Silver Clusters of Photographic Interest III. Formation of Reduction-Sensitization Centers in Emulsion Layers on Storage and Mechanism for Stabilization by TAI

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Comparison of the increase in sensitivity of AgBr emulsion layers caused by their storage in Ar gas at 70°C for 72 h with that caused by reduction-sensitization of the same emulsions revealed that R centers of reduction-sensitization were formed on the emulsion grains during the storage. The driving force for the electron transfer from gelatin to AgBr grains on storage for formation of R centers was confirmed by ultraviolet photoelectron spectroscopy (UPS) measurement, whereby the Fermi level of gelatin was higher than that of AgBr. It was however proposed for the formation of R centers on storage that the electron transfer took place by a two-electron process without creating any free electron or any single silver atom in the AgBr grain. Fog centers as well as reduction-sensitization centers were formed on sulfur-plus-gold-sensitized grains during storage. A stabilizer 4-hydroxy-6-methyl-1,3,3a-7-tetraazaindene (TAI) depressed the sensitivity increase and fog formation in layers of sulfur-plus-gold-sensitized AgBr emulsions on storage. The observation provided evidence for the mechanism of stabilization of emulsion layers by TAI, according to which TAI depresses sensitometric change on storage by preventing formation of reduction-sensitization centers.

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Introduction

The formation of reduction-sensitization centers owing to the reduction of silver ions on silver halide grains by gelatin was observed in several phenomena including reduction-sensitization by digesting emulsions at low pAg (i.e., silver digestion) as reported by Wood,[1] formation of silver clusters during precipitation of silver halide emulsion grains as suggested by Pouradier[2] and confirmed by Tani and Suzumoto[3] and by Nakatsugawa and Tani,[4] and reduction-sensitization by digesting emulsions at high pH as reported by DeFrancisco and coworkers.[5]

The formation of reduction-sensitization centers owing to the reduction of silver ions on silver halide grains by gelatin is important for understanding various photographic phenomena, because photographic emulsions are composed of suspensions of silver halide grains in gelatin or in aqueous gelatin solutions and reduction-sensitization centers have significant influence on various photographic phenomena.[6] However, little analysis has been undertaken on the formation of reduction-sensitization centers as a result of the reduction of silver ions on silver halide grains by gelatin.

In this series of investigations,[7–9] reduction-sensitization of fine grain AgBr emulsions was studied by digesting them in the presence of DMAB and other sensitizers and by characterizing reduction-sensitization centers on the basis of measurements of sensitometry of emulsion layers, photoconductivity and ionic conductivity of emulsion grains, and diffuse reflectance spectra of emulsions. As a result of the above experiments, reduction-sensitization centers acting as positive hole traps and electron traps could be separately prepared and characterized according to our proposal, as dimers of silver atoms formed at electrically neutral sites and at positively charged kink sites (i.e., R centers and P centers), respectively.

The present investigation was undertaken to confirm formation of reduction-sensitization centers in emulsion layers on storage by observing the phenomenon under such a simplified condition that nothing but the interaction of AgBr grains with gelatin could be the cause for the phenomenon taking place. The result was also compared with the phenomena caused by normal reduction-sensitization, which were well established in this series of investigations. The materials and experimental conditions employed in this study were the same as those in the previous investigations so that the observed phenomena could be analyzed on the basis of established results.[7–9]

We believe that the formation of reduction-sensitization centers on storage causes the photographic instability of emulsion layers, because it should increase their sensitivity and might cause the formation of fog centers, especially in sulfur-plus-gold-sensitized emulsions. We also believe a compound that depresses the formation of reduction-sensitization centers in an emulsion layer on storage photographically, stabilizes the emulsion.

Birr discovered 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) as a stabilizer, which depresses sensitometric change of an emulsion on storage.[10] It was noted that sulfur-plus-gold sensitization was realized in practice, when Koslowski succeeded in stabilizing gold-enhanced fog us-

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ing TAI.[11] The stabilizing effect of TAI has been studied mainly in relation to the change in the condition of sulfur-sensitization centers on storage.[6] Although an idea for the stabilizing effect of TAI in relation to the change in the condition of reduction-sensitization on storage was noted,[11a] any evidence for the change in the condition of reduction of reduction-sensitization in emulsion layers on storage was not described.

