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

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Behavior of the delayed formation of latent image specks in a vacuum on sulfur+gold-sensitized emulsions with cubic and octahedral grains was studied. The fraction of developed grains P increased by storing in a vacuum after exposure. In the cubic grain emulsion P exhibited an exponential one-step increase. On the octahedral grain emulsion P indicated a two-step increase. The first step was exponential and the second step was S-shaped. The delayed formation diminished with the increase of sensitization level and disappeared completely at the highest level. Latent subimage specks in the sulfur+gold-sensitized emulsion were developable by absorbing one photon, but not by adding one silver atom in the delayed formation process. The mechanism of the two-step increase in developability is also discussed.

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Introduction

We have found the phenomenon of delayed formation of latent image specks in a vacuum and reported some experimental results.[1–9] Accordingly, new developable latent image specks are formed after exposure, when the exposed photographic film is stored in a vacuum.[1] We considered this phenomenon as a coagulation of a small photolytic silver cluster with atomic silver, as expressed by the equation,[1]

$$\mathrm{Ag}_{n-1} + \mathrm{Ag} \rightarrow \mathrm{Ag}_n, \qquad (1)$$

where, Ag_{n-1} is an undevelopable latent subimage 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 obtain developability.

Only SSAS can migrate on an AgBr grain, other specks such as LSIS cannot. When SSAS encounters LSIS, this undevelopable LSIS absorbs it and grows into a developable speck. We also considered the migration mechanism of SSAS.[1,8,10] Although there were three possible mechanisms, namely migration of electrons, migration of positive holes, and migration of silver atoms, the experimental results suggested the migration of silver atoms to be the most likely one.[8,10]

The delayed formation did not take place in room air but took place weakly under intermediate conditions such as wet nitrogen or weak vacuum.[2] Lifetime of SSAS is not as long as for other silver clusters. Mitchell estimated the lifetime of the Ag atom in an AgBr grain to be about 1 sec.[11] This lifetime, in room air, would be insufficient to allow encounter with the other silver atom clusters. The lifetime will be prolonged in the vacuum or other conditions where there are less oxidizing species, and as a result, SSAS can encounter the LSIS to enable the delayed formation of latent image.

Malinowsky also suggested latent image formation by the process of coagulation of silver atoms, so-called "supersaturation mechanism."[12] He assumed the migration of the silver atom species in his theory. He considered that this process took place under room air conditions, in a shorter period.

We regarded this phenomenon as a kind of latensification process, where LSIS acquires developability on storage in vacuum. Up to now, we have mainly been interested in SSAS, its character or migration mechanism, etc. However, as LSIS becomes developable and so detectable as delayed formation of latent image, we acquire useful information about LSIS and the smallest size of developable silver specks.

Previously we reported the effect of gold latensification on delayed formation in cubic grain emulsions.[1,8] Although the results were a little complicated and substantial fog often appeared, similar sensitivity increases were observed with gold latensification and with storage in a vacuum. In several instances the sensitivity did not increase further with successive treatments. This suggested that each treatment produced the same effect. However, in other cases the result was a little different. The successive treatments increased the sensitivity more than the single treatment did. This suggested that there is a speck that acquires developability through two successive processes.

We have also reported the effect of sulfur[6,7] or reduction[10] sensitization on the delayed formation of latent image. The delayed formation was diminished by the latter with increasing sensitization level.[10] It was also diminished[6] or depressed[7] by the former at low sensitization levels, though it was restored again at a higher sensitization level.[6,7] However, we have not yet examined the effect of sulfur+gold sensitization. It is well

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known that the critical developable size of latent image specks decreases on sulfur+gold-sensitization. Therefore, it should be very interesting to observe how delayed formation appears in the case of sulfur+gold-sensitized emulsion.

We have also reported on the kinetics of increase of developable grains by delayed formation of latent image. In many cases we observed an exponential growth, as approximated by the following equation[1,4,5]:

$$P = P_0 + \Delta P \{1 - \exp(-K \bullet t)\}, \quad (2)$$

where P was a fraction of the number of developed grains relative to the total number of grains, t was the storage time in a vacuum after exposure, P_0 was the value of P at $t = 0$, ΔP was a coefficient, and K was the apparent rate constant. This equation suggested that the developable latent image specks were formed through a one-step process.[1]

In the meantime, we have occasionally observed a two-step increase of P. The first step was exponential, and the second step was described by an S-shaped curve with a large induction period. We first observed this phenomenon in the phenosafranine-treated emulsion[8] and then with octahedral grains without any sensitization or addenda.[9] We have proposed the two-step coagulation of LSIS and SSAS as one possible mechanism of the two-step increase.[9] This was represented as Eqs. 3 and 4:

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

$$Ag_{n-1} + Ag \rightarrow Ag_n. \quad (4)$$

However we could not provide a satisfactory explanation why the second increase did not take place in the cubic grain emulsion or what was the difference between the cubic and octahedral grain emulsions.

