Enhancement of Silver Nuclei Formation by Sulfur Sensitization Centers on Silver Bromide Grains

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Heavy hydrogen hypersensitization formed P centers, which were silver nuclei acting as electron traps on octahedral silver bromide grains in coated emulsion layers. The number of P centers was evaluated by measuring the diffuse reflectance spectrum of a stack of 10 coated emulsion layers. Sulfur sensitization centers increased the rate of formation of P centers, and decreased its activation energy. The observed activation energies were 0.87 eV in a primitive emulsion and 0.52 eV in an excessively sulfur sensitized one. This result supports an idea that sulfur sensitization centers formed on silver bromide emulsion grains catalyze silver nuclei formation, and that this is one of the essential functions of sulfur sensitization centers.

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Introduction

Sulfur sensitization is indispensable to produce highly sensitive photographic silver halide emulsions. In the processes for latent image formation, sulfur sensitization centers perform the following functions: trapping and detrapping of photoelectrons, enhancement of formation and stabilization of minute silver nuclei.[1]

The enhancement of minute silver nuclei formation by sulfur sensitization centers was proposed for the first time by Sheppard, Trivelli and Loveland[2] in their model of latent image formation. Mitchell[3] reported that movement of silver clusters in large sheet crystal of silver bromide was depressed in the presence of silver sulfide clusters. Tamura, Hada, Fujiwara and Ikenoue[4] observed by means of a double flash method that sulfur sensitization centers prolonged the life time of latent preimage centers formed on silver halide grains in room air.

Babcock, Ferguson, Lewis and James[5] showed that hydrogen gas was an effective reduction sensitizer for coated emulsion layers, bringing about hydrogen hypersensitization. Janusonis[6] reported that the activation energy for the increase in sensitivity of cubic silver bromide grains in hydrogen hypersensitization was 0.83 eV. Tani and Murofushi[7] observed by means of diffuse reflectance spectra of thick emulsion layers together with photoconductivity of emulsion grains that there are two types of reduction sensitization centers (i.e., R centers acting as positive hole traps and P centers acting as electron traps), and that P centers on silver bromide emulsion grains had a sharp absorption peak at 474 nm. Oku and Kawasaki[8] reported that the relative amount of silver nuclei formed on reduction sensitized and hydrogen hypersensitized silver bromide emulsion grains could be estimated by means of the absorption spectrum of a stack of 10 coated film samples.

By means of the diffuse reflectance spectrum of a stack of 10 coated emulsion layers on film base, we quantitatively observed that sulfur sensitized centers formed on silver bromide grains enhanced minute silver nuclei formation by the hydrogen hypersensitization treatment.

Experimental

An emulsion containing octahedral silver bromide grains with 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 to an aqueous gelatin solution maintained at pH 2 and pAg 8.3. 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 and reduction sensitization were carried out by digesting the above emulsion for 60 min at 60°C in the presence of sodium thiosulfate pentahydrate and dimethylamine borane (**DMAB**) as sensitizers, respectively. The emulsions were coated on TAC film base of 126 μm thickness. A prepared film sample had an emulsion layer of 5 μm thickness and a silver bromide coating weight of 2.1 g/m^2.

Each film sample was exposed for 10 sec to a tungsten lamp with color temperature of 2856 K through a continuous wedge, developed for 10 min at 20°C by use of MAA-1 surface developer. The optical density of a developed film sample was measured using a Fuji Densitometer, and sensitivity was given as the reciprocal of exposure required to give optical density of 0.2 above fog.