The results obtained in this investigation could verify formation of reduction-sensitization centers on AgBr grains in emulsion layers on storage and provide the grounds for proposal of a mechanism for stabilization of emulsion layers, according to which stabilizers depress sensitometric change on storage by limiting the formation of reduction-sensitization centers.

Experimental

The emulsions used were the same as those used in the previous investigation,[7,8] composed of octahedral or cubic AgBr grains with equivalent circular diameter of 0.2 μm suspended in aqueous solutions of an inert and deionized gelatin provided by Nitta Gelatin Co., Ltd., (Yao, Osaka) and prepared at pH 2 at 75°C for 60 min by a controlled double-jet method[12,13] to minimize formation of reduction-sensitization centers during precipitation.[3,4] These emulsions were reduction-sensitized by digesting them at 60°C for 60 min in the presence of various amounts of dimethylamine borane (DMAB). They were sulfur-plus-gold-sensitized by digesting them at 60°C for 60 min in the presence of various amounts of sodium thiosulfate as a sulfur sensitizer, potassium chloroaurate as a gold sensitizer, and potassium thiocyanate as a stabilizer for a gold sensitizer.

The above-stated emulsions were coated on triacetate cellulose (TAC) film base with 1.74 g of AgBr/m^2 and 1.27 g of gelatin/m^2 and used as film samples for the measurements of sensitometry and microwave photoconductivity.

The film samples were exposed at room temperature for 10 s to a tungsten lamp (color temperature: 2856 K) through a continuous wedge. Exposed films were developed[14] at 20°C for 10 min by use of a surface developer MAA-1, fixed, washed, dried, and subjected to the measurement of optical density. Photographic sensitivity of a film sample was given by the reciprocal of the exposure to give the optical density of 0.1 above fog density.

To observe the formation of reduction-sensitization centers on AgBr grains in emulsion layers on storage, film samples were evacuated, stored at a fixed temperature for a fixed period in Ar, and subjected to the above-stated sensitometry.

The photoconductivity of AgBr grains in the emulsion layers was measured at −100°C by means of a 9-GHz microwave photoconductivity apparatus.[15,16] Ultraviolet photoelectron spectroscopy (UPS) was also applied to an evaporated thin AgBr layer and a thin gelatin layer to measure the Fermi levels of AgBr and gelatin. A UPS apparatus was used with the retardation potential technique designed under the guidance of Seki.[17]

Results and Discussions

Figure 1 shows the photographic sensitivity, fog density, and microwave photoconductivity of octahedral AgBr grains with equivalent circular diameter of 0.2 μm in emulsions, which were reduction-sensitized by digesting them at 60°C for 60 min in the presence of DMAB in the amount indicated on the abscissa. Sensitivity increased through two steps with increasing amounts of DMAB. The photoconductivity of the emulsion grains was hardly influenced by the sensitization centers bringing about the sensitivity increase

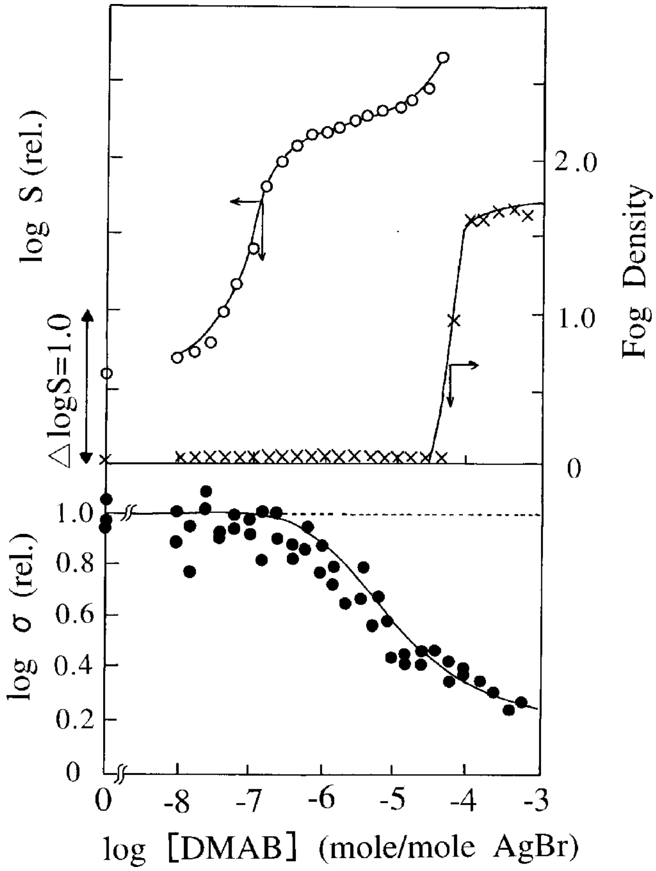

Figure 1. Photographic sensitivity (*S*, ❍), fog density (×), and photoconductivity (σ, ●) of octahedral AgBr emulsions, unsensitized and reduction-sensitized at 60°C for 60 min in the presence of DMAB with the amount indicated in the abscissa.

