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Silver Clusters of Photographic Interest IV: Reduction Sensitization of Silver Chloride and Silver Bromide Emulsions

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Digestion of AgBr emulsions with increasing amounts of reduction sensitizers achieved stepwise increase in sensitivity corresponding to the formation of two kinds of sensitization centers, designated R centers, acting as positive-hole traps, and P centers, acting as electron traps. It has been proposed that R and P centers are silver dimers formed at electrically neutral and positively charged surface sites on AgBr grains, respectively. The formation of P centers was depressed by addition of TAI and PMT, which are preferably adsorbed to positively charged surface sites on the grains, and enhanced by cyanine dyes, which are preferably adsorbed to negatively charged surface sites. Reduction sensitization of AgCl emulsions was less effective than that of AgBr emulsions in that the former brought about less increase in sensitivity and more increase in fog density than the latter with increasing amounts of sensitizers. Reduction sensitization of AgCl emulsions was significantly improved by digesting the emulsions for reduction sensitization in the presence of PMT and TAI. From the fact that the sensitivity increase of AgCl emulsions was not associated with a decrease in photoconductivity with photoelectrons as carriers and was not observed in the presence of hydrogen hypersensitization centers acting as positive-hole traps, it is considered that, in AgCl emulsions, reduction sensitization centers were solely R centers, while P centers acted as fog centers. The developability of P centers in AgCl emulsions was however very weak. It was found that R centers exhibited their absorption band, whose peak wavelength (420 nm) was close to that of the absorption band of Ag2 in rare gas (412 nm). This result supports the proposed model where an R center is a silver dimer at a neutral site that physically interacts with the surface of silver halide.

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Introduction

In this series of investigations,[1–3] we have demonstrated from various kinds of experiments with fine AgBr emulsions that there are two types of silver clusters of photographic interest; P centers acting as electron traps and R centers acting as positive-hole traps. Digestion of AgBr emulsions for their reduction sensitization with increasing amounts of sensitizers achieved stepwise increase in sensitivity, which corresponded to the formation of R centers followed by the formation of P centers, and made it possible to observe separately the effects caused by those centers. It was also pointed out that both R and P centers produced by reduction sensitization are composed of dimers of silver atoms.

Silver clusters acting as positive-hole traps and electron traps have been studied by several groups of investigators for many years,[4] assigned by the present author to silver clusters forrned at neutral sites and positively charged sites, respectively,[5] and named by Hamilton and Baetzold as R and P centers, respectively.[6] In the second paper of this series,[2] the present author revised this model according to where a P center of reduction sensitization is composed of a silver cluster ion Ag_3^+ formed by chemical combination between Ag_2 and Ag^+ at a positively charged surface site while an R center is composed of Ag_2 that physically interacts with a neutral surface site. The revised model provides a reasonable explanation for the distinct difference in properties between R and P centers. Figure 1 illustrates the model of R and P centers together with a prediction that the formation of P centers would be depressed by compounds preferably adsorbed to positively charged sites on silver halide grains and enhanced by compounds preferably adsorbed to negatively charged sites and neutral sites.

Keen attention has been paid recently to highly sensitive AgCl emulsions, because it is expected that they can meet the demand of the times, achieving rapid and environmentally friendly processing. It is also expected that the dependence of the properties and behavior of silver

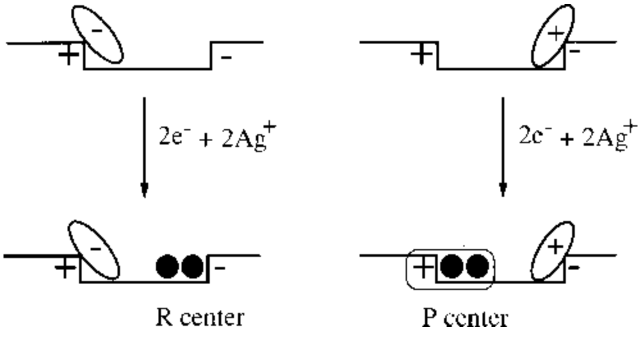

Figure 1. Model and formation of R and P centers of reduction sensitization.

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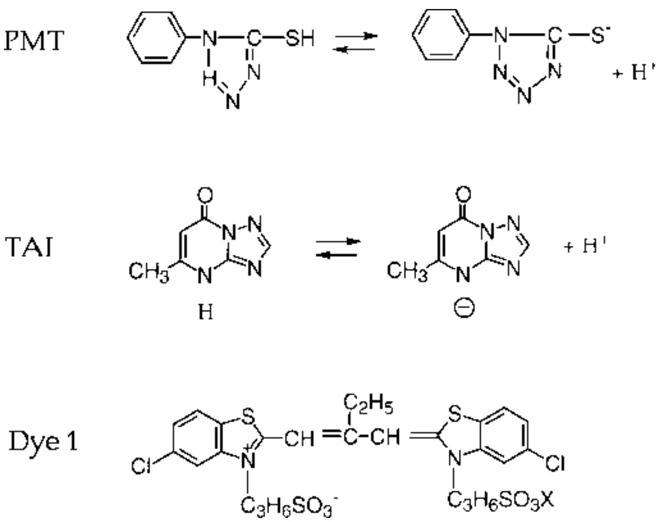

