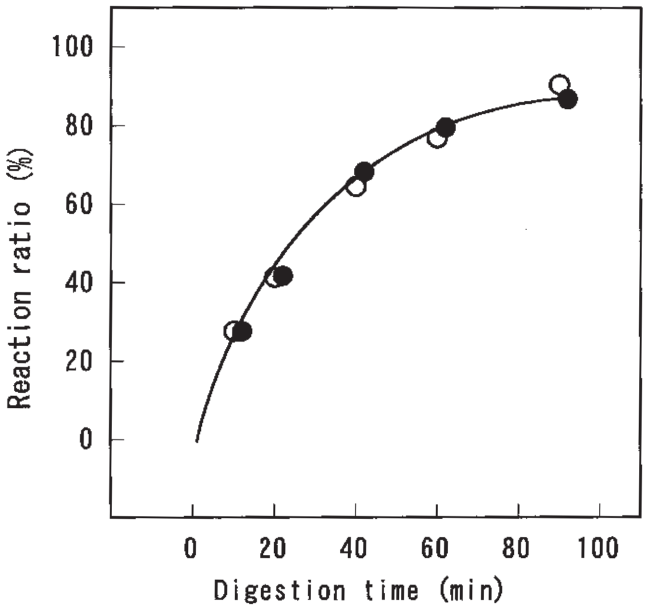
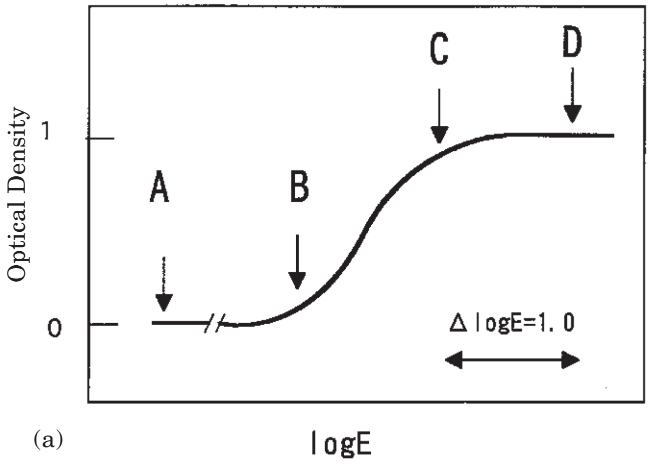
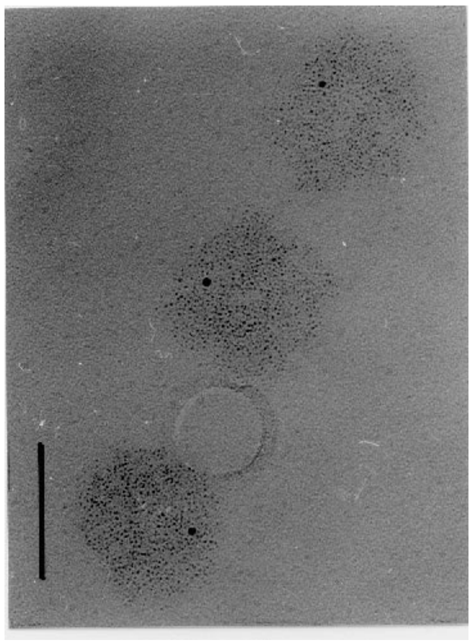