in the first step and was significantly decreased by the sensitization centers bringing about the sensitivity increase in the second step. This result provided the evidence for the idea proposed in the series of these investigations[8,9] that the sensitivity increases in the first and second steps were ascribed to the effects caused by hole-trapping R centers and electron-trapping P centers, respectively.

Figure 2 shows photographic sensitivity and fog density of unsensitized and reduction-sensitized octahedral AgBr emulsion layers stored at 70°C for 0, 72, and 96 h in dry Ar gas. The reduction-sensitization was carried out by digesting the emulsions at 60°C for 60 min in the presence of DMAB in the amount shown on the abscissa In the latter case, sensitivity increased through two steps with increasing amounts of DMAB in accordance with the previous papers,[8] and as seen in Fig. 1. The sensitivity increases in the first and second steps were thus ascribed to the effects caused by R and P centers of reduction-sensitization, respectively.

As seen in Fig. 2, storage in dry Ar gas at 70°C for 72 and 96 h significantly increased the sensitivity of the unsensitized emulsion, and the sensitivity increase was detected and saturated on storage at 4 and 72 h, respectively. After storage in dry Ar gas, the sensitivity increase caused by R centers of reduction-sensitization could hardly be observed, whereas the sensitivity increase caused by P centers of reduction-sensitization remained. The sensitivity achieved by storage in dry Ar gas was nearly the same as that achieved by R centers of reduction-sensitization. We propose from these results that R centers of reduction-

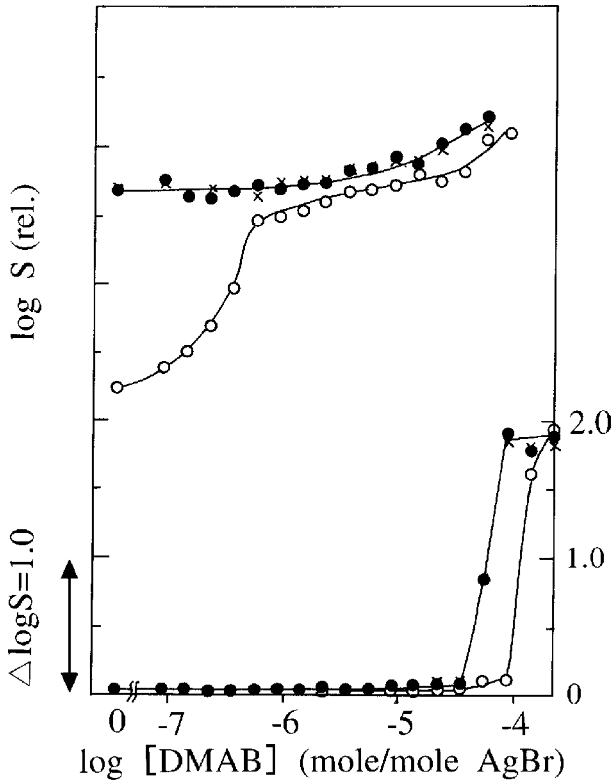

Figure 2. Photographic sensitivity (S) and fog density of unsensitized and reduction- sensitized octahedral AgBr emulsion layers stored in dry Ar gas at 70°C for 0(○), 72(●), and 96 h (×). The reduction sensitization was carried out by digesting the above-stated emulsions in the presence of DMAB in the amounts indicated in the abscissa.