Figure 2. Compounds used for controlling the formation of R and P centers of reduction sensitization.

clusters on substrates such as AgBr and AgCl provides valuable knowledge for understanding the mechanism of photographic sensitivity. In this work, the author has studied reduction sensitization of AgCl emulsions by controlling the formation of reduction sensitization centers in the light of the knowledge of silver clusters on AgBr emulsion grains obtained in this series of investigations. The results obtained could extend knowledge concerning silver clusters in AgBr emulsions to the AgCl environment and make clear the differences in properties and behavior of silver clusters on AgCl and AgBr emulsions.

Experimental

The emulsion mainly used in this study was composed of monodispersed cubic AgCl grains with equivalent circular diameter of 0.2 μm. The emulsions composed of octahedral and cubic AgBr emulsions with equivalent circular diameter of 0.2 μm were also used as references. These emulsions were reduction-sensitized by digesting them for 60 min at 60°C in the presence of various amountss of dimethylamineborane (DMAB) and thiourea dioxide. To control the formation of reduction sensitization centers, silver-complexing agents, 1-phenyl-5-mercaptotetrazole (PMT), 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI), and 3,3′-disulfopropyl-5,5′-dichloro-9-ethyl-thiacarbocyanine dye (Dye 1) were added to the above-stated emulsions before their digestion for reduction sensitization. As shown in Fig. 2, it is known that molecules of PMT and TAI are dissociated in emulsions to give their anions, which are preferably adsorbed to positively charged sites on the surface of silver halide grains.[7] It is also known that cyanine dye molecules are preferably adsorbed to negatively charged sites and neutral sites on the surface of silver halide grains regardless of their substituents, their positively charged chromophore being responsible for their adsorption to the grains.[8] Layers of the above emulsions were prepared by coating them on TAC film bases and subjected to measurements of sensitometry and photoconductivity.

The coated emulsion layers were exposed to a tungsten lamp with color temperature of 2856 K for 10 sec through a continuous wedge, developed for 10 min at 20°C by use of a surface developer[9] MAA-1, washed, dried, and evaluated by densitometry. The sensitivity was given as the reciprocal of the exposure required to give an optical density of 0.1 above fog density. The photoconductivity of the emulsion grains was measured at –100°C by use of a 9-GHz microwave photoconductivity apparatus and given as the signal intensity.

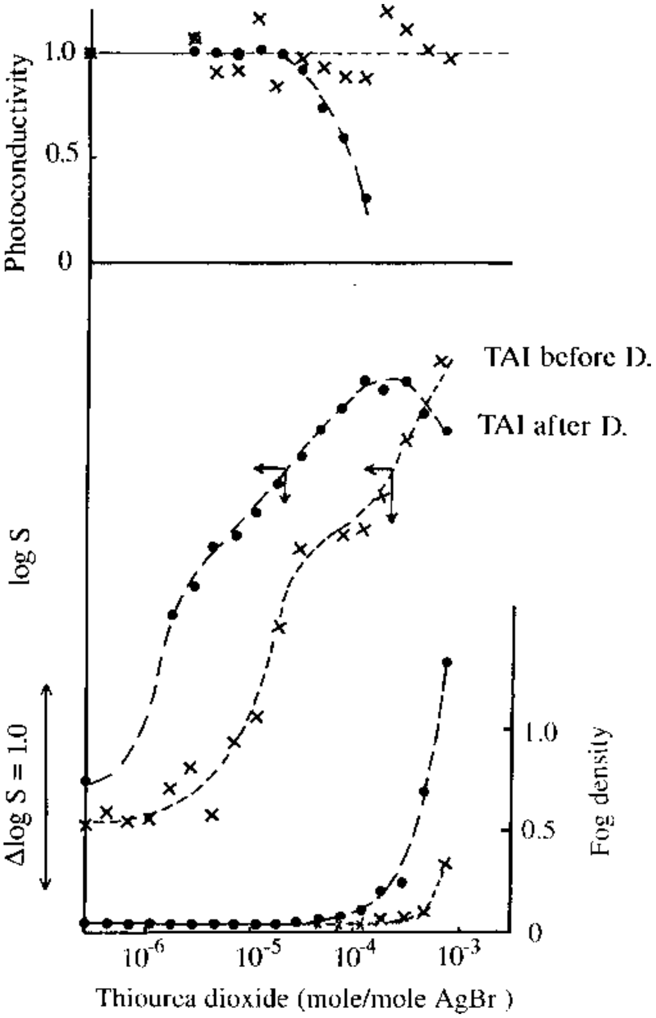

Figure 3. Sensitivity, fog density, and photoconductivity of octahedral AgBr emulsions, to which TAI was added before (×) and after (●) the digestion for their reduction sensitization with thiourea dioxide.