Thus we could have useful information about LSIS by comparing the behaviors of the delayed formation in the cubic and the octahedral grain emulsions. Therefore we studied the phenomena of the delayed formation on the sulfur+gold-sensitized cubic and octahedral grain emulsions.

Experimental

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

Two kinds of sensitizer were used. One was a complex of sodium gold-thiosulfate, $Na_3\{Au(S_2O_3)_2\} \bullet 2H_2O$, and the other was a combination of sodium thiosulfate, $Na_2S_2O_3 \bullet 2H_2O$ and sodium tetrachloroaurate, $NaAuCl_4 \bullet 2H_2O$. Both $Na_2S_2O_3$ and $NaAuCl_4$ were of commercial origin and $Na_3\{Au(S_2O_3)_2\}$ was synthesized from both. We symbolized the treatment using the complex as (SG) and that using the combination as (S+G).

For the treatment of (SG) we added certain amounts of the complex at 65°C to the cubic grain emulsion, and at 60°C to the octahedral grain emulsion, followed by heating for 60 min. The amounts of complex were 0.1, 0.2, 0.5, 1, and 2 μmol per AgBr mol for the cubic grain emulsion and 0.2, 0.6, and 1.5 μmol per AgBr mol for the octahedral one. The mole ratio of gold to sulfur was 1:2. We will represent them as Cub(0.1 μ SG) or Oct(1.5 μ SG), etc.

For the treatment of (S+G) we used the cubic grain emulsion. We added $Na_2S_2O_3$ and $NaAuCl_4$ successively at 1 min intervals at 65°C, followed by heating for 60 min. The amounts of $NaAuCl_4$ were 0.1, 0.5, and 1 μmol per AgBr mol and the mole amount of $Na_2S_2O_3$ was twice as much as $NaAuCl_4$ to keep the mole ratio of gold to sulfur 1:2. We will represent them as Cub(0.1 μ S+G), etc.

A control sample represented as U was prepared without any addition of the sensitizers or heating. The 0 SG sample was prepared with heating for 60 min without any addition of the sensitizers. Those emulsions were coated in thin mono-grain layers on a polyester base to avoid the effects of moisture and oxygen occluding in the gelatin layer.

The experimental apparatus and procedures were the same as described in the earlier papers.[1–10] Frames of a sample film strip were exposed for 1 sec under blue light at 20°C in a vacuum chamber (ca. 10^{-3} to approximately 10^{-4} Pa) one after another at certain intervals. They were stored in vacuum until room air was introduced to the chamber. Afterwards, the film strip was immediately developed with modified M-AA-1 surface developer for 10 min at 20°C. (The amount of sodium metaborate in the developer was doubled to depress the formation of filamentary silver.) This made it easier to count the developed grains with an optical microscope in the next step. We carried out sensitometry in room air condition with a JIS III type sensitometer to compare the sensitivity of each emulsion.

We counted the numbers of developed and undeveloped emulsion grains in a fixed area of each film strip with an optical microscope and calculated P_{dev}, the fraction of grains developed. The fraction of grains developed without exposure, P_{fog}, was also calculated. To eliminate the effect of fog we evaluated the fraction P by the following equation, and used this P value instead of the usual optical density.

$$P = (P_{dev} - P_{fog}) / (1 - P_{fog}). \quad (5)$$

Experimental Results

Characteristic curves at various sensitization levels exposed in room air are shown in Fig. 1 for Cub(SG) samples, in Fig. 2 for Cub(S+G) samples, and in Fig. 3 for Oct(SG) samples. The ordinate of each figure does not represent the optical density, but rather the P value. The P value increased remarkably with the sensitization level on every sample. It increased monotonically and finally fog appeared at the highest sensitization level. The fog values for each sample are shown in Table I, and every curve was corrected for the fog by Eq. 5. The fog induced by the combination seems to be larger than that induced by the complex.