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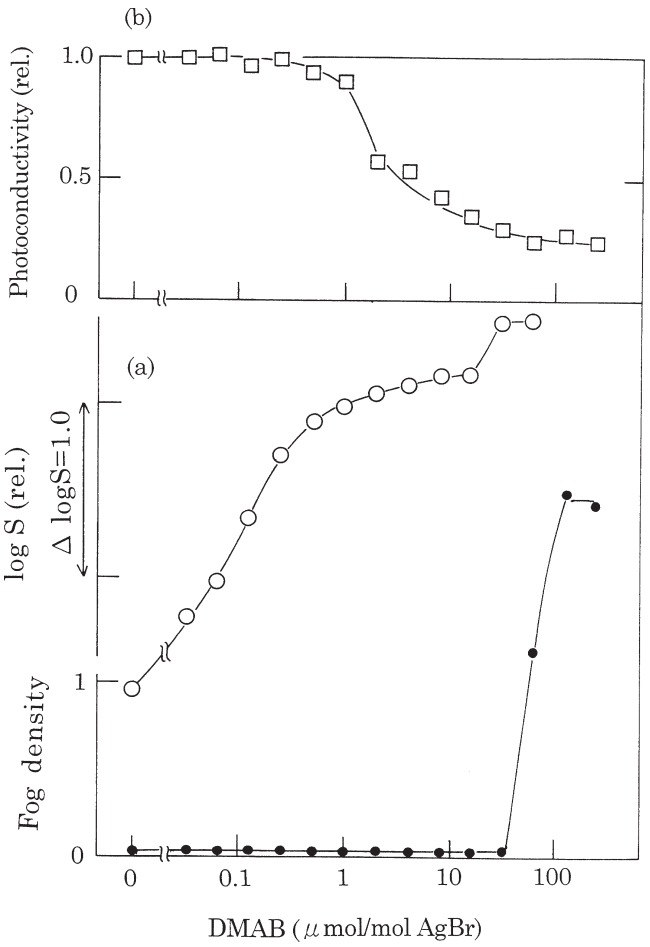

Figure 1. Photographic sensitivity (S) and fog density; (a) and photoconductivity; (b) of octahedral silver bromide emulsion grains as a function of the amount of **DMAB** used for reduction sensitization.

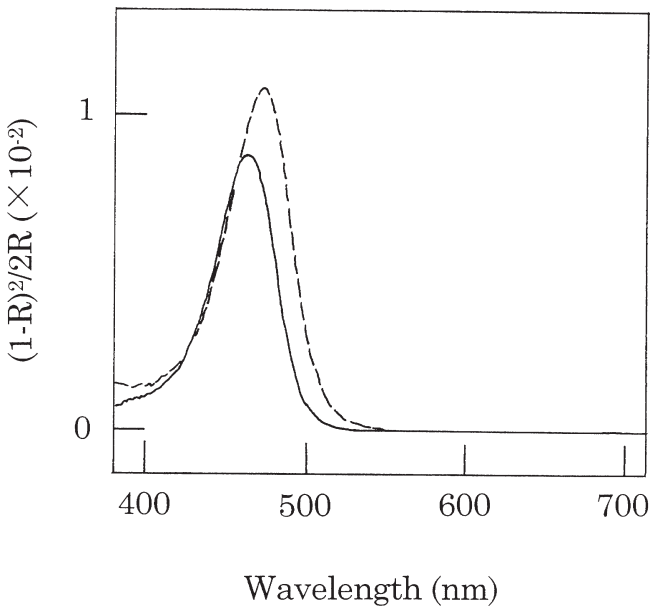

Figure 2. Absorption spectra of P centers in a silver bromide emulsion, which was reduction sensitized with **DMAB** of 32 μmol/mol AgBr. The spectra were expressed by $(1 - R)^2/2R$, where R was the diffuse reflectance at the absorption peak of P centers of a stack of 10 coated emulsion film samples (solid line) and the corresponding thick liquid emulsion layer in 1 cm cell (broken line).

Hydrogen hypersensitization treatment was carried out by degassing film samples in a vacuum vessel, and keeping them under hydrogen gas at 0.3 kg/cm^2 pressure and fixed temperatures for fixed periods of time.