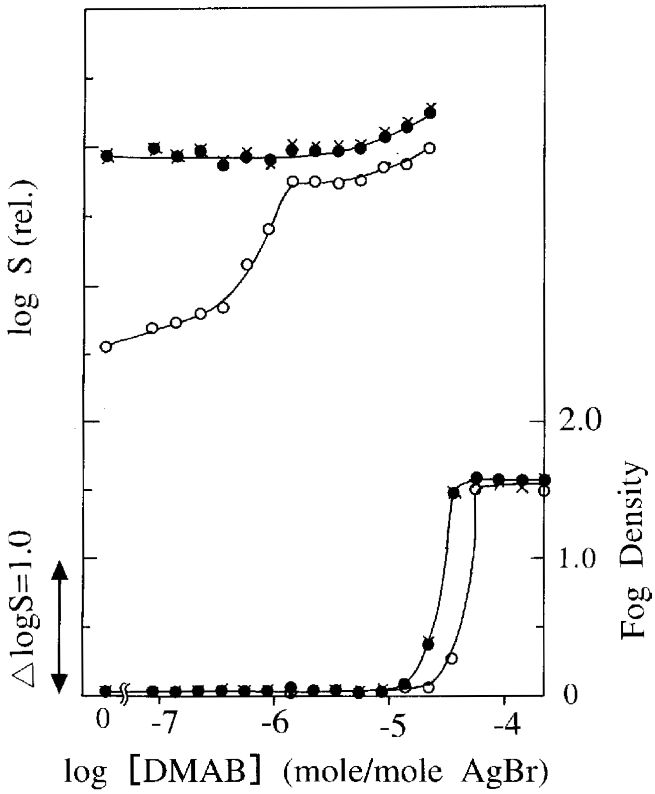

Figure 3. Photographic sensitivity (S) and fog density of unsensitized and reduction-sensitized cubic AgBr emulsion layers, stored in dry Ar gas at 70°C for 0(○), 72(●), and 96 h (×). The reduction-sensitization was carried out by digesting the above-stated emulsions in the presence of DMAB in the amounts indicated in the abscissa.

sensitization were formed on the unsensitized emulsion grains on their storage in dry Ar gas at 70°C for 72 and 96 h owing to reduction of silver ions on the grains by gelatin, because the emulsion grains were surrounded only by gelatin in an inactive atmosphere during storage.

Following the results shown in Fig. 2, Fig. 3 shows photographic sensitivity and fog density of unsensitized and reduction-sensitized cubic AgBr emulsion layers, which were stored in dry Ar at 70°C for 72 and 96 h. Sensitivity increased through two steps by reduction-sensitization with increasing amounts of DMAB in accordance with the results in the previous article.[8] The sensitivity increases in the first and second steps were ascribed to the effects caused by R and P centers, respectively.

In a similar fashion to the results with octahedral AgBr emulsions, the sensitivity of unsensitized cubic AgBr emulsions significantly increased by storage in dry Ar gas. After storage in dry Ar gas, the sensitivity increase caused by R centers of reduction-sensitization was hardly observed, whereas the sensitivity increase caused by P centers remained. The sensitivity achieved by the image in dry Ar gas was nearly the same as that achieved by R centers of reduction-sensitization. We likewise propose that R centers of reduction-sensitization were also formed on cubic AgBr grains in emulsion layers owing to reduction of silver ions on the grains by gelatin on storage in dry Ar gas.

Following the results shown in Fig. 2, Fig. 4 shows photoconductivity along with photographic sensitivity of unsensitized and reduction-sensitized octahedral AgBr grains in emulsion layers stored in dry Ar gas at 70°C for 72 h. As seen here, storage in dry Ar gas hardly influenced the photoconductivity of unsensitized grains in contrast to the fact that the image significantly increased the grain sensitivity. This result also supports the idea that the storage of the emulsion layers in dry Ar gas caused the formation of R centers of reduction-sensitization on the grains.

Figure 5 shows photographic sensitivity and fog density of sulfur-plus-gold-sensitized emulsion layers stored in dry Ar gas at 70°C for 0 and 18 h. The sulfur-plus-gold sensitization was carried out by digesting the emulsions at 60°C for 60 min in the presence of sulfur and gold sensitizers with the amounts indicated in the abscissa. As shown, storage increased the sensitivities and fog densities of the sulfur-plus-gold-sensitized emulsions. This result suggests that storage caused the formation of reduction-sensitization centers on the emulsion grains. Most of the reduction-sensitization centers contributed to the sensitivity increase, but some were converted by gold ions into fog centers composed of gold atoms.