TABLE I. Amount of Fog at Each Sensitization Level Represented as *P* Values

Sensitization level	Fog
Cub (U)	0.00
Cub (SG)	
0 SG	0.00
0.1 μ SG	0.00
0.2 μ SG	0.04
0.5 μ SG	0.07
1 μ SG	0.09
2 μ SG	0.10
Cub (S+G)	
0.1 μ S+G	0.01
0.5 μ S+G	0.04
1 μ S+G	0.30
Oct (SG)	
U	0.00
0.2 μ SG	0.00
0.6 μ SG	0.01
1.5 μ SG	0.02

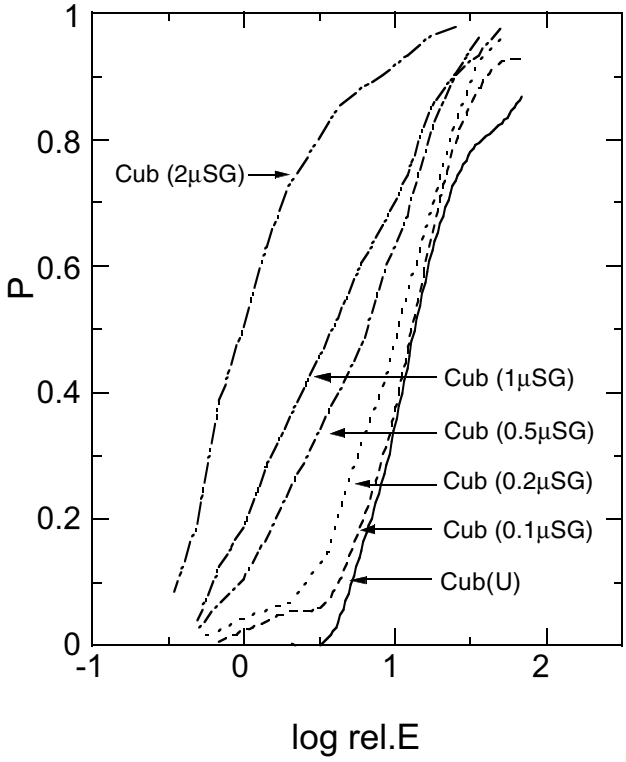

Figure 1. Characteristic curves of the Cub(SG) samples at various levels of sulfur+gold sensitization exposed in room air.

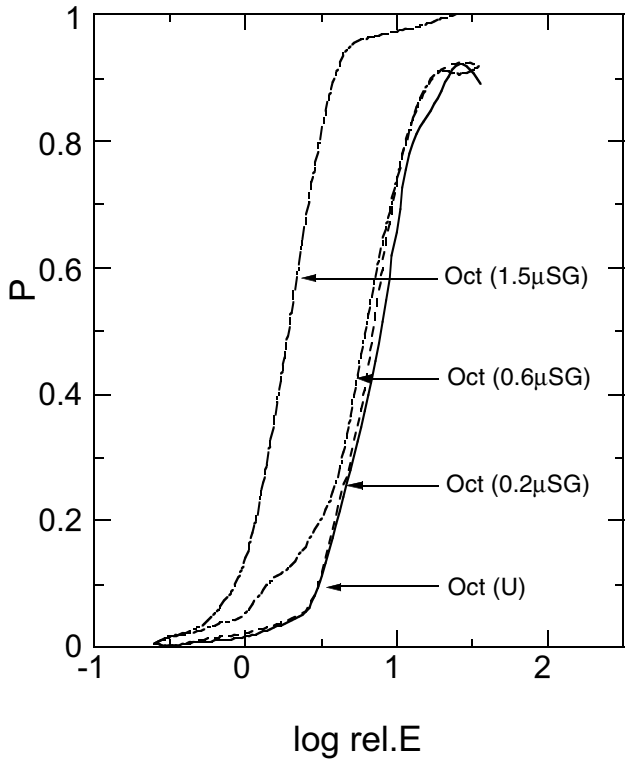

Figure 3. Characteristic curves of the Oct(SG) samples at various levels of sulfur+gold sensitization exposed in room air for the Oct(SG) samples.

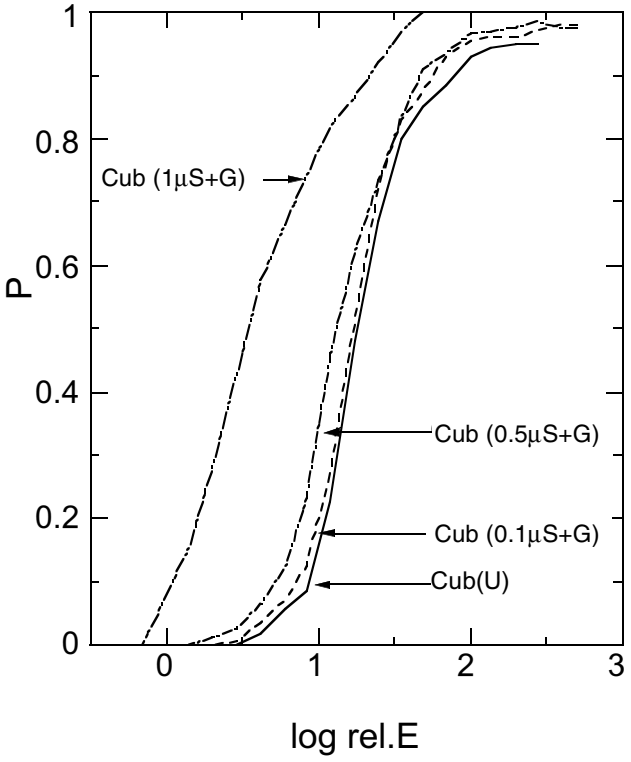

Figure 2. Characteristic curves of the Cub(S+G) samples at various levels of sulfur+gold sensitization exposed in room air.