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

The visible range diffuse reflectance spectra of a stack of 10 coated film samples and of a liquid thick emulsion layer in a 1 cm cell were measured by means of a color analyzer spectrophotometer model 307 made by Hitachi Seisakusho Co., equipped with an integrating sphere. A sample with unsensitized emulsion was used as a reference. The absorption spectra of sensitization centers were obtained by conversion from the above diffuse reflectance spectra, using the Kubelka–Munk equation, as shown below.[10]

$$K/S = (1 - R)^2/2R = c\varepsilon/S, \quad (1)$$

where R is the diffuse reflectance of the emulsion layer with infinite thickness for light which is absorbed by sensitization centers. K and S are absorption and scatter coefficients of the layer, respectively and c and ε are the concentration and molecular extinction coefficient of sensitization centers, respectively. Therefore, the value of $(1 - R)^2/2R$ gave the relative concentration of sensitization centers formed on silver bromide grains.

Results and Discussions

Figure 1 shows photographic sensitivity, fog density and photoconductivity of octahedral silver bromide emulsion grains with photoelectrons as carriers as a function of the amount of **DMAB** used for reduction sensitization. As is well known,[11] the sensitivity increased through two steps with increasing the amount of **DMAB**. The first step was ascribed to the formation of R centers, since it was not associated with a decrease in the photoconductivity. The second step was ascribed to the formation of P centers, since it was associated with a decrease in the photoconductivity.

Figure 2 shows the absorption spectra of P centers in terms of $(1 - R)^2/2R$, as given by diffuse reflectance spectra of reduction sensitized silver bromide emulsion grains. The wavelength of the absorption peak with a stack of 10 coated film samples (solid line) was a little shorter than that with the corresponding thick emulsion layer in the 1 cm cell (broken line).

Figure 3 shows the value of $(1 - R)^2/2R$ at the wavelength of the absorption peak of P centers as a function of the amount of DMAB, giving straight lines with slope of 1.8 for both a stack of 10 coated film samples and the corresponding thick liquid emulsion. Therefore, we concluded that the value of $(1 - R)^2/2R$ as given by the reflectance spectrum of a stack of 10 coated film samples gave the relative concentration of silver nuclei formed on silver bromide grains.

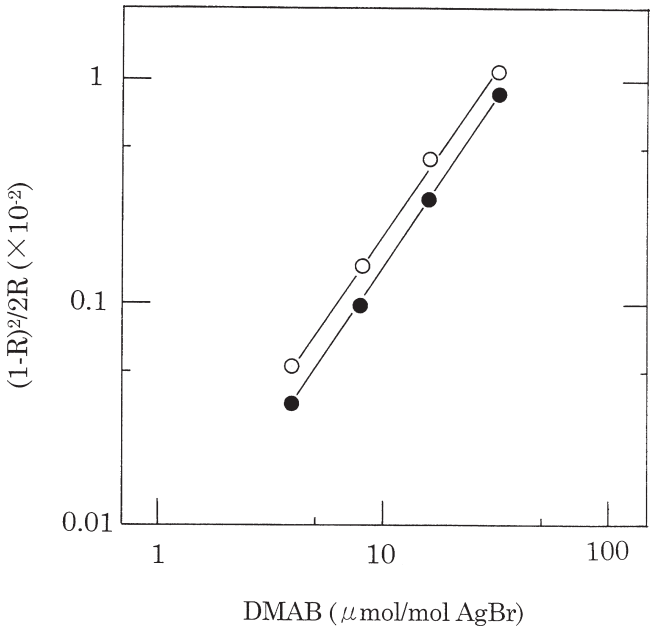

Figure 3. Relationship between the amount of **DMAB** and $(1 - R)^2/2R$ at the absorption peak of P centers of a stack of 10 coated emulsion film samples (●) and the corresponding thick liquid emulsion layer (○).