The diffuse reflectance spectra of the emulsions were measured and transformed according to the Kubelk–Munk equation to obtain the absorption spectra and concentrations of reduction sensitization centers and fog centers.[1]

To obtain information on the rate of development of fog centers formed by reduction sensitization, optical density of a coated emulsion layer at 1090 nm was measured as a function of time of development using equipment developed by Ohzeki.[10]

Results and Discussion

Figure 3 shows sensitivity, fog density, and photoconductivity of reduction-sensitized octahedral AgBr emulsions to which TAI was added before and after the digestion for reduction sensitization in the presence of thiourea dioxide in the amount indicated on the abscissa. Figure 4 shows the relation between sensitivity and photoconductivity of the emulsions shown in Fig. 3. As discussed in this series of investigations, we consider that the sensitivity increase without decrease in photoconductivity was brought about by R centers, while the sensitivity increase with decrease in photoconductivity was brought about by

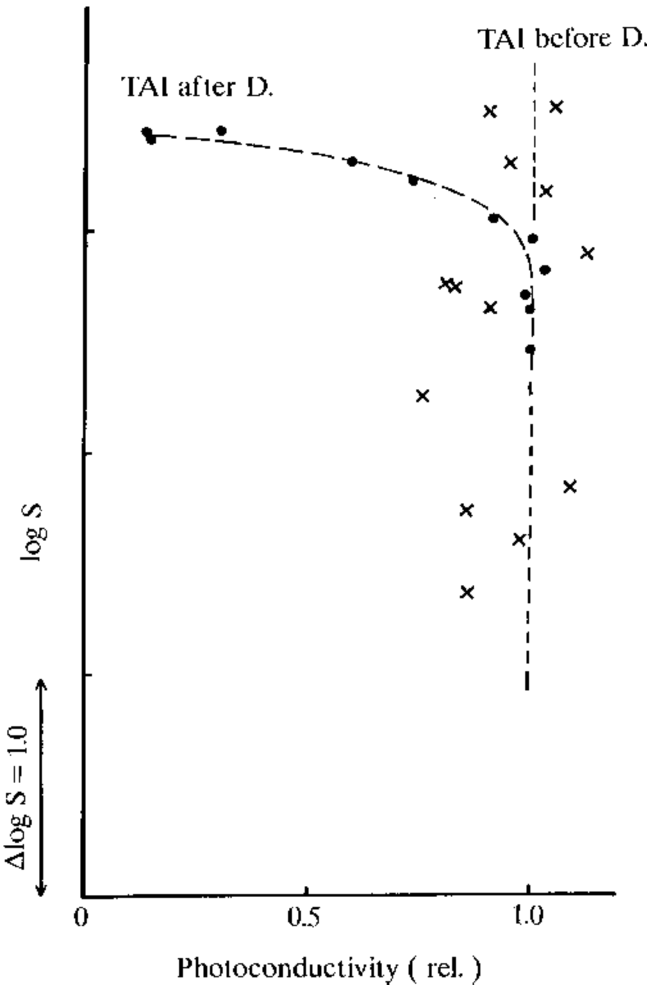

Figure 4. Relation between sensitivity and photoconductivity of the reduction-sensitized AgBr emulsions shown in Fig. 3.

P centers. Accordingly, Fig. 4 indicates that addition of TAI to the emulsions before their digestion for reduction sensitization could depress the formation of P centers. Similar results were obtained by use of cubic AgBr emulsions. The addition of PMT before digestion for reduction sensitization gave similar results.

In a previous work,[1] it was shown that the sensitivity of reduction-sensitized AgBr grains increased in two steps with increasing amounts of reduction sensitizer; the first and second steps were ascribed to the contributions by R centers and by P centers, respectively, because only the second step was associated with the decrease in the microwave photoconductivity of the grains. As seen in Fig. 3, sensitivity increased stepwise with increasing amounts of reduction sensitizer when TAI was added before the digestion. However, the discrimination between the first and second steps in this work was much less distinct than that in the former case, and the second step was not associated with a decrease in the conductivity of the grains. We therefore infer that the weak stepwise increase in sensitivity observed in Fig. 3 does not necessarily indicate the separate formation of R centers and P centers with increasing amounts of reduction sensitizer.