We obtained a set of characteristic curves of samples exposed and stored in a vacuum for certain periods. From these curves we took P values at the same exposure value and plotted them against the storage time t, as shown in Fig. 4(a) for the unsensitized cubic grain emulsion and in Fig 4(b) for the octahedral one. The exposure value was taken at the point of $P_0 = 0.3$ for each sample.

In the cubic sample the increase of P with the storage time in vacuum after exposure corresponded to the exponential curve. Every sample indicated the exponential one-step increase. We approximated the growth rate by Eq. 2 and evaluated ΔP and K values. On the octahedral sample P also corresponded to the exponential increase at first stage, but after provisional saturation P increased again showing the S-shaped curve and then reached a second saturation level. This was the same behavior in the octahedral sample as previously reported.[9] We approximated the growth rate during the first stage of increase by Eq. 2.

Three results for the cubic sample and two results for the octahedral sample are shown in Fig. 4. Those results were obtained from different experiments under the same conditions. In the cubic case, two curves out of three overlapped, while one curve exhibited smaller ΔP and K. In the octahedral case the two curves overlapped. We sometimes observed that some curves did not overlap in spite of the same experimental condition, which brought about the decrease of ΔP in many cases. We suppose that a little moisture and oxygen may still remain behind in the emulsion layer after one day evacuation, and those residues sometimes diminish the delayed formation and decrease ΔP, although we have no supporting evidence for this speculation.

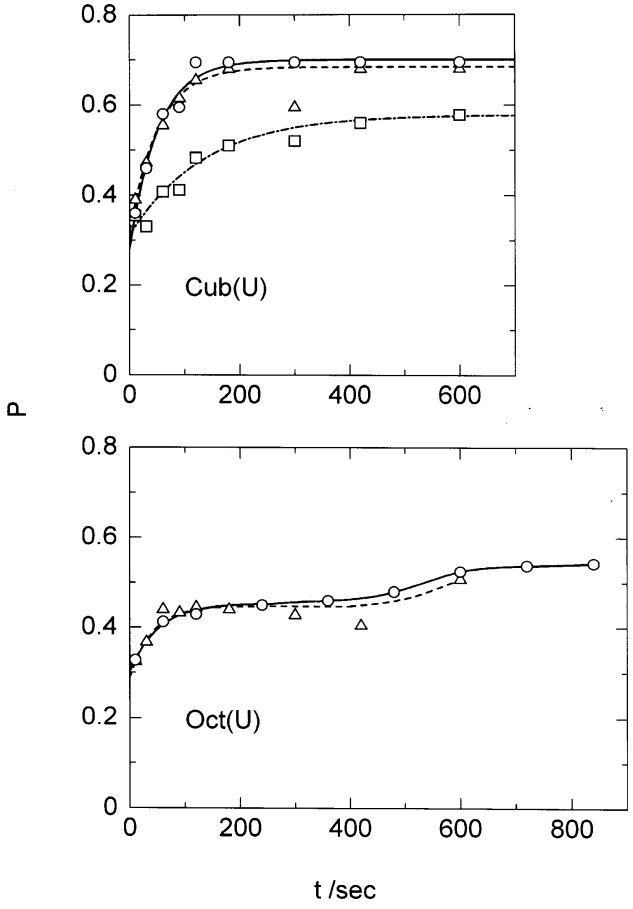

Figure 4. Increase of P in unsensitized emulsions with the time of storage in a vacuum after exposure at a certain exposure value. The exposure value gives each sample P_0 = 0.3. Each curve in the same figure was obtained from different experiments under the same conditions. Top: cubic grain emulsion; bottom: octahedral grain emulsion.