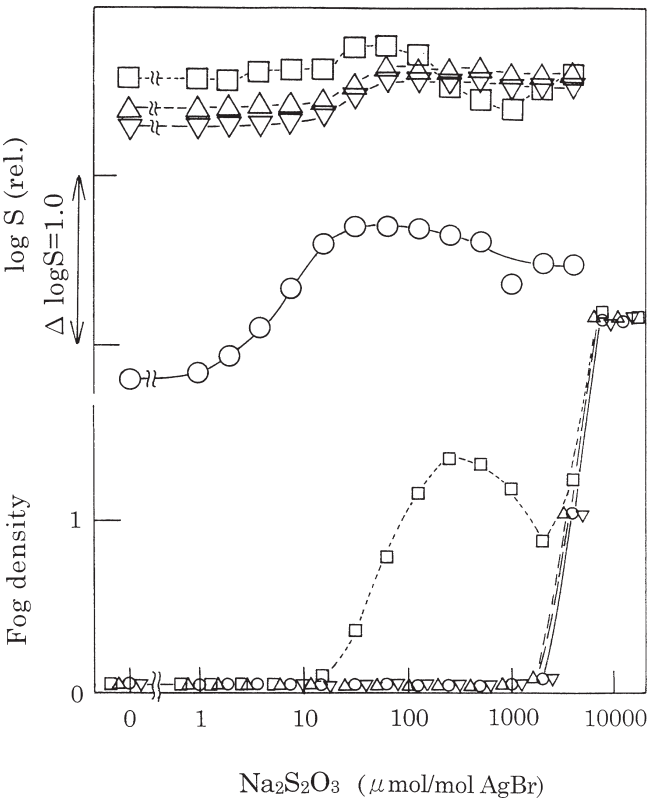

Figure 4. Photographic sensitivity (S) and fog density of sulfur sensitized silver bromide emulsions (○) as a function of the amount of sodium thiosulfate used for sulfur sensitization and of those hydrogen hypersensitized for 3 hr at 25°C (▽), 40°C (△) and 60°C (❑).

Figure 4 shows photographic sensitivity and fog density of sulfur sensitized silver bromide grains as a function of the amount of sodium thiosulfate used as sensitizer. The results with hydrogen hypersensitized grains are also shown in this figure. The sensitivity increased with increasing the amount of the sensitizer and reached its maximum with about 32 μmol/mol AgBr sensitizer, and fog appeared with sensitizer levels of more than 2 μmol/mol AgBr. The sensitivity increased significantly when the samples were kept under hydrogen gas at 25°C for 3 hr. Fog appeared in some samples when they were treated at 60°C for 3 hr with hydrogen gas.

Figure 5 shows the photoconductivity of octahedral silver bromide grains in primitive emulsions, which were kept in air and in hydrogen gas. The photoconductivity of the grains in emulsions which were hydrogen hypersensitized at 25°C, 40°C and 60°C decreased to 97%, 54% and 34% of that of the grains in an unsensitized emulsion.

Figure 6(1) shows the absorption spectra in terms of $(1 - R)^2/2R$ of a stack of 10 coated film samples of a primitive silver bromide emulsion without (a) and with (b) hydrogen hypersensitization treatment at 60°C for 3 hr. An absorption band with a sharp peak at 464 nm was obtained in a primitive silver bromide emulsion treated with the hydrogen hypersensitization treatment, as was observed in Fig. 2 for film samples of a reduction sensitized emulsion. Figures 6(2) and 6(3) show the absorption spectra of sulfur sensitized silver bromide emulsions with sodium thiosulfate levels of 64 and 256 μmol/mol AgBr. The peak amplitude at 464 nm observed with hydrogen hypersensitization treatment increased with increasing the amount of sulfur sensitizer. The absorption bands observed in the absence of hydrogen hypersensitization treatment were ascribed to sulfur sensitization centers, and did not change on keeping in a vacuum vessel without hydrogen gas for 3 hr at 60°C. The absorption peak of P centers was not observed in a

