Effects of Iridium doping and Chemical Sensitization on Reciprocity Law Failure and Latent Image Stability

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Abstract

It is known that Iridium doping into silver halide micro crystals has significant effects not only on the reciprocity law failure characteristics, but also on the behavior of latent image formation and its preservation. To understand the phenomena more in detail, authors investigated the effects of Iridium doping on the formation processes and the formed states of silver sulfide clusters on silver chloride micro crystals, by electron microscopic observation method. The result was that the presence of Iridium ion significantly influenced the sulfur sensitization reaction and the formation of silver sulfide clusters on silver chloride micro crystals. Authors considered that these phenomena also contributed to the effects of Iridium doping on the reciprocity law failure characteristics and the latent image behavior.

Introduction

Iridium doping is one of the most famous measures to improve the reciprocity law failure characteristics of silver halide emulsions. In addition, Iridium doping is also known to affect the behavior of latent image formation and its preservation, and it often causes the formation of unstable latent images. Some studies were made to understand the phenomena and its mechanisms. For example, Zwicky reported the mechanism of the delayed formation of latent image caused by iridium doping into silver halide emulsion¹. But the most of the studies suggested the main factors of the phenomena were related to the electron traps generated by Iridium doping in the silver halide crystals.

On the other hand, it is also well known that the state of silver sulfide formed through chemical digestion greatly influences the photographic characteristics of silver halide emulsions. Since the number, the size, and their distribution of silver sulfide on silver halide micro crystals are considered to be important factors, which dominate photographic performances, several studies were made to characterize the state of silver sulfide clusters formed on silver chloride micro crystals. For example, Farnell, Flint and Birch reported the distribution of silver sulfide on sensitized tabular grains of silver bromide $emulsion^{2}$.

Some Studies were also made to characterize the emulsion under the variously combined conditions of Iridium doping and chemical sensitization. For example, Owaki and Hirano observed the delayed formation of latent image, which was considered to be caused by thermally ejected electron from silver atoms formed in adjacent to iridium ions³⁾. They concluded that delayed formation of latent image was caused by the influence of chemical sensitization, but no suggestion was made to speculate the relationship between Iridium doping and the state of silver sulfide clusters on silver chloride micro crystals.

To understand the behavior of Iridium doping more in detail, authors investigated the formation process and the states of silver sulfide clusters in the presence of Iridium ions by using sulfur or gold and sulfur chemical sensitization.

Experiments

Emulsions, used in this study, were prepared by a controlled double jet technique, and consisted of cubic silver chloride grains. Potassium hexachloroiridate(IV) was added as an Iridium dopant during silver chloride crystal formation. Sodium thiosulfate was used as a sulfur sensitizer, and tetrachloroaurate(III) was used as a gold sensitizer.

Radio-chemical tracer experiments were conducted to measure the reaction rate and the quantity of silver sulfide formed by chemical sensitization, by using sodium thiosulfate with the outer sulfur atom labeled by radioactive isotope (S^{35}).

To observe the size and number distribution of silver sulfide clusters formed on silver chloride grains, authors used gelatin shells (replicas) method of silver chloride grains for transmission electron microscope (TEM) observation ^{2),5),6}.

Results and Discussions

The reaction rate of silver sulfide formation, in which sodium thiosulfate was used as a chemical sensitizer, was increased by the presence of Iridium ions (Fig.1). The number of silver sulfide clusters formed on silver chloride emulsion grains was increased in the presence of Iridium ions (Table 1). The average size of silver sulfide clusters formed on silver chloride emulsion grains was reduced by the presence of Iridium ions. (Fig.2, Table1)

These results indicate that the presence of Iridium ion influenced the sulfur sensitization reaction, and so that the formed state of silver sulfide clusters on silver chloride emulsion grains.

Authors considered that these phenomena contributed to unique effects of Iridium doping on the characteristics of silver chloride emulsions, such as unstable latent image forming or change of reciprocity law failure characteristics.

Conclusion

It was observed that the presence of Iridium ion accelerated the reaction of silver sulfide formation, increased the number, and reduced the average size of silver sulfide clusters formed on silver chloride emulsion grains.

The influence of Iridium on chemical sensitization was considered to be one of the important factors why Iridium doping showed unique effects on the characteristics of silver chloride emulsions.

References

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Biography

Masanobu Miyoshi received his bachelor of engineering in Applied Chemistry in 1977, and master of engineering in 1979 from Kyushu University at Fukuoka, Japan. Since 1979 he has worked in R&D Center for photosensitive materials at Konica Corporation in Kanagawa, Japan. His work has primarily focused on the development of photosensitive color print materials, including amateur and professional color papers, and other silver-based display materials. He is a member of the IS&T.



Table 1 Effect of iridum complex doping on number and average size

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Chemical sensitizer	Adding of dopant during crystal formation	Average number of silver sulfide clusters per grain	Average size of silver chloride clusters(*10 ⁻ ¹⁰ m)	Distribution of silver sulfide clusters on silver chloride grains
Sodium thiosulfate	Potassium hexachloroiri date(IV)	87	38	Big clusters on coners, Small clusters on planes
	Non	49	45	Big clusters on coners, Small clusters on planes



Fig.2 Effect of iridum complex doping on size distribution of silver sulfide clusters after chemical sensitization by sodium thiosulfate