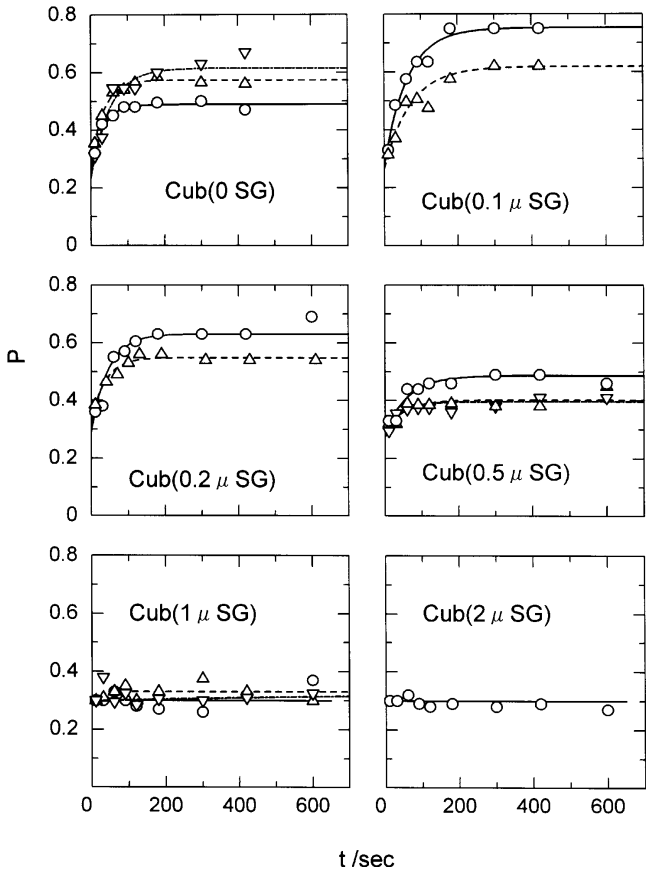

Figure 5. Increase of P in the Cub(SG) samples of various sensitization levels with the time of storage in a vacuum after exposure at a certain exposure value. The exposure value is the one that gives P_0 = 0.3 for each sample. Each curve in the same figure was obtained from different experiments on the same condition.

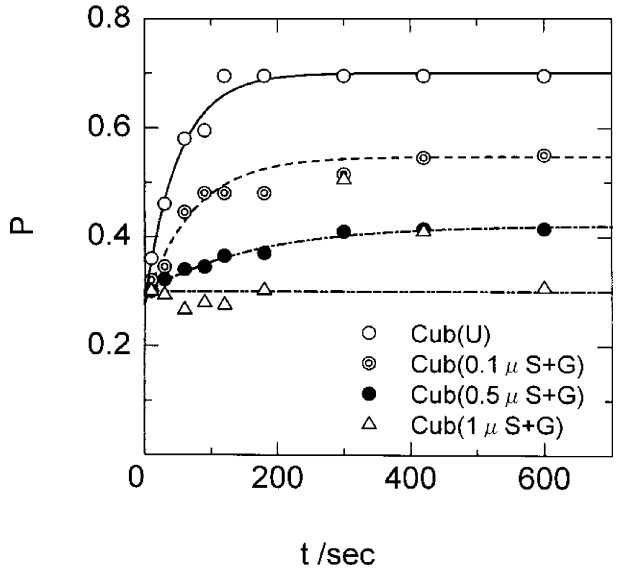

Figure 6. Increase of P in the Cub(S+G) samples of various sensitization levels with the time of storage in a vacuum after exposure at a certain exposure value. The exposure value is the one that gives P_0 = 0.3 for each sample.

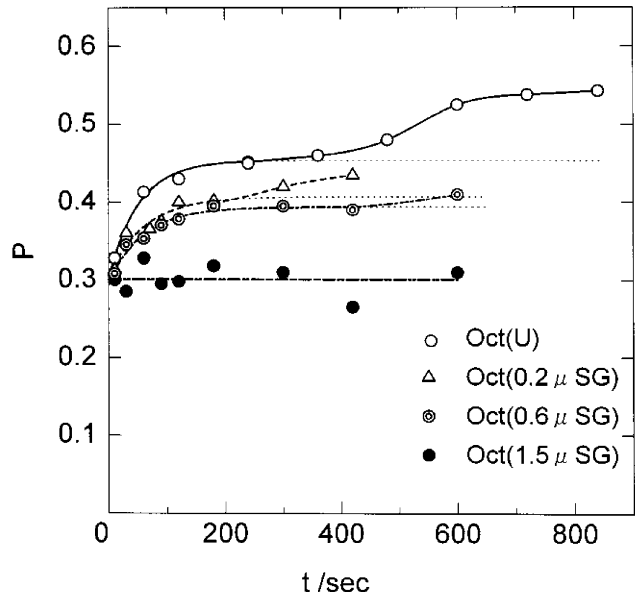

Figure 7. Increase of P in the Oct(SG) samples of various sensitization levels with the time of storage in a vacuum after exposure at a certain exposure value. The exposure value is the one that gives P_0 = 0.3 for each sample.