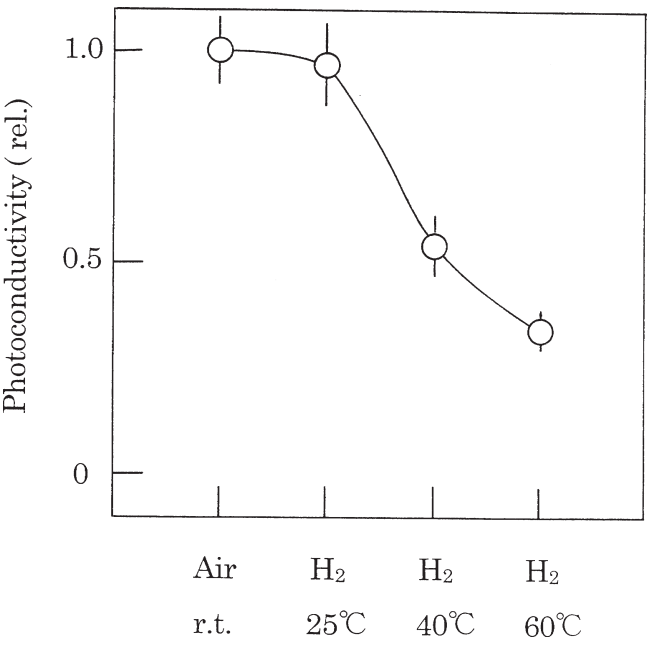

Figure 5. Photoconductivity of unsensitized octahedral silver bromide emulsion grains kept in air at room temperature (r.t.) and those kept in hydrogen gas at 25°C, 40°C and 60°C for 3 hr.

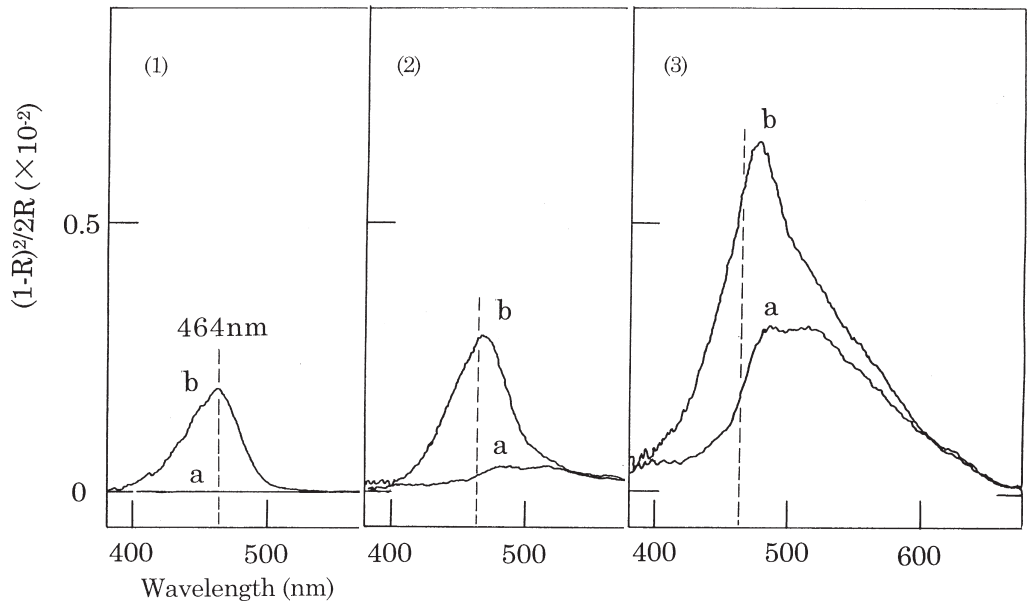

Figure 6. Absorption spectra of a primitive emulsion (1) and sulfur sensitized ones with sodium thiosulfate levels of 64; (2) and 256; (3) μmol/mol AgBr. The spectra were expressed by $(1 - R)^2/2R$, where R is the diffuse reflectance of a stack of 10 coated layers of silver bromide emulsion grains without (a) and with (b) hydrogen hypersensitization treatment at 60°C for 3 hr.

