

Effect of Gold + Sulfur Sensitization on the Delayed Formation of Latent Image Specks in a Vacuum

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Abstract

Behavior of the delayed formation of latent image specks in a vacuum for gold+sulfur sensitized emulsions with cubic and octahedral grains was studied. Sensitivity increase by storing in a vacuum after exposure diminished and disappeared finally with the sensitization level. This behavior was the same at both emulsions. However, the octahedral grain emulsion showed two-step increase, while the cubic grain emulsion showed one-step increase. Latent sub-image specks become developable in the delayed formation process, and the gold+sulfur sensitization also makes those specks developable without the process. The difference between cubic and octahedral grain emulsions was discussed.

Introduction

The delayed formation of latent image specks in a vacuum is the phenomenon that new latent image specks are formed in storage when the photographic film is exposed and stored in a vacuum.[1] We have reported that the increasing rate of developed grains by this process was approximated by the following equation,[1,2]

$$P = P_0 + \Delta P \{ 1 - \exp(- K \cdot t)\} \quad (1)$$

where, P is a fraction of the number of developed grains relative to the total number of grains, t is a storage time in a vacuum after exposure, P_0 is a value of P at t = 0, ΔP is an increasing value of P, and K is an apparent rate constant. This equation indicates that P increases exponentially and then saturates, and this suggests that the developable latent image specks are formed by one-step process. Hence, we considered this phenomenon as a coagulation of small photolitic silver clusters expressed by the equation,[1]

$$Ag_{n-1} + Ag \rightarrow Ag_n \quad (2)$$

where, Ag_{n-1} is an undevelopable latent sub-image speck (LSIS), Ag is a single silver atom species (SSAS), Ag_n is a latent image speck, and n is the minimum number of silver atoms to get the developability.

We regard this phenomenon as a kind of latensification process, where the undevelopable LSIS are latensified by the storage in a vacuum. Previously we have reported the effect of gold latensification to the delayed formation for cubic grain emulsions.[1,3] The same sensitivity was obtained by the gold latensification or by the storage in a vacuum. For the successive treatments the sensitivity did not show any increase in several cases. LSIS got the developability by either of the two. This indicates that each treatment gives the same effect but double treatments do not increase the sensitivity more. However, in other cases the result was a little different. When the both treatments were given to the sample successively, the sensitivity increased more than a single treatment by either of the two.

Previously we have reported the effect of sulfur[4] or reduction[5] sensitization. The latter depressed the delayed formation and the former did not, but we have not examined with the gold+sulfur sensitization. This is very interesting, especially from a view of effect of gold.

Moreover, we observed the two-step increase of sensitivity by the delayed formation for the phenosafranine-added emulsions.[3] This was the first observation of the two-step increase. We secondly observed it by the octahedral grain emulsion without any sensitization and addenda.[6] Then we studied phenomena of the delayed formation for cubic and octahedral grain emulsions with gold+sulfur sensitization.

Experimental

Two photographic emulsions were used. Both consisted of pure silver bromide monodisperse grains, and one consisted of cubic grains of 0.8 μm edge length and the other consisted of octahedral grains of 0.8 μm diameter.

For the treatment of sensitization we added a certain amount of sensitizer to the cubic grain emulsion at 65°C and also to the octahedral grain emulsion at 60°C, followed by

heating for 60 min. The sensitizer used was a complex of sodium gold-thiosulfate, $Na_3\{Au(S_2O_3)_2\}\cdot 2H_2O$. The amounts of sensitizer were 0.1, 0.2, 0.5, 1 and 2 μ mol per AgBr mol for the cubic grain emulsion and 0.2, 0.6 and 1.5 μ mol per AgBr mol for the octahedral one. We will represent them as Cub(0.1 μ SG) or Oct(1.5 μ SG), etc. A control sample was represented as U. These emulsions were coated into mono-grain layer on a polyester base.

The experimental apparatus and procedures were the same as described in earlier papers.[1-6] Frames of the sample film strip were exposed for 1 sec under blue light at 20°C in a vacuum chamber (ca. 10^{-3} ~ 10^{-4} Pa) one after another at certain intervals. It was stored in a vacuum until room air was introduced to the chamber. Afterwards, the film strip was immediately developed with M-AA-1 surface developer for 10 min at 20°C. Fixation was not carried out.

We counted the numbers of developed and undeveloped emulsion grains in a fixed area of each frame with an optical microscope and calculated P, the fraction of grains developed. We used this P value instead of the usual optical density. A set of characteristic curves of samples exposed and stored in a vacuum for certain periods was obtained. From these curves we took values of P at the same exposure and plotted them against the storage time t.

Experimental Results

At the cubic grain emulsions P shows an exponential one-step increase by the delayed formation. We approximated the increasing rate by Equation (1) and estimated ΔP and K values. On the other hand, the plottings of P versus t for the octahedral grain emulsions are shown in Fig. 1. The exposure value was taken at the point of P_0=0.3. At the unsensitized emulsion P also shows an exponential increase at first stage, but after provisional saturation P increased again showing an S-shaped curve and then reached a second saturation level. This is the same behavior as the previous report.[6] We approximated the increasing rate by Equation (1) for the first stage of increase.