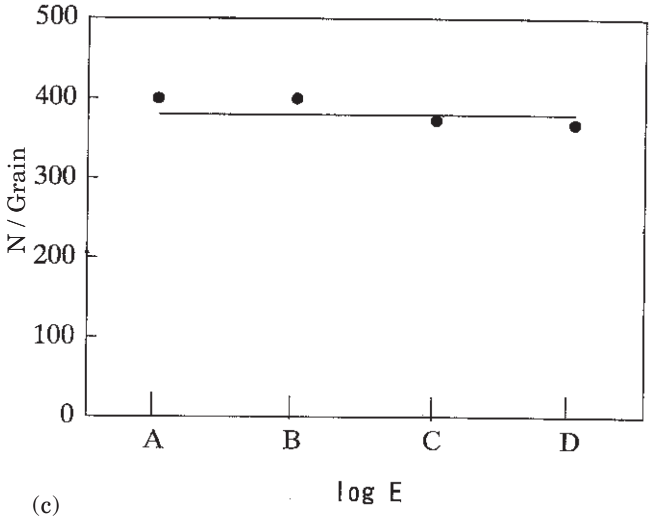
Figure 9. Reaction ratio of sodium thiosulfate labeled with radioactive ^{35}S on octahedral silver bromide grains in emulsions as a function of digestion time at 60°C with 16 (●) and 130(○) μmol/molAgBr sodium thiosulfate.



(a)



(b)



(c)

Figure 10. (a) Normalized characteristic curve for the emulsion sensitized with 16 μmol/molAgBr sodium thiosulfate; (b) An electron micrograph of gelatinate shells of the sensitized grains, that were exposed to light at the exposure level indicated by D in Fig. 10(a), and subjected to amplification treatment. The length of the bar in this figure indicates to 0.2 μm; (c) The average number (N) of the observed centers per grain in the sulfur sensitized emulsions, which were unexposed (A) and exposed to light at the exposure levels indicated by B, C and D in Fig. 10(a).

assumption that all the silver sulfide centers formed on the grains could be observed by means of the method described above, the number of sulfide ions contained in each observed center was estimated as shown in Table I. In the emulsion with maximum sensitivity, which was digested in the presence of 16 μmol/molAgBr sodium thiosulfate, each sulfur sensitization center contained two sulfide ions on the average.

Figure 10(b) shows an electron micrograph of gelatinate shells of the grains of the emulsion with maximum sensitivity, which had been exposed to light at the exposure level marked with D on the normalized characteristic curve in Fig. 10(a), and treated by the amplification method. Many small centers observed on each grain were ascribed to sulfur sensitization centers, while one large center on each grain was ascribed to a latent image center. As shown in Fig. 10(c), it was found that the average number of observed sulfur sensitization centers per exposed grain was equivalent to that of the observed centers per unexposed grain, and independent of exposure.

Discussion

Owing to the concentration principle, photoelectrons and interstitial silver ions take part in the formation of only one silver cluster, i.e., latent image center, on each grain in spite of the presence of many sulfur sensitization centers on it, as shown in Fig. 10(b). However, the results shown in Figs. 10(b) and 10(c) indicate that a silver cluster was formed and grown at every sulfur sensitization center by the amplification treatment. Thus the silver cluster formation at a sulfur sensitization center by amplification treatment takes place independently of the concentration principle. This consideration was supported by the following observation. Namely, sulfur sensitization centers enhanced the formation of silver clusters by hydrogen hypersensitization treatment.[12] Silver cluster formation independent of the concentration principle has therefore been proposed and observed as the mechanism of the formation of reduction sensitization centers.[13]

As seen in Figs. 5, 8 and Table I, the changes in the sensitivity, photoconductivity, and number of sensitization centers per grain in sulfur sensitized emulsions with variation in the amount of the sensitizer correlated well with each other, and indicated that as many as 3200 per μm^2 electron-trapping sensitization centers were formed by sulfur sensitization on octahedral silver bromide grains in emulsions. The comparison of the amount of silver sulfide formed in the emulsion with the number of observed centers per grain indicated that each sulfur sensitization center contained two sulfide ions at maximum sensitivity. This result gave experimental evidence for the hypothesis that a sulfur sensitization center is a dimer of silver sulfide, as proposed by Keevert and Gokhale,[1] Kanzaki and Tadakuma,[2] and Tani.[3]

The number of sulfide ions in each sulfur sensitization center strikingly increased with increasing amount of the sensitizer as shown in Table I, and became clusters of silver sulfides acting as fog centers. It has been reported that the fog centers have the crystal structure of silver sulfide[14] and a very broad absorption spectrum ranging from 500 nm beyond 780 nm.[15]