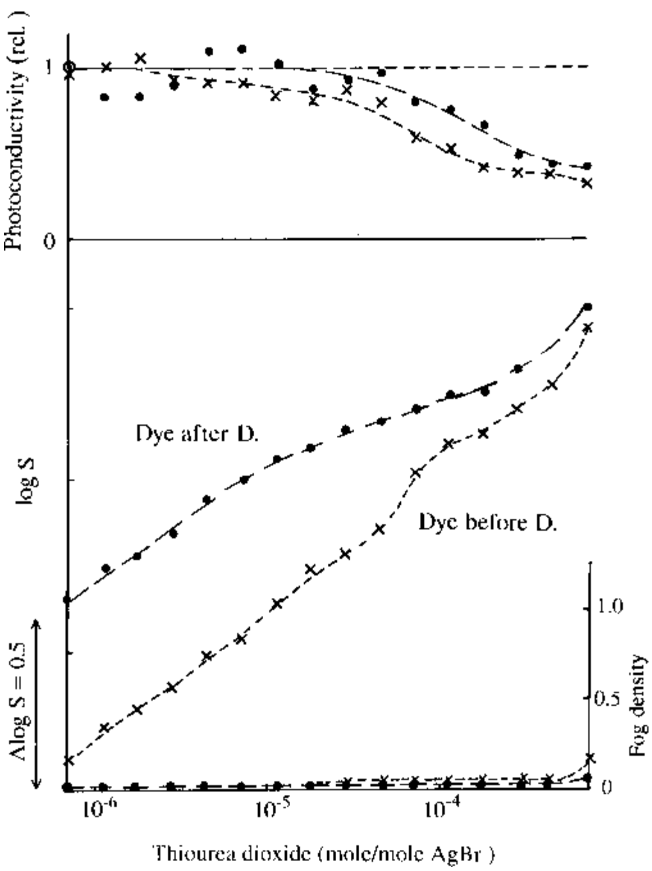

Figure 5. Sensitivity, fog density, and photoconductivity of octahedral AgBr emulsions, to which Dye 1 was added before (×) and after (●) the digestion for their reduction sensitization with thiourea dioxide.

Figure 5 shows sensitivity, fog density, and photoconductivity of reduction-sensitized octahedral AgBr emulsions to which Dye 1 was added before and after digestion for reduction sensitization in the presence of thiourea dioxide in the amounts indicated on the abscissa. Figure 6 shows the relation between sensitivity and photoconductivity of the emulsions shown in Fig. 5. Accordingly it appears that the addition of Dye 1 to the emulsions before their digestion for reduction sensitization may enhance the formation of P centers. Similar results were obtained using cubic AgBr emulsions.

The above results can be taken as verifying the prediction for control of R and P centers illustrated in Fig. 1. Namely, the formation of P centers could be enhanced by compounds preferably adsorbed to negatively charged sites and neutral sites on silver halide grains and depressed by compounds preferably adsorbed to positively charged sites.

Figure 7 shows the sensitivity and fog density of cubic AgCl emulsions, which were reduction-sensitized with DMAB in the amounts indicated on the abscissa. With increasing amounts of DMAB, reduction sensitization achieved only a weak sensitivity increase, which was then followed by severe fog formation. By comparing the result in Fig. 7 with those in Figs. 3 and 5, we judge that reduction sensitization is less effective for AgCl emulsions than for AgBr emulsions.

To improve reduction sensitization of AgCl emulsions, an attempt was made to modify the formation of reduction sensitization centers according to the prediction illustrated in Fig. 1 as verified by the results of the experiments with AgBr emulsions shown in Figs. 3 to 6. Figure 7 also shows the sensitivity and fog density of AgCl emulsions, which were reduction-sensitized in the presence of TAI. As seen in this figure, TAI could improve reduction sensitization of AgCl emulsions by depressing the

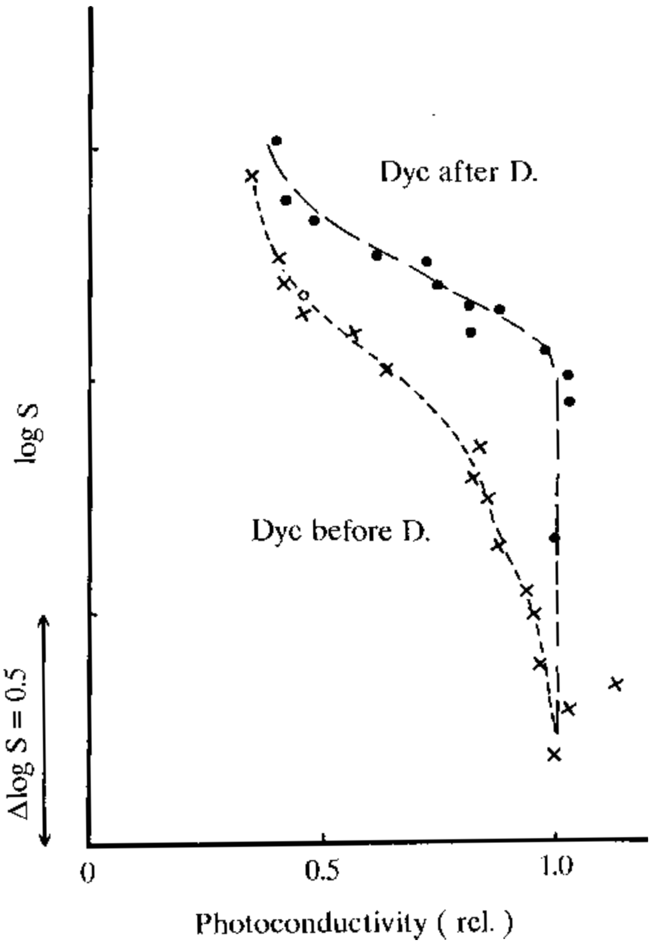

Figure 6. Relation between sensitivity and photoconductivity of the reduction-sensitized AgBr emulsions shown in Fig. 5.