Following the results shown in Fig. 5, Fig. 6 shows photographic sensitivity and fog density of sulfur-plus-gold-sensitized octahedral AgBr emulsion layers without and with TAI stored in dry Ar gas at 70°C for 18 h. The increases in sensitivity and fog density of the sulfur-plus-gold-sensitized emulsions caused by the storage in dry Ar gas were less owing to the addition of TAI to the emulsions.

To obtain knowledge of the driving force for the reduction of silver ions on AgBr by gelatin in the dry and inactive condition, UPS was applied to a thin layer of gelatin and an evaporated AgBr layer to obtain their electronic states according to the procedure reported in the literature[17] using the apparatus described in **Experimental** section. Although a dried gelatin layer in the ground state

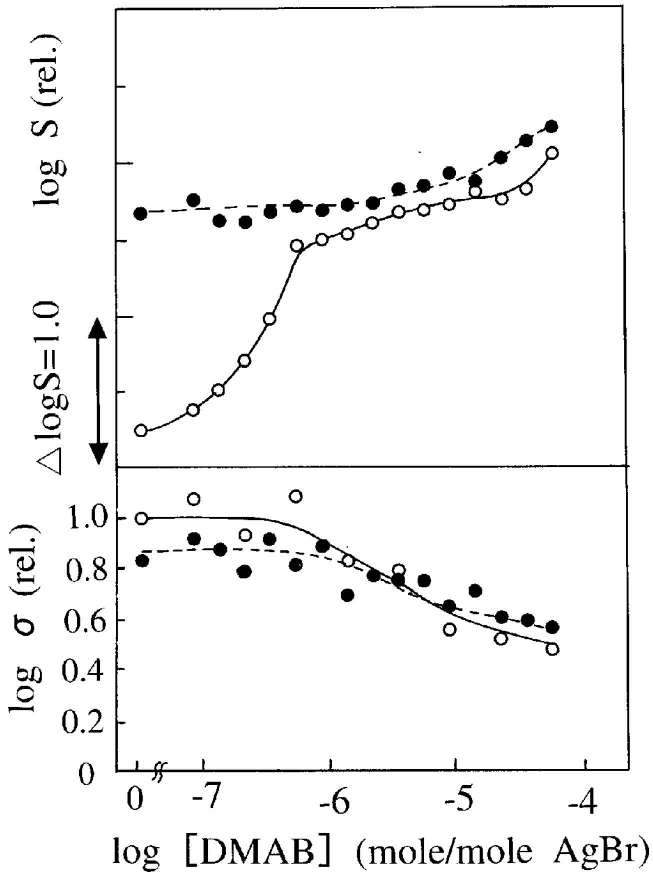

Figure 4. Photographic sensitivity (*S*) and photoconductivity of unsensitized and reduction-sensitized octahedral AgBr grains in emulsion layers, stored in dry Ar gas at 70°C for 0(○) and 72 h (●). The reduction-sensitization was carried out by digesting the above-stated emulsions in the presence of DMAB in the amounts indicated in the abscissa. The photoconductivity of the emulsion grains was measured at –100°C by a microwave photoconductivity apparatus.