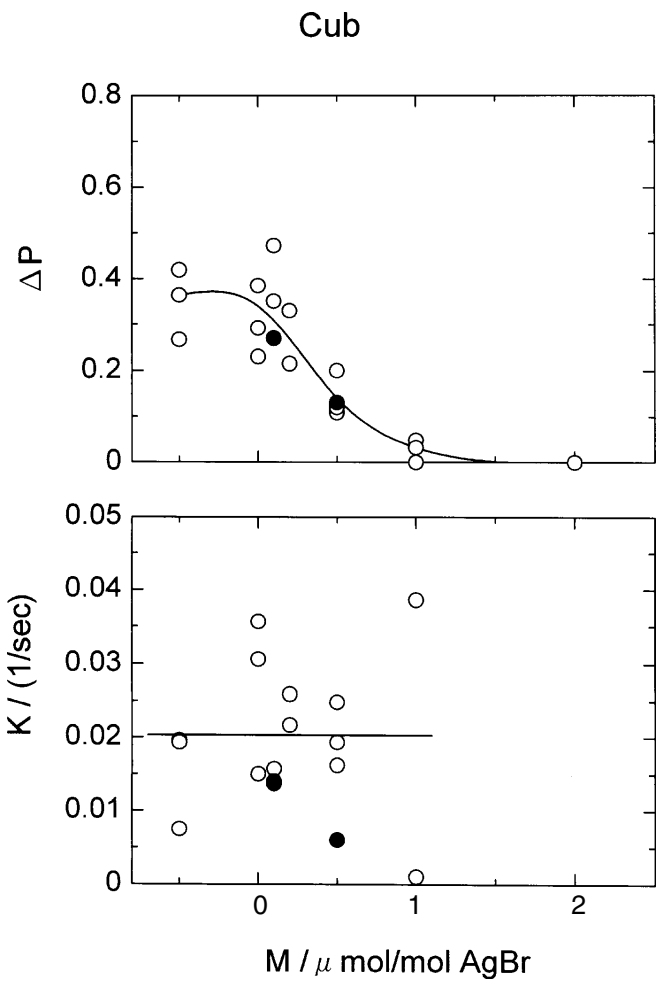

Figure 8. Relationships of ΔP and K to the sensitization level for the Cub(SG) and Cub(S+G) samples. Open circles represent the result for Cub(SG) and closed circles for Cub(S+G). The abscissa is taken as the amount of sensitizer M. Unsensitized emulsion is represented on the left side of M = 0 point. Top: ΔP versus M; bottom: K versus M.

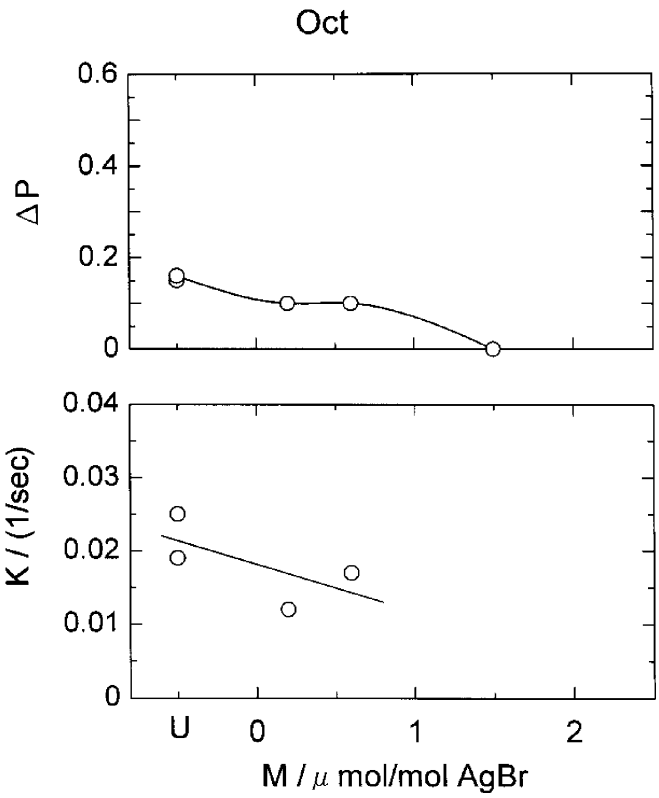

Figure 9. Relationships of ΔP and K to the sensitization level for the Oct(SG) samples. The abscissa is taken as the amount of sensitizer M. Unsensitized emulsion is represented on the left side of M = 0 point. Top: ΔP versus M, bottom: K versus M.

