Study of the Delayed Formation of Latent Image Specks in a Vacuum for Emulsions with added Phenosafranine by the Arrested Development Technique

Ken'ichi Kuge,▲ Yasuhiro Watanabe, Tsugio Gomi, and Nobuo Mii▲

Faculty of Engineering, Chiba University, Chiba, Japan

Effects of phenosafranine (**Ps**) on the delayed formation of latent image specks in a vacuum and on the dispersion of latent image specks at sulfur-sensitized octahedral grain emulsions were studied by the arrested development technique. **Ps** desensitized in room air especially at unsensitized emulsion, while it was not the case in a vacuum. **Ps** did not affect the dispersion of latent image specks in room air and in a vacuum as well, while high level of sulfur sensitization enhanced the dispersion. Low levels of **Ps** and sulfur sensitization depressed the delayed formation, and high levels of both enhanced it. The sulfur sensitization may enhance the delayed formation due to the dispersion of latent image specks, while **Ps** may do so due to the formation of single silver atom species (SSAS). An emulsion grain is divided into several domains and the delayed formation proceeds when a latent sub-image speck and SSAS form in the same domain. There are two types of small silver species; growing species and non-growing. The former is a precursor of the latent image speck acting as an electron trap. The later, such as SSAS, cannot trap electrons and it requires a certain aggregation process to grow a larger speck.

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Introduction

The delayed formation of latent image specks in a vacuum is considered to be a coagulation of dispersed photolitic silver specks, expressed by the following equation,[1]

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

where Ag_{n-1} is an undevelopable latent sub-image speck (LSIS), Ag is a single silver atom species (SSAS), Ag_n is a developable latent image speck (LIS), and n is a minimum number of silver atoms to acquire the developability. Therefore, the delayed formation would be closely related to the dispersion of latent image specks.

The arrested development technique is one of the adequate methods for examining the dispersion thereof. Previously we reported on the relationship with respect to the sulfur-sensitized emulsion.[2] For the unsensitized emulsion, delayed formation was observed, while LIS was always one speck per grain. This suggests that some SSAS must form independently of the dispersion. For the weakly sensitized emulsion, the delayed formation and the dispersion were not observed, while both were observed for the strongly sensitized one. We considered that no SSAS formed in the former, and some SSAS formed again in the latter. Characteristics of LSIS and SSAS are distinctly different and only LIS and LSIS are included in the so-called latent image specks in the dispersion. We cannot discuss SSAS in the same way.

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On the other hand, we reported the behavior of delayed formation at the phenosafranine (**Ps**)-added emulsion.[3] **Ps** is a desensitizing dye which captures photoelectrons and acts as a loss site for them. The delayed formation appeared in the **Ps**-added emulsion. Moreover, the two step increase of sensitivity by the delayed formation was observed occasionally. **Ps** has some other effects besides desensitization; one possible effect is the enhancement of dispersion.

It is very interesting to see whether the dispersion is enhanced and how the delayed formation appears at the **Ps**-added emulsion. Thus we studied the dispersion of latent image specks in room air and vacuum conditions by the arrested development technique.

Experimental

The photographic emulsion used was pure silver bromide monodisperse octahedral grains of 0.38 μm diameter. This was sulfur sensitized by sodium thiosulfate at 55° C for 60 min. The amounts of sensitizer were 20, 40, 80 and 160 μ mole per AgBr mole. We will represent them as symbols of 20 μS or 160 μS, etc. Those emulsions were the identical ones in the previous papers.[2,4]

Phenosafranine was added just before coating. The amounts of **Ps** were 0.3, 3, 30 and 300 μ mole per AgBr mole. We will represent them as symbols of 0.3 μ **Ps**, etc. A control sample represented as U was prepared without any addition of the sulfur-sensitizer and heating. Those emulsions were coated in a thin mono-grain layer on a polyester base in order to avoid the effects of moisture and oxygen occluding in the gelatin layer.

Experimental apparatus and procedures for the delayed formation were the same as described in the earlier papers.[2] Blue light exposure was given for 1 s at 20°C in a vacuum chamber (ca. 10^{-5} ~ 10^{-6} Torr or 10^{-3} ~

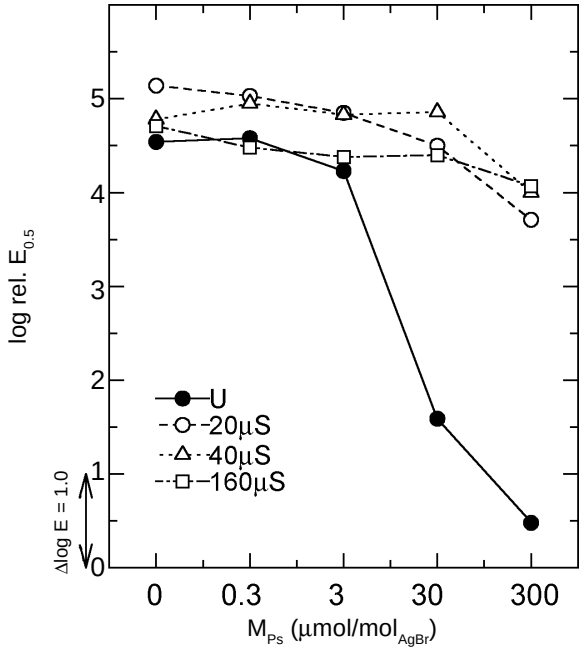

Figure 1. Relative sensitivity of the sulfur-sensitized and phenosafranine-added emulsions exposed in room air.

10^{-4} Pa) through a step wedge. The first exposure was given on one frame of a sample film strip and the second one was given on the other frame 10 min after the first exposure. Room air was introduced to the chamber just after the second exposure. The first frame was stored for 10 min in a vacuum after exposure and the second was not. Afterwards, the film strip was immediately developed with the arrested developer for 15 min at 20°C. The arrested developer used here was the phenylenediamine developer with the quaternary ammonium salt same as the one in the previous study.[4]

We observed carbon replicas of the developed grains with the electron microscope and counted the number of small developed silver clusters on a grain. We consider that those clusters form on LIS. We obtained $f(n)$ = fraction of grains having n developed clusters per grain, v = average number of them per grain, and p = fraction of grains having a particular number of developed clusters. We also obtained Δv and Δp = differences of v and p between the samples with and without storage in a vacuum after exposure. We calculated the Poisson distribution $p(n