For the sulfur+gold-sensitized emulsions, the behavior of increasing step was almost same as the unsensitized ones. At the cubic ones the pattern of increase was the exponential one-step increase. And at the octahedral ones P shows a two-step increase. First, exponential one and second, S-shaped one. We also approximated the increasing rate by Equation (1) for the first stage. Changes of ΔP and K to the sensitization level are shown in Table I. ΔP decreased with the sensitization level and finally became zero. At the highest level of sensitization the delayed formation did not occur. This behavior was same for both emulsions.

Discussion

At high level of sulfur+gold sensitization the delayed formation was depressed completely. Previously we have reported the effect of sulfur or reduction sensitization to the delayed formation.[4,5] At the sulfur sensitization ΔP was almost same as that of unsensitized one, while it decreased at the reduction sensitization. However, the latter did not depress the delayed formation completely.

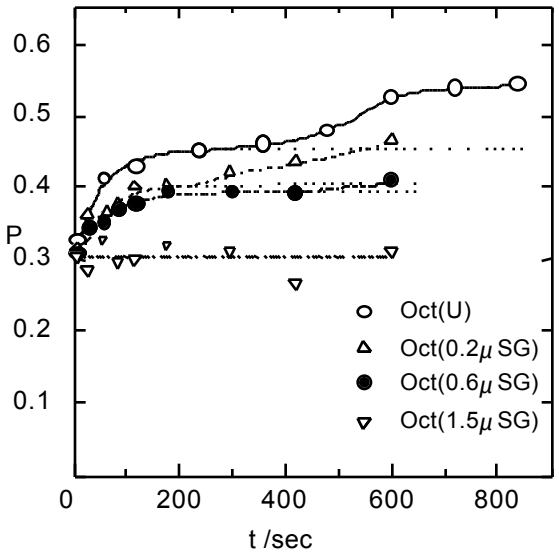

Figure 1. Increase of P at a certain exposure value with the time of storage in a vacuum after exposure for sulfur+gold-sensitized octahedral grain emulsions. The exposure value is the one that gives P_0 = 0.3 for each sample.

Many authors suggested that the sulfur+gold-sensitization decreased the number of photolitic metal atoms to the minimum in latent image speck to get the developability, and this was one effect of the sensitization. Hence, when the so-called latent sub-image specks got the developability in the sulfur+gold-sensitized emulsion, the delayed formation would not take place. In practice ΔP decreased with the sensitization level and became zero at the highest level. This suggests that the probability of LSIS getting the developablity increases with the sensitization level and finally almost all of LSIS become developable at the highest level. In other words, the minimum number of photolitic metal atoms for getting the developability would decrease at the sulfur+gold sensitization.

The sulfur+gold-sensitization depressed the delayed formation, but it did not alter the increasing pattern of P, whether to take the one-step or two-step increase. Those patterns would be a character of grains with different crystal habits, and never be affected by the sensitization. We have considered the mechanism of delayed formation at the one-step increase as Equation (2).

Table I. ΔP and K of the delayed formation with the sensitization level

Cubic Grain Emulsion		
Sensitization level	**ΔP**	**K (sec^{-1})**
U	0.28	$7.0 \times 10\text{-}^{3}$
0.1 μ SG	0.32	1.1×10^{-2}
0.2 μ SG	0.25	2.6×10^{-2}
0.5 μ SG	0.10	1.4×10^{-2}
1 μ SG	0	—
2 μ SG	0	—
Octahedral Grain Emulsion		
Sensitization level	**ΔP**	**K (sec^{-1})**
U	0.15	1.9×10^{-2}
0.2 μ SG	0.10	1.6×10^{-2}
0.6 μ SG	0.10	1.7×10^{-2}
1.5 μ SG	0	—

Hence, there are two possible mechanisms for the two-step increase. One is the two-step coagulation of SSAS as shown in Equation (3).

$$Ag_{n-2} + Ag \rightarrow Ag_{n-1} \quad (3\text{-}1)$$

$$Ag_{n-1} + Ag \rightarrow Ag_{n} \quad (3\text{-}2)$$

In this case there are two kinds of LSIS, Ag_{n-1} and Ag_{n-2}. If n was four, they would be Ag_3 and Ag_2 specks. The large induction period at the second increase will be explained well in this mechanism.

However, the two-step increase did not appear at the cubic grain emulsion, and the sulfur+gold sensitization depressed the delayed formation at both cubic and octahedral grain emulsions. Hence, this mechanism will suggest that Ag_2 specks do not exist in cubic grain emulsion and they become developable at sulfur+gold-sensitized octahedral grain emulsion.

And the other is a two pass mechanism of different rate constants to the coagulation of SSAS as shown in Eq. (4).

$$Ag_{n-1} + Ag \xrightarrow{k_1} Ag_{n} \quad (4\text{-}1)$$

$$Ag_{n-1} + Ag \xrightarrow{k_2} Ag_{n} \quad (4\text{-}2)$$

If it was a simple parallel reaction with different rate constant, the reaction rate would be shown as an exponential curve. As the second increase started after the first increase finished, the reaction (4-2) must start after the reaction (4-1) finishing. It is required to explain this large induction period at the second step increase.

References

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