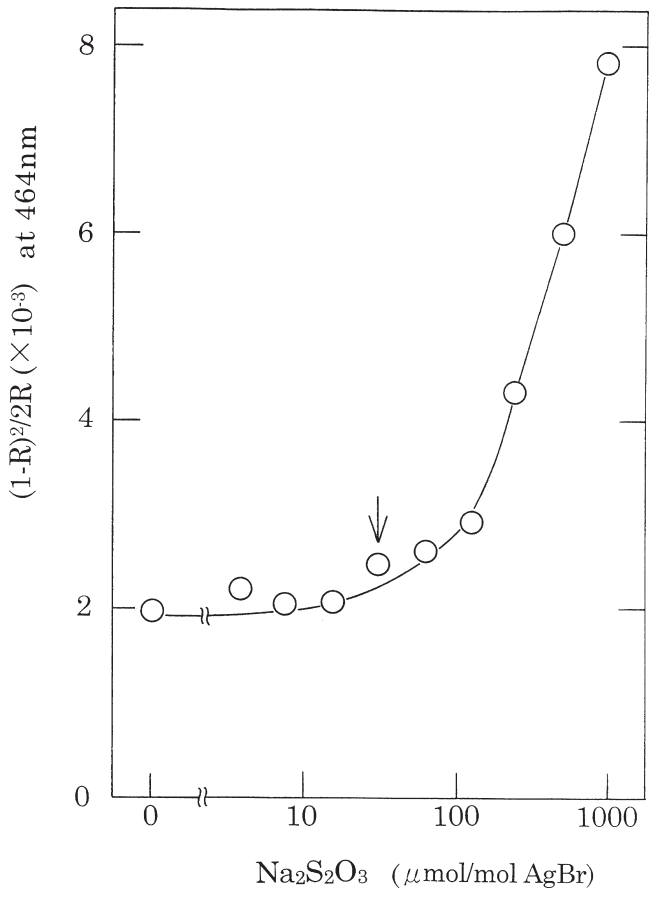

Figure 7. The formation of P centers by hydrogen hypersensitization at 60°C for 3 hr in terms of $(1 - R)^2/2R$ at 464 nm as a function of the amount of a sulfur sensitizer. An arrow refers to the condition for the maximum sensitivity.

primitive silver bromide emulsion treated at 25°C for 3 hr with hydrogen gas.

Figure 7 shows the formation of P centers by hydrogen hypersensitization treatment at 60°C for 3 hr as expressed by $(1 - R)^2/2R$ at 464 nm as a function of the amount of sulfur sensitizer. In this figure an arrow referred to the condition for the maximum sensitivity. The concentration of P centers formed by the hydrogen hypersensitization treatment increased with uperlinearly as the amount of sulfur sensitizer was increased.

Figure 8 shows the formation of P centers in an unsensitized emulsion and sulfur sensitized ones, as expressed by $(1 - R)^2/2R$ at 464 nm as a function of time for hydrogen hypersensitization treatment at 60°C. The number of P centers thus formed increased with treatment time and the rate increased with the amount of sulfur sensitizer.

Figure 9 shows the temperature dependence of the zero-order rate constant for formation of P centers in primitive and sulfur sensitized emulsions by hydrogen hypersensitization treatment evaluated at 3 hr treatment time. The slope of each straight line in this figure gave the activation energy of the rate of formation of P centers.

Figure 10 shows the activation energy of rate of formation of P centers by hydrogen hypersensitization treatment as a function of the amount of sulfur sensitizer. The activation energy decreased with increasing the amount of a sulfur sensitizer. The activation energies were 0.87 eV for a primitive silver bromide emulsion, 0.61 eV for an optimally sulfur sensitized one, and 0.52 eV for an excessively sulfur sensitized one.

As shown in Fig. 4, the photographic sensitivity of a silver bromide emulsion was significantly increased by hydrogen hypersensitization treatment at 25°C. The photoconductivity of the hydrogen hypersensitized grains was the same as that of unsensitized ones as shown in Fig. 5. The hydrogen hypersensitized emulsion did not exhibit any absorption band corresponding