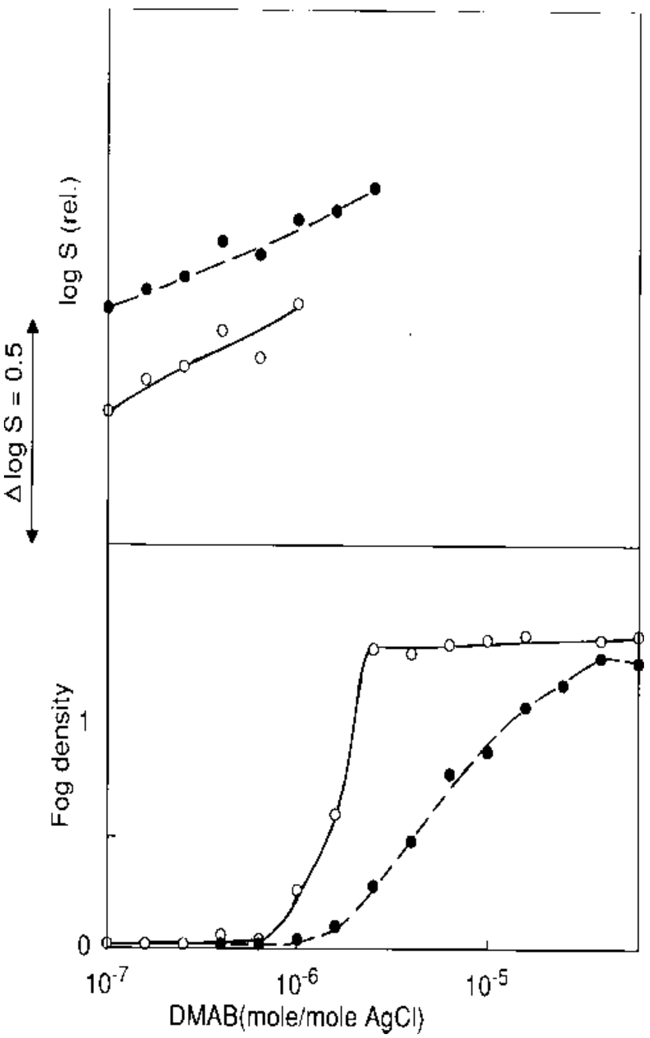

Figure 7. Sensitivity and fog density of AgCl emulsions reduction-sensitized with DMAB in the absence (O) and presence of (●) TAI of 0.014 mole/mole AgCl added before digestion for their reduction sensitization.

formation of fog centers and increasing the degree of the sensitivity increase caused by reduction sensitization. According to the above prediction, this result indicates that reduction sensitization of AgCl emulsions may be improved by depressing the formation of P centers.

Significant improvement in reduction sensitization of AgCl emulsions was achieved by adding PMT to the emulsions before their digestion for reduction sensitization. Figure 8 shows the sensitivity and fog density of AgCl emulsions to which PMT was added before and after their digestion for reduction sensitization. As seen in this figure, the addition of PMT before the digestion brought about significant sensitivity increase with marked reduction of fog density.

Figure 9 shows the photoconductivity along with sensitivity and fog density of reduction-sensitized AgCl grains in emulsions digested for reduction sensitization in the absence and presence of PMT. We note that fog centers markedly decreased the conductivity of the grains in the presence of PMT, while they had little influence on the photoconductivity of the grains in the absence of PMT. As described in a former article,[11] photoelectrons produced in AgCl grains are captured by electron traps on the surface, i.e., silver ions at surface kink site, according to diffusion-limited kinetics. This means that the introduction of any additional electron traps to the grain surface cannot influence the photoconductivity of AgCl grains unless silver ions at surface kink sites are modified. Taking into account the fact that PMT ions strongly interact with silver ions at surface kink sites, the results obtained in Ref. 11 clearly explain why the photoconductivity of AgCl grains in the absence of PMT was not influenced by electron traps such as fog centers, while the photoconductivity of AgCl grains in the presence of PMT was sensitive to and decreased by electron traps.

As seen in Fig. 9, the significant increase in sensitivity caused by reduction sensitization in the presence of PMT was not associated with decrease in photoconductivity of the emulsion grains. This result indicates that the significant increase in sensitivity caused by reduction sensitization in the presence of PMT was not a consequence of P centers acting as electron traps, but of R centers acting as positive-hole traps, and in AgCl emulsions the sensitivity increase caused by reduction sensitization is solely due to R centers, contrary to the case of AgBr emulsions, in which the sensitivity increase caused by reduction sensitization is due to both R centers and P centers.[1]

Figure 10 shows the sensitivity and fog density of AgCl emulsions, reduction-sensitized in the presence of PMT and then hydrogen-hypersensitized. As seen in this figure, the maximum sensitivity achieved with reduction sensitization was nearly equal to the sensitivity achieved with hydrogen hypersensitization, whereby sensitivities