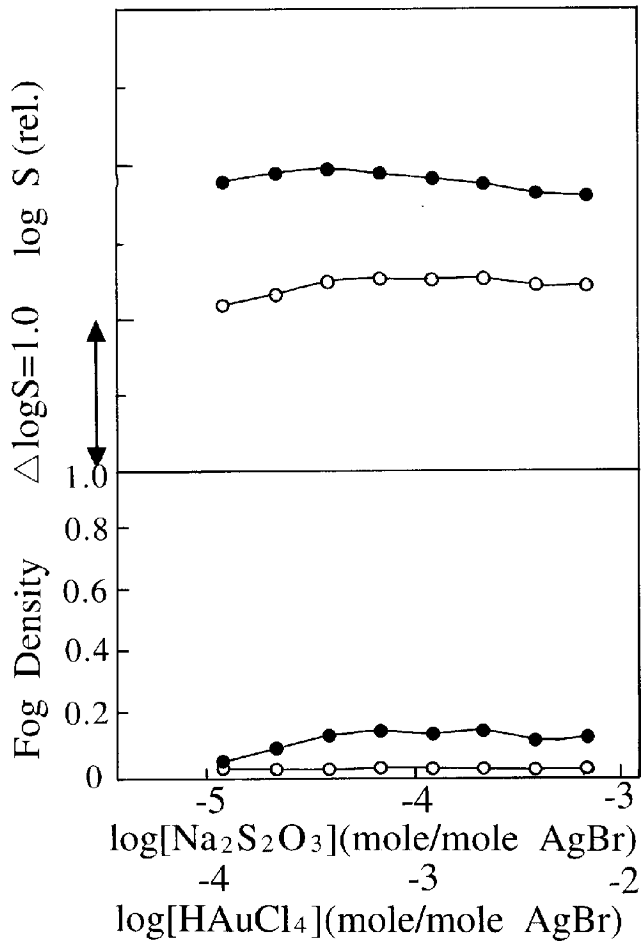

Figure 5. Photographic sensitivity (*S*) and fog density of sulfur-plus-gold-sensitized octahedral silver bromide emulsion layers, stored in dry Ar gas at 70°C for 0(○) and 18 h (●). The sulfur-plus-gold sensitized was carried out by digesting the emulsions at 60°C for 60 min in the presence of sulfur and gold sensitizers with the amounts indicated in the abscissa.

is an insulator, it has its own Fermi level that can be determined by means of UPS because the gelatin is electronically excited and can therefore exchange electrons with AgBr to equalize the Fermi levels during the measurement of their UPS.[17] In gelatin in an emulsion layer, there is some reducing substituents and/or impurities that can transfer electrons to silver halide to form silver clusters during storage. It is not clear at present how those substituents and/or impurities in a gelatin layer are related to the gelatin's Fermi level.

The resulting electronic energy level diagram of gelatin and AgBr is shown in Fig. 7. As indicated, it was found that the Fermi level of gelatin was higher than that of AgBr, indicating the presence of a driving force for electron transfer from gelatin to AgBr when they are in contact with each other. Based on this result, we propose that the reduction of silver ions on AgBr grains by gelatin occurs because of the electron transfer from gelatin to AgBr grains in emulsion layers during storage.

Discussion

Formation of Silver Clusters. As described in the previous section, reduction-sensitization centers were formed on AgBr emulsion grains during storage of emulsion layers owing to reduction of silver ions on the grains by gelatin. This phenomenon should be very important for sensitivity and stability of silver halide photographic materials, because silver halide grains are always surrounded by gelatin and reduction-sensitization centers have significant influence on the sensitivity and stability of the photographic materials.

We suggest that this phenomenon involved the formation of silver clusters brought about by reduction of silver ions on AgBr grains as a result of electron transfer from gelatin to the grains. It seems meaningful to compare electron transfer to AgBr by this reduction reaction to the formation of silver clusters with light-induced electron transfer from photoexcited sensitizing dyes to AgBr. Note that formation of reduction-sensitization centers during storage was very slow. The sensitivity increase by the reduction-sensitization centers was detected and saturated on storage in dry Ar gas at 70°C at 4 and 72 h, respectively. But electron transfer from sensitizing dyes is the excited state to AgBr emulsion grains takes place in several picoseconds when the energy level of the excited electrons in a dye are[18] above the bottom of the conduction band of AgBr. We therefore propose that the energy level of the electrons transferred from gelatin to AgBr emulsion grains should be much lower than the bottom of the conduction band of AgBr.

It has been shown that Lowes hypothesis[7] really takes place according to the following steps: Namely, an R center