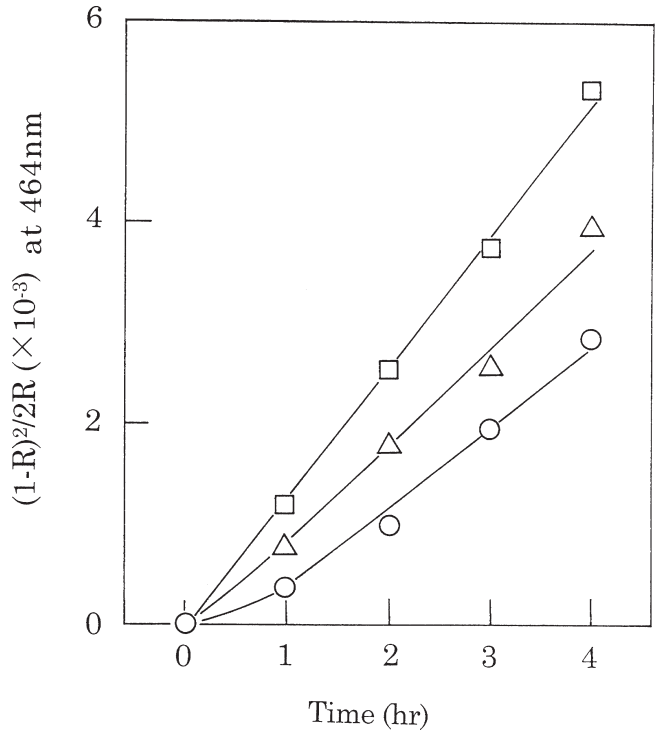

Figure 8. The formation of P centers in terms of $(1 - R)^2/2R$ at 464nm as a function of time for hydrogen hypersensitization treatment at 60°C of a primitive emulsion (○) and sulfur sensitized ones with sodium thiosulfate of 64 (△) and 256 (❑) μmol/mol AgBr.

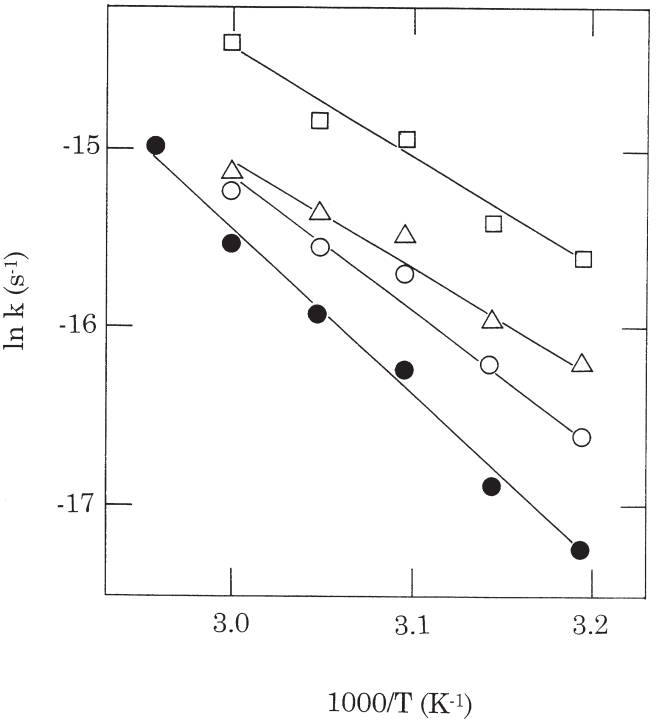

Figure 9. Temperature dependence of the rate constant (k) of the formation of P centers by hydrogen hypersensitization treatment for 3 hr of a primitive emulsion (●) and sulfur sensitized ones with sodium thiosulfate of 32 (○),128 (△), and 512 (❑) μmol/mol AgBr.

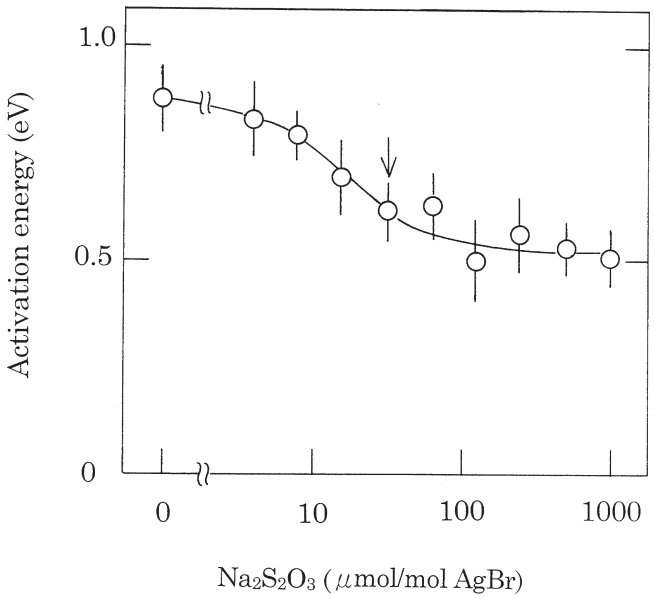

Figure 10. Activation energy of the rate of the formation of P centers by hydrogen hypersensitization treatment as a function of the amount of sodium thiosulfate for a sulfur sensitizer. An arrow refers to the condition for the maximum sensitivity.