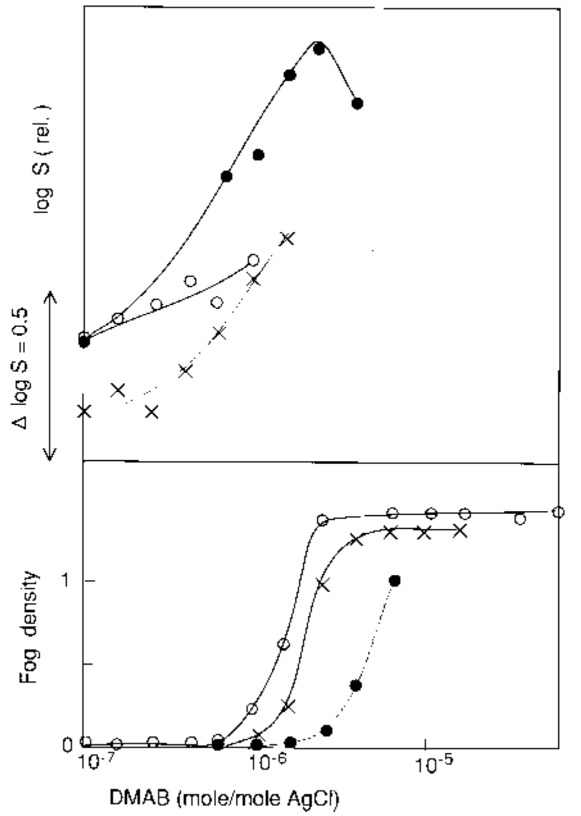

Figure 8. Sensitivity and fog density of AgCl emulsions reduction-sensitized with DMAB in the absence (O) and presence (●, ×) of PMT of 0.0025 mole/mole AgCl added before (●) and after (×) digestion for reduction sensitization.

of the emulsion reduction-sensitized with various amounts of DMAB and then hydrogen hypersensitized were independent of the amounts of DMAB. Because hydrogen hypersensitization solely provides silver centers acting as positive-hole traps,[12] the result in Fig. 10 confirms that the sensitivity increase of AgCl emulsions caused by reduction sensitization was brought about by R centers.

As described above, compounds preferably adsorbed to positively charged surface sites that depress the formation of P centers.on AgBr grains can reduce fog density, and the sensitivity increase then observed is accordingly brought about by R centers. These results indicate that P centers, which we propose to be composed of Ag_2 clusters at positively charged kink sites, act as fog centers on AgCl emulsions and only R centers are reduction sensitization centers for AgCl emulsions.

Figure 11 shows the developed optical density as a function of time of development for coated layers of AgCl emulsions fogged to various levels by reduction sensitization. The rate of development was very small especially in partially fogged emulsions, but increased with increasing amounts of DMAB used as reduction sensitizer. Because the rate of development of the smallest latent images centers comprising four or five silver atoms is rapid,[10] this result supports the idea that P centers composed of silver dimers, smaller than the smallest latent image centers, are fog centers with a small propensity for development in reduction-sensitized AgCl emulsions.

A DMAB molecule should be able to reduce six silver ions.[13,14] The total number of silver atoms in fog centers in reduction-sensitized AgBr emulsions, estimated by elec-

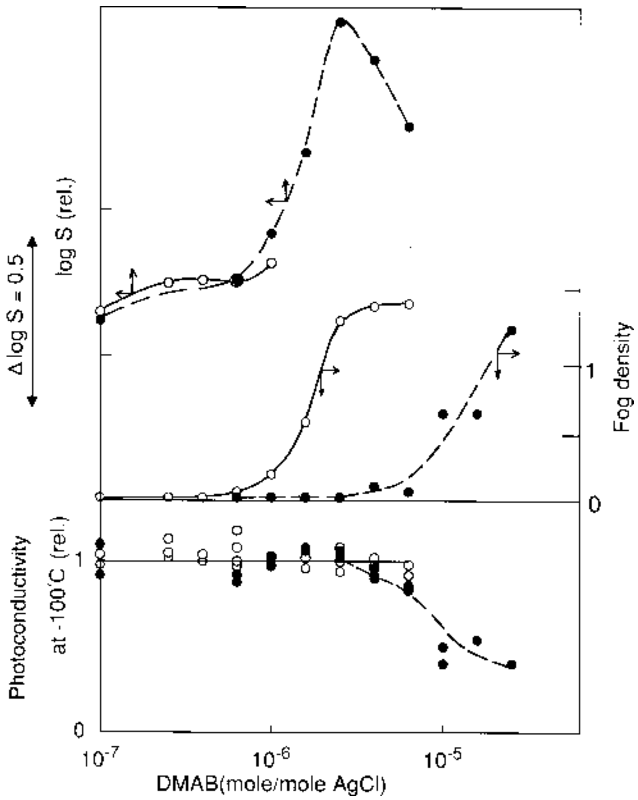

Figure 9. Sensitivity, fog density, and photoconductivity of AgCl emulsions reduction-sensitized with DMAB in the absence (O) and presence (●) of PMT of 0.0025 mole/mole AgCl.