The P–t plottings are shown in Fig. 5 for the Cub(SG) samples, in Fig. 6 for the Cub(S+G), and in Fig. 7 for the Oct(SG). On the cubic samples the increase of P always showed the exponential one-step increase similar to the unsensitized one. But ΔP decreased with the sensitization level. The ΔP was equal to zero, and so the delayed formation was not observed at the highest sensitization level of the Cub(2 μSG) and Cub(1 μS+G) samples.

The behavior of the octahedral samples was also similar to the unsensitized one. The value P exhibited a two-step increase, the first step was exponential, and the second step was S-shaped. We approximated the increasing rate for the first stage by Eq. 2. Again, ΔP, decreased with the sensitization level and the S-shaped second increase diminished simultaneously. Although the second growth step may diminish faster than the first one, it never disappeared before the first one did. Anyway, at the highest level of sensitization of Oct(1.5 μSG), the delayed formation was not observed at all.

Relationships of ΔP and K to the sensitization level are shown in Fig. 8 for the Cub(SG) and Cub(S+G) samples and in Fig. 9 for the Oct(SG) samples. The sensitization level is represented by the amount of sensitizer M and the unsensitized samples are represented on the left side of the M = 0 point. The top figures show the relationship between DP and M, and the bottom ones show that between K and M.

Those figures also indicate clearly that ΔP decreases with sensitization level. On the contrary, K does not show clear dependence on the sensitization level; some scatter is seen. On the whole, K seems to show a constant value in the cubic grain emulsion and decreases slightly with the sensitization level in the octahedral one. The K value on the octahedral sample was a little smaller than for the cubic one.

Discussion

The sulfur+gold sensitization depressed the delayed formation of latent image completely on both the cubic and the octahedral grain emulsions. Previously we reported the effect of sulfur or reduction sensitization on the delayed formation.[6,7,10] At the lowest level of sulfur sensitization ΔP decreased for a large cubic grain emulsion[6] and disappeared for a small octahedral one.[7] With the reduction sensitization ΔP decreased with the sensitization level but did not disappear even at the highest level.[10]

There are two possible explanations for the depression in the sulfur+gold-sensitized emulsion. One is a lack of LSIS and the other is a lack of SSAS.

Many authors suggest that the minimum number of photolytic metal atoms comprising the developable speck decreases with sulfur+gold sensitization.[13] But this does

not mean that the developable latent image speck is formed by absorbing one photon per grain in the sulfur+gold-sensitized emulsion. Sensitivity on the sulfur+gold-sensitized emulsions does not seem to reach the one photon level.[14] The undevelopable specks must be formed, and they acquire developability when one more photon is absorbed.

First of all, we must define LSIS. One definition is that LSIS is the speck that acquires developability when the grain absorbs another photon. We will call this process the "one photon event." The other definition is that LSIS is the Ag_{n-1} speck and acquires developability in a process of adding one more silver atom. We will call this one the "one silver atom event." Normally those two definitions may be the same. The LSIS gets one more silver atom through the one photon event and also through the delayed formation process. However, in the sulfur+gold-sensitized emulsion the two are not equal because the latent image specks contain gold atoms.

The result here suggests that LSIS in the sulfur+gold-sensitized emulsion does not acquire developability by the one silver atom event, but does so by the one photon event. Probably there is a large gap in size between developable and undevelopable specks.

One possible explanation for this large gap is the disproportionation reaction proposed by Spencer.[15] This is the reaction of Au(I) ions catalyzed by a silver atom speck during exposure. In the sulfur+gold sensitized emulsion there are some Au(I) ions, and the newly generated silver atom speck triggers the following disproportionation reaction to generate gold atoms:

$$3\mathrm{Au(I)} + \mathrm{Ag}_m \rightarrow \mathrm{Au}_2\mathrm{Ag}_m + \mathrm{Au(III)}. \qquad (6)$$

When n is equal to 4 as proposed by many authors,[13] the Ag_{n-2} speck would correspond to Ag_2 and Ag_{n-1} specks would correspond to Ag_3. If the Ag_2 speck cannot trigger this reaction, it always stays in the two atom speck. And if the Ag_3 speck can trigger it, as Spencer suggested,[15] the Ag_3 speck becomes a five atom speck by this reaction. When the Ag_2 speck grows to a Ag_3 speck through the one photon event, this speck grows immediately to the five atom speck, which is fully developable.

Then, there are no three atom and four atom specks, that is, Ag_3 and Ag_4 specks, and the large size gap between the developable and undevelopable specks appears in the sulfur+gold-sensitized emulsion. At high sensitization levels, Reaction 6 can take place in every grain and the delayed formation does not proceed, as there are no Ag_3 specks.