Conclusions

In this study, we could successfully observe sulfur sensitization centers formed on octahedral silver bromide grains in emulsions by means of an amplification treatment with a special physical developer. By this treatment, a silver cluster was deposited on each center. The number of the observed centers per grain and sensitivity of sulfur sensitized emulsions increased with increasing the amount of a sulfur sensitizer, and the former reached a plateau when the latter reached the maximum. The number of the centers per grain in the emulsion with the maximum sensitivity was as many as 3200 per μm^2, and was the same as the number of fog centers per grain formed with excessive amount of sensitizer. The observed sulfur sensitization centers were uniformly distributed on the grains. The comparison of the number of the observed centers per grain with the amount of silver sulfide formed indicated that each sulfur sensitization center contained two sulfide ions in the emulsion with the maximum sensitivity. The number of sulfide ions in each sulfur sensitization center strikingly increased with increasing the amount of the sensitizer, and became silver sulfide clusters, which could be observed without any amplification treatment, and acted as fog centers.

Acknowledgment. The authors thank Dr. Tadaaki Tani of Ashigara Research Laboratories of Fuji Photo Film Co., Ltd. for his helpful discussion.

References

1. J. E. Keevert and V. V. Gokhale, *J. Imaging Sci.* **31**, 243 (1987).
2. H. Kanzaki and Y. Tadakuma, *J. Phys. Chem. Solids* **55**, 631 (1994).
3. (a) T. Tani, *J. Imaging Sci. Technol.* **39**, 386 (1996); (b) T. Tani, *J. Imaging Sci. Technol.* **42**, 135 (1998); (c) T. Tani and Y. Yoshida, *J. Imaging Sci. Technol.* **44**, 242 (2000).
4. (a) D. J. Cash, *J. Photogr. Sci.* **20**, 223 (1972); (b) D. J. Cash, *J. Photogr. Sci.* **25**, 203 (1977).
5. Y. Tadakuma, Y. Yoshida and H. Kanzaki, A Study of Aggregation Process of Sulfur Sensitization Centers on AgBr Emulsion Grains, *Annual Conference of Soc. Photogr. Sci. Technol., Jpn., SPSTJ*, Tokyo, Japan, 1990, p. 98.
6. J. A. Aznarez, *J. Photogr. Sci.* **25**, 53 (1977).
7. G. C. Farnell, R. B. Flint and D. C. Birch, *J. Photogr. Sci.* **25**, 203 (1977).
8. T. Tani, *J. Imaging Sci.Technol.* **39**, 386 (1995).
9. T. Kaneda, *J. Imaging Sci.* **3**, 115 (1989).
10. (a) H. Frieser and E. Ranz, *Ber. Bunsenges. Phys. Chem.* **68**, 389 (1964); (b) H. Mifune and Y. Yoshida, *J. Soc. Photogr. Sci. Tech. Jpn.* **61**, 372 (1998).
11. T. H. James, W. Vanselow and R. F. Quirk, *PSA J.* **14**, 349 (1948).
12. (a) H. Mifune, Enhancement of Silver Nuclei Formation by Sulfur Sensitization Centers on Silver Bromide Grains, *Annual Conference of Soc. Photogr. Sci. Technol. Jpn., SPSTJ*, Tokyo, Japan, 2000, pg. 135; (b) H. Mifune, *J. Imaging Sci. Technol.* **46,** 117 (2002).
13. T. Tani, T. Tasaka, M. Murofushi, K. Hosoi, and A. Hirano, *Imaging Sci. J.* **47**, 1 (1999).
14. T. Shiozawa and T .Kobayashi, *Phys. stat. sol. (a)*, **110**, 375 (1988).
15. K. Morimura and H. Mifune, *J. Soc. Photogr. Sci. Tech. Jpn.* **59**, 435 (1996).