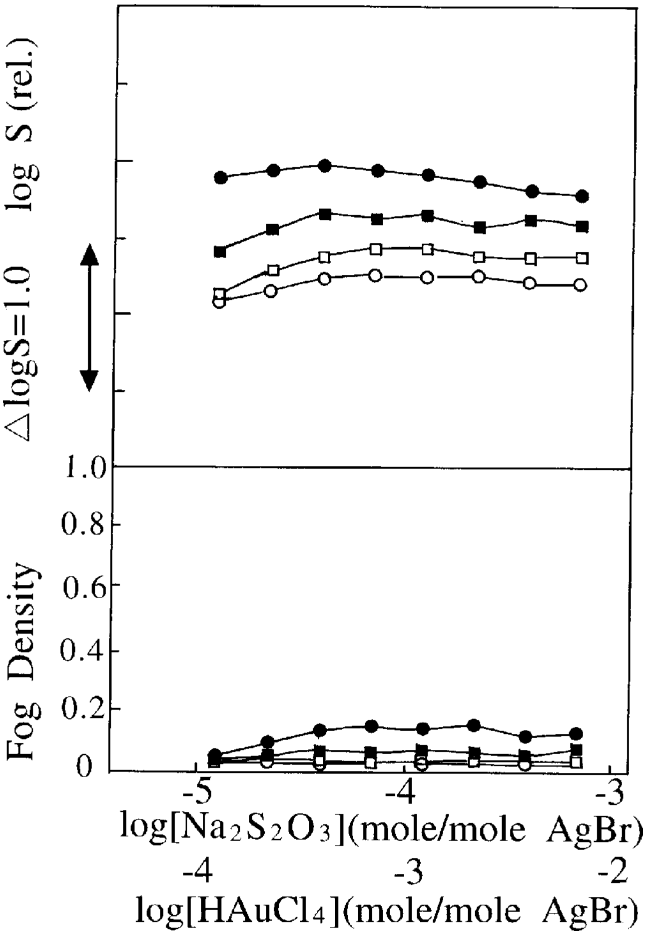

Figure 6. Photographic sensitivity (S) and fog density of sulfur-plus-gold-sensitized octahedral silver bromide emulsion layers without (○,●) and with (□, ■) TAI, stored in dry Ar gas at 70°C for 0(○,□) and 18 hours (●,■). The sulfur-plus-gold sensitization was carried out by digesting the emulsions at 60°C for 60 min in the presence of sulfur and gold sensitizers with the amounts indicated in the abscissa. The amount of TAI added to the above-stated emulsions was 2×10^{-2} mole/mole AgBr.

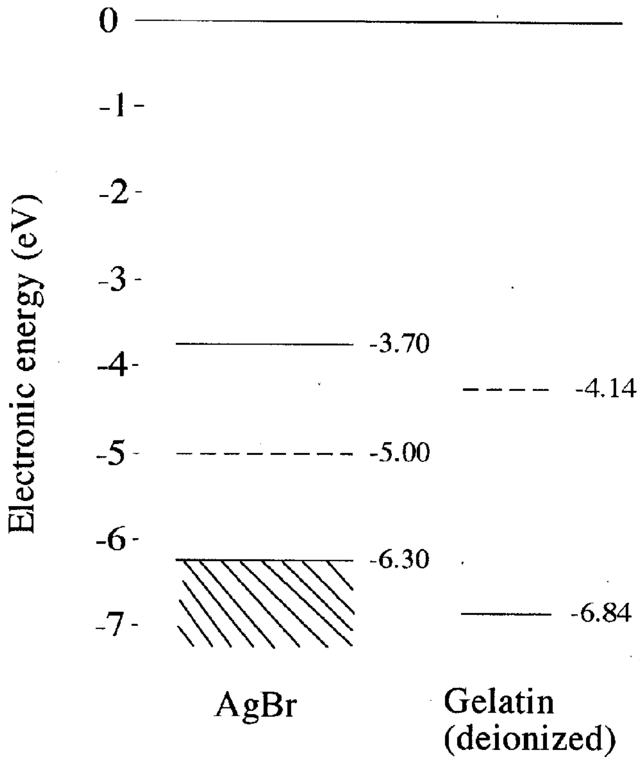

Figure 7. The UPS energy level diagram of thin layers of AgBr and gelatin where broken lines indicate their Fermi levels. The UPS measurement also gave the top of the valence band of AgBr and the highest occupied electronic energy level of gelatin as –6.30 and –6.84 eV, respectively. By taking[21] the band gap of AgBr as 260 eV, the bottom of the conduction band of AgBr was evaluated to be –3.70 eV.

is oxidized by a positive hole to give Ag_2^+ (step 1), which undergoes ionic relaxation to give a silver atom and an interstitial silver ion (step 2). A silver atom then dissociates to give a free electron and an interstitial silver ion (step 3).

$$Ag_2(\text{R center}) + h^+ \longrightarrow Ag_2^+, \quad (1)$$

$$Ag_2^+ \longrightarrow Ag + Ag^+, \quad (2)$$

$$Ag \longrightarrow Ag^+ + e^-. \quad (3)$$

Step 2 was originally proposed by Mitchell,[18] and Step 3 was proposed according to the analysis of low-intensity reciprocity failure.[19] Accordingly, appearance of free electrons leads to the formation of a silver cluster acting as an electron trap (i.e., P center) on a grain following the mechanism of the formation of a latent image center.[7] Namely, only one P center is formed and grown on such a fine AgBr grain according to the concentration principle[7] when free electrons take part in the formation of the silver cluster.

