Silver Clusters of Photographic Interest: Reduction Sensitization of Silver Chloride Emulsions

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Abstract

It was found that the addition of PMT and TAI to AgBr emulsions before their digestion for reduction sensitization with DMAB depressed the formation of P centers. The digestion for reduction sensitization of a cubic AgCl emulsion with increasing amount of DMAB brought about only slight sensitivity increase before the appearance of severe fog. The addition of PMT and TAI to the AgCl emulsion before the digestion depressed the fog formation and achieved significant sensitivity increase. The analysis of the above-stated phenomena revealed that the sensitivity increase was brought about by R centers, while P centers initiated development. The absorption band of R centers on AgCl grains appeared at 420 nm, being in good accord with that of Ag_2 in a rare gas matrix.

Introduction

In the papers of this series, a model has been proposed[1] and revised[2] for R centers acting as traps for positive holes and P centers acting as traps for photoelectrons on fine AgBr emulsion grains. The revised model has proposed that a P center is a Ag_3^+, which is formed by the combination of a Ag_2 with a Ag^+ at a kink site, and that the lowest unoccupied electronic energy level of a P center is much lower than that of an R center.

This study was an extension of the studies in this series on AgBr emulsions to a AgCl emulsion, and provided a new knowledge on silver clusters of photographic interests.

Experiments

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 for references. These emulsions were subjected to digestion for reduction sensitization with dimethylamineborane (DMAB). In order to control the formation of reduction sensitization centers by silver-complexing agents, 1-phenyl-5-mercapto-tetrazole (PMT) and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) were used in this study. The layers of the above-stated emulsions were prepared by coating them on TAC film bases and subjected to the measurements of sensitometry and photoconductivity.

The coated emulsion layers were exposed to a tungsten lamp with color temperature of 2856K for 10 sec through a continuous wedge, developed for 10 min at 20°C by use of a surface developer MAA-1, washed, dried, and subjected to the measurement of optical density. The sensitivity was given by the reciprocal of the exposure required to give an optical density of 0.1 above fog density. The photoconductivity of the above-stated emulsion grains was measured at - 100°C by use of a 9 GHz microwave photoconductivity apparatus,[3] and given by its signal intensity.

The diffuse reflectance spectra of the above-stated reduction-sensitized emulsions were measured and treated by the Kubelka-Munk equation[1,4] in order to obtain the absorption spectra and concentrations of reduction sensitization centers and fog centers.

Results and Discussions

Figure 1 shows the sensitivity and fog density of the AgCl emulsion, which was reduction-sensitized with increasing amount of DMAB. The reduction sensitization could bring about only slight sensitivity increase before the appearance of severe fog. The addition of TAI and PMT to the AgCl emulsion before the digestion for the reduction sensitization could depress the fog formation and bring about significant sensitivity increase. The result with PMT is shown in Figure 1, and was studied in more details.

As shown in Figure 1, hydrogen hypersensitization could bring about significant sensitivity increase without causing fog formation for the AgCl emulsion, and its sensitizing effect was not additive to that of the reduction sensitization in the presence of PMT. Since hydrogen hypersensitization centers are almost entirely positive hole traps under normal condition,[6] it is considered that the reduction sensitization centers formed in the presence of PMT were R centers. This idea was further supported by the observation that the reduction sensitization centers formed in the presence of PMT did not decrease the photoconductivity of the grains, as shown in Figure 1.

Since PMT depresses the formation of P centers, it is considered that the depression of the formation of P centers on the AgCl grains by PMT could depress the fog formation and bring about significant sensitivity increase. It is therefore considered that the sensitivity increase was almost entirely caused by R centers, and that P centers on the surface of AgCl grains initiated development. The development caused by P centers was however very slow. Taking into account the consideration that many P centers should be formed on each grain, the probability of each P center to initiate development was very small.

In the diffuse reflectance spectra of the AgCl emulsions, which were reduction-sensitized in the presence of PMT, R centers gave the absorption band at 420 nm, being in good accord with that of Ag_2 suspended in a rare gas matrix, which appeared at 419 nm according to the measurement by Ozin et al.[7] This result supports the present model that R centers are composed of Ag_2.

On the contrary to the fact that P centers did not initiate development in AgBr emulsions, they could initiate development in a AgCl emulsion, although the probability of each P center to initiate development was very small. The observed difference in developability of P centers between AgBr and AgCl emulsions was ascribed to the difference in the silver potential of the centers during development arising from the difference in solubility between them. The revised model for a P center[2] as a Ag_3^+ support an idea that the lowest unoccupied electronic energy level of a P center is so deep that at least one of many P centers on a AgCl grain could accept an electron from a developer to initiate the development of the grain.

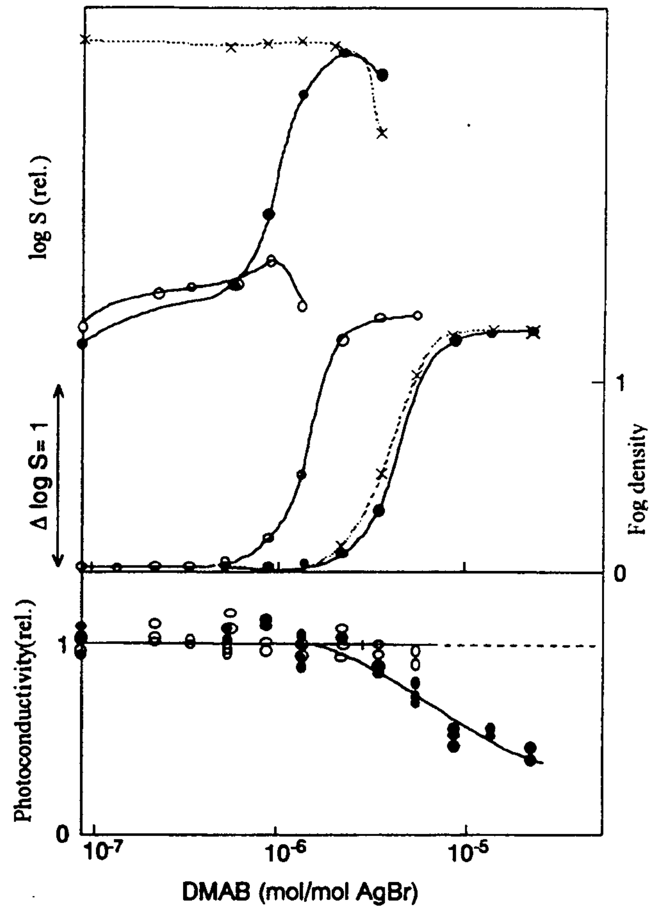

Figure 1. Sensitivity, fog density and microwave photoconductivity of cubic silver chloride emulsions, which were reduction sensitized in the absence (O) and presence (●) of PMT (5.1 mmole/mole AgCl), and sensitivity and fog density of the emulsions, which were reduction-sensitized in the presence of PMT and hydrogen-hypersensitized at 40°C for 4 hours (×) The reduction sensitization was carried out by digested the emulsions at 60°C for 60 min in the presence of DMAB as a reduction sensitizer with amount shown in the abscissa.

References

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