The other possible explanation for this gap is that the developability is different for the three atom specks which are Ag_3 and Ag_2Au speck. Kawasaki, Yoshiki, and Oku suggested that the two atom speck did not include a gold atom, but the three atom speck did in the sulfur+gold sensitized emulsion.[16] Therefore, when the Ag_2 speck grows to the Ag_2Au speck not by reducing Ag(I) but Au(I) ion through the one photon event, no Ag_3 speck is formed. If the Ag_2Au speck is developable while the Ag_3 speck is not, the delayed formation would not appear as, again, there are no Ag_3 specks. In both cases the Ag_3 speck does not exist and so the delayed formation does not take place in the sulfur+gold sensitized emulsion.

Next, we consider the other possibility, namely, the lack of SSAS. Previously we explained the decrease of ΔP in the weakly sulfur-sensitized emulsions are due to the lack of SSAS. We have suggested that sulfur sensitization depressed formation of SSAS by promoting the growth of other silver specks. However, the delayed formation appeared in highly sulfur-sensitized emulsion, and so SSAS was generated again. If the sulfur+gold sensitization depresses the formation of SSAS more effectively than the sulfur sensitization, the delayed formation would not appear.

We must consider the propriety of this explanation from the viewpoint of the reaction rate of delayed formation. The apparent rate constant K is almost constant in the cubic samples and slightly decreased with sensitization level in the octahedral samples, while ΔP is decreased with the sensitization level in both emulsions. According to the kinetic analysis, we proposed that K reflected both the number of LSIS and the number of SSAS in a grain.[4,5] If SSAS decreased and finally disappeared with the level of sulfur+gold sensitization, both ΔP and K would decrease with the level. This discrepancy can be explained by the concept of divided domain in a grain.[3]

As suggested previously, a large grain may be divided into several domains, wherein the latent image formation proceeds independently.[3] If both SSAS and LSIS were formed in the same domain, the delayed formation would proceed, and if each were formed in a different domain, it would not. When only one SSAS was formed in every domain, K would not change, and when two or more SSAS were formed in a domain, K would decrease along with the total number of SSAS. Accordingly, the cubic grain corresponded to the former case and the octahedral grain corresponded to the latter case.

We considered that the mechanism of two-step increase was represented as Eqs. 3 and 4. However, we must explain the difference between cubic and octahedral grain emulsions, that is, the lack of a second step in the cubic case. This suggests the lack of an Ag_{n-2} or Ag_2 speck. This leads to the incomprehensible consideration that there is no Ag_2 speck when the second increase of P does not appear, and so there is no Ag_2 speck in the cubic grain emulsion.

Another explanation is the difference of number of SSAS in a divided domain. In the octahedral grains there are many SSAS and so there are two or more SSAS in a domain, while there is only one SSAS in a domain in the cubic grains. When there is only one SSAS in the domain, only the first reaction proceeds and only the first increase appears. In addition, when there are two or more SSAS in the domain, the successive reactions can proceed and the second increase appears. The appearance of second increase in the cubic grain emulsion with phenosafranine will be due to the increase of SSAS in a domain by the phenosafranine.

If the disappearance of delayed formation at the high level of sensitization was due to the decrease of SSAS, the second increase would disappear faster than the first increase. On the contrary, when this disappearance was due to the developability at the Ag_2Au speck, only the second increase would appear because the successive reactions of Eqs. 3 and 4 proceed. Both increases in Fig. 7 seem to disappear simultaneously, and this suggests that the above two mechanisms are unlikely. However, it is a little difficult to judge from this result only and we must accumulate further results.

We consider another possible mechanism for the second increase. That is, a two-pass mechanism of different rate constants as shown in the following equations:

$$\mathrm{Ag}_3 + \mathrm{Ag} \xrightarrow{k_1} \mathrm{Ag}_4, \qquad (7)$$

$$\mathrm{Ag}_3 + \mathrm{Ag} \xrightarrow{k_2} \mathrm{Ag}_4. \qquad (8)$$

The second increase must have a large induction period and must start after the first increase is finished. If these were simple simultaneous reactions with different rate constants, the reaction rate profile would show one overlapped exponential curve. We must explain the large induction period in the reaction of Eq. 8, but we do not yet have the detailed mechanisms corresponding to Eq. 7 and Eq. 8.

There are many hypotheses and we must choose the most reasonable explanation. Because the second increase seems to disappear simultaneously with the first increase, the following process is considered more reasonable. The disappearance of delayed formation at the high level of sulfur+gold sensitization is due to the lack of Ag_3 speck, and this lack is due to the disproportionation reaction of Au(I) ions on the Ag_3 speck. The second increase on the octahedral grain emulsion is due to the successive growth of the Ag_{n-2} speck in a divided domain, where two or more SSAS exist. But there is still some possibility that the sulfur+gold sensitization depresses the formation of SSAS.

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