to P centers. These results indicated that the hydrogen hypersensitization treatment at 25°C for 3 hr formed only R centers on primitive grains.

The photographic sensitivity of the grains treated with hydrogen gas at 60°C was a little higher than that of the grains treated with hydrogen gas at 25°C. The photoconductivity of the former grains was smaller by about 34% than that of the latter grains. These results indicated that the hydrogen hypersensitization treatment at 60°C for 3 hr also formed P centers on primitive grains. This idea was supported by the observation in this study that the absorption band of P centers peaking at 464 nm was given by the hydrogen hypersensitization at 60°C. Babcock and others[5] also reported that P centers were formed by excessive hydrogen hypersensitization treatment.

Janusonis[6] reported that the activation energy for sensitivity increase of cubic silver bromide grains of 0.2 μm by hydrogen hypersensitization was 0.83 eV. Murofushi and Tani[12] estimated by means of diffuse reflectance spectra that the activation energy of the rate of the formation of P centers on 0.2 μm octahedral silver bromide emulsion grains by reduction sensitization with DMAB as a sensitizer was 0.78 eV. Although the former and the latter values were ascribed to the formation of R centers and P centers, respectively, they were close to each other, and also close to the value obtained in this work for the formation of P centers by hydrogen hypersensitization (i.e., 0.87 eV). As shown in Fig. 1, R centers were formed by a smaller amount of sensitizer than P centers. This observation was consistent with the fact that an activation energy of the formation of R centers was smaller than that of P centers.

Babcock and others[5] also reported that the sensitivity increase for hydrogen hypersensitization was larger in sulfur sensitized silver bromide emulsions than in unsensitized ones, and proposed the idea that silver sulfide nuclei catalyzed hydrogen hypersensitization. It was

observed in this work that sulfur sensitization centers formed on silver bromide grains enhanced the formation of P centers, and decreased the activation energy for their formation. However, we do not know the detailed mechanism for hydrogen hypersensitization. It was concluded that sulfur sensitization centers stabilize one or more of the transition states on the reaction pathway. It may also be inferred that a P center should be formed adjacent to a sulfur sensitization center, owing to the catalytic action toward formation of the former by the latter.

The author and collaborators[13] observed and analyzed all the sulfur sensitization centers formed on octahedral silver bromide grains in emulsion by means of an amplification treatment with a special physical developer. In this amplification treatment, silver clusters were deposited on the sulfur sensitization centers. We believe that the enhancement of silver nuclei formation by sulfur sensitization centers on silver bromide grains as proved in the present work played a significant role in the above stated amplification treatment.

Enhancement of silver nuclei formation by sulfur sensitization centers in this study was observed in hydrogen hypersensitization, which does not involve formation of photoelectrons. However, it is believed that minute silver cluster, Ag_2, similar to a P center is formed as an intermediate in the latent image formation process. It is thus possible that the catalytic action of sulfur sensitization centers toward silver nuclei formation on hydrogen hypersensitization is analogous to their action toward the formation of silver nuclei on light exposure.

Conclusion

Sulfur sensitization centers formed on octahedral silver bromide emulsion grains increased the rate of the formation of P centers by hydrogen hypersensitization. The observed activation energies of the rate of the formation of P centers were 0.87 eV in a primitive emulsion, 0.61 eV for an optimally sulfur sensitized one and 0.52 eV in an excessively sulfur sensitized one. This result supports an idea that sulfur sensitization centers catalyze silver nuclei formation and that this is one of the essential functions of sulfur sensitization centers.

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