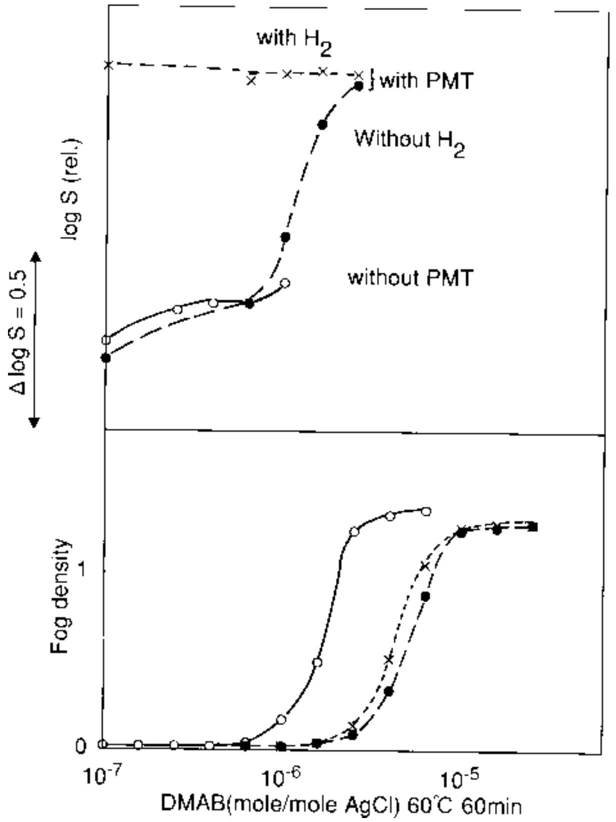

Figure 10. Sensitivity and fog density of AgCl emulsions reduction-sensitized with DMAB in the absence (O) and presence (●, ×) of PMT of 0.0025 mole/mole AgCl. The fresh (O, ●) and hydrogen-hypersensitized (×) coated emulsion layers were subjected to sensitometry.

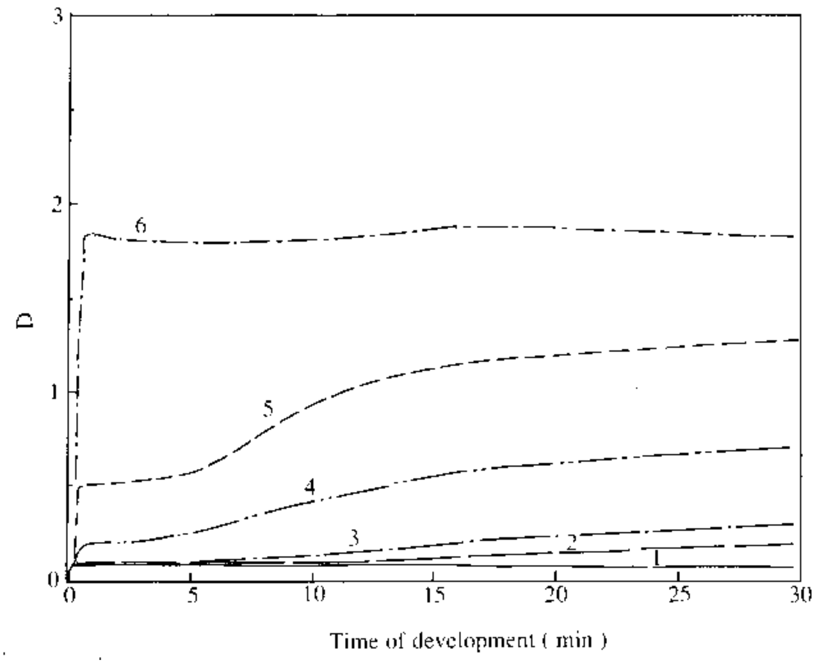

Figure 11. Optical density at 1090 nm as a function of time of development of coated layers of AgCl emulsions reduction-sensitized with DMAB of 0 (1), 0.4 (2), 0.6 (3), 1.0 (4), 1.6 (5), and 2.5 (6) $\times 10^{-6}$ mole/mole AgCl.

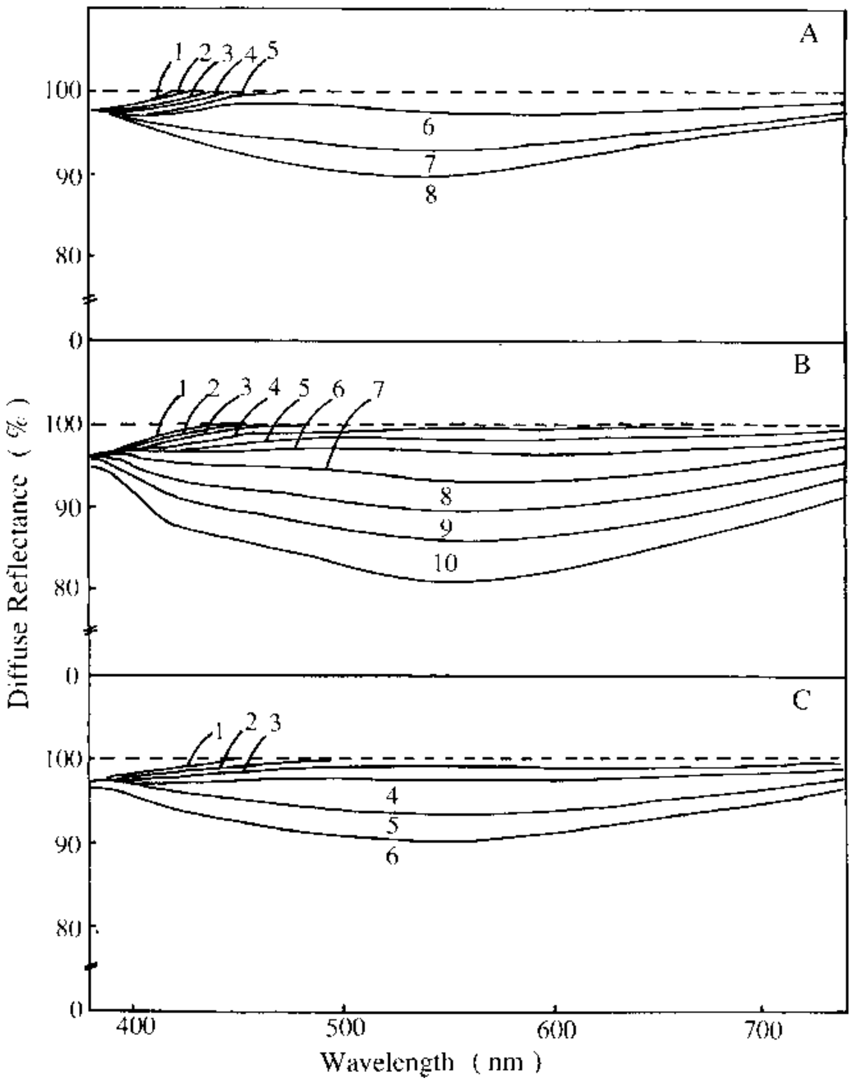

Figure 12. Diffuse reflectance spectra of AgCl emulsions reduction-sensitized with DMAB in the absence (A) and presence of PMT of 0.0025 mole/mole AgCl added before (B) and after (C) the digestion for reduction sensitization. The amounts of DMAB added to the emulsions were 0 (1), 0.6 (2), 1.0 (3), 1.6 (4), 2.5 (5), 4.0 (6), 6.3 (7), 10 (8), 16 (9), and 25 (10) $\times 10^{-6}$ mole/mole AgCl.

tron microscopy was larger by as much as six times the number of DMAB molecules used for the reduction-sensitization,[15] indicating that the yield for reduction of silver ions on silver halide grains by DMAB was surprisingly high. Accordingly as many as 600 P centers per grain were formed in emulsion 4 of Fig. 11, that was slightly fogged by reduction sensitization with DMAB at 1.0×10^{-6} mole/mole AgCl. This result indicates that no more than one among 600 P centers on a AgCl grain may initiate development of the grain during development by MAA-1 at 20°C for 10 min and developability of a P center itself is therefore very small.

Because P centers as well as latent subimage centers on AgBr grains could initiate development under more intense conditions of development,[16] we do not consider that the difference in developability between P centers on AgCl and AgBr grains is significant, but rather that it reflects the difference in the rate of development between silver clusters on AgCl and AgBr grains.

Figure 12 shows the diffuse reflectance spectra of reduction-sensitized AgCl emulsions to which PMT was added before and after the digestion for reduction sensitization. Reduction sensitization of AgCl emulsions gave rise to two absorption bands. One of them appeared at around 420 nm, and the other broad one then appeared with increasing amounts of DMAB for reduction sensitization at around 540 nm. The absorption band at 540 nm could be clearly ascribed to fog centers, because the amounts of DMAB for the appearance of the 540 nm band as seen in Fig. 12 coincided well with that for the appearance of fog centers as seen in Figs. 8 through 10.

We therefore infer that R centers of reduction sensitization give rise to the other absorption band which appears at 420 nm. In accord with this assignment, the amounts of DMAB for the appearance of the absorption band at 420 nm as seen in Fig. 12 coincided with that for the appearance of the sensitivity increase caused by R centers as seen in Figs. 8 through 10, although the absorption band was too weak for us to estimate the concentration of these centers as a function of the amounts of DMAB.

The wavelength of the absorption peak for R centers, observed at 412 nm on AgCl grains, is close to the wavelength of one of the absorption peaks of silver dimers, observed at 412 nm in rare gas matrix by Ozin and Huber.[17] The wavelengths of other absorption peaks were too short to be discriminated from the absorption band of AgCl in the diffuse reflectance spectra of AgCl emulsions. The wavelength of the absorption band of R centers is also close to that of the absorption peak of silver dimers in the gas phase.[18] This result supports the proposed model, according to which R centers are silver dimers formed at electrically neutral kink sites, which thus physically interact with the surface of the silver halide. ▲

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