It was obvious in this investigation that the electrons transferred from gelatin to an AgBr grain during storage were disposed to form many R centers on the grain. We therefore suggest that the electron transfer from gelatin to an AgBr grain takes place by creating neither any free electrons nor free silver atoms in the grain, which is contrary to the electron transfer in spectral sensitization that creates free electron in an AgBr grain.[20] Namely, there is an essential difference between the electron transfer processes by reduction reaction and the light-induced electron transfer (i.e., spectral sensitization) for the formation of silver clusters.

To analyze the proposed difference, it is meaningful to compare the following two electron transfer processes:

$$R + Ag^+ \longrightarrow R^+ + Ag, \quad (4)$$

$$R + 2Ag^+ \longrightarrow R^{2+} + Ag_2. \quad (5)$$

The electron transfer for spectral sensitization corresponds to process 4. It is proposed in this article that the electron transfer for the formation of a reduction-sensitization center by reduction reaction correspond to process 5.

In the case of spectral sensitization, R in Eq. 4 corresponds to a sensitizing dye molecule in the excited state in which only one electron is excited to the higher molecular orbital and available for the electron transfer within the lifetime of the excited dye molecule. Therefore, one electron is transferred from the excited dye molecule to the conduction band of silver halide in spectral sensitization contributing to the formation and growth of one silver cluster acting as an electron trap on a grain.

But formation of a silver cluster by thermal reduction proceeds not through process 4, but through process 5 owing to the following reason: In process 5, R is in the ground state and has two electrons in the highest occupied molecular orbital both of which are available for electron transfer. In addition, a dimer of two silver atoms is much more stable than two isolated silver atoms owing to the large binding energy of the dimer.[7–9,21] It is therefore expected that the formation energy of a silver cluster through process 5 is smaller than that through process 4 leading directly to the formation of a silver cluster by the reduction reaction.

No analysis could be made in this investigation on the chemical composition of the gelatin that transferred electrons to AgBr emulsion grains during storage. However, the difference in Fermi level between gelatin and AgBr provides the driving force for electron transfer from gelatin to the grains. Namely, the Fermi level of AgBr is situated nearly at the middle of its forbidden band, lower than the Fermi level of gelatin. Electron transfer from gelatin to AgBr emulsion grains and formation of reduction-sensitization centers there could accordingly take place, raising the Fermi level of the grains until it became equal to that of gelatin. The detailed elementary processes for achieving process 5 could not however be clarified in this study.

Mechanism of Stabilization by TAI. As described in the previous section, reduction-sensitization centers were formed on AgBr emulsion grains during storage of emulsion layers owing to two-electron reduction of silver ions on the grains by gelatin. This phenomenon should be very important for stability of silver halide photographic materials because formation of reduction-sensitization centers during storage should have significant influence on both sensitivity and fog density of photographic materials.

As Yoshida, Mifune, and Tani reported,[22] it is known that application of gold sensitization to reduction-sensitized emulsions causes formation of fog centers by converting reduction-sensitization centers into clusters of gold atoms that act as fog centers owing to the development-enhancing effect of gold atoms.[6] It is therefore expected that formation of reduction-sensitization centers on silver halide grains in sulfur-plus-gold-sensitized emulsion layers during storage might cause an increase in fog density in addition to the increase in sensitivity. As shown in Fig. 5, storage in Ar gas actually increased the sensitivity and fog density of sulfur-plus-gold-sensitized emulsions. This result indicates that storage caused the formation of reduction-sensitization centers on the emulsion grains, most of which contributed to the sensitivity increase, and some of which were converted into fog centers composed of gold atoms.

As shown in Fig. 6, increases in the sensitivity and fog density of the sulfur-plus-gold-sensitized emulsions by storage in dry Ar gas was less because of the addition of TAI to the emulsions. Namely, TAI could stabilize sulfur-plus-gold-sensitized emulsion layers by inhibiting the formation of reduction-sensitization centers during storage. As indicated by Eq. 5, the formation of reduction-sensitization centers during storage depends upon the activity of silver ions. It is well known that TAI decreases the activity of silver ions by forming its sliver ions on the grain surface.[6,11a] Thus TAI could depress the formation of reduction-sensitization centers on emulsion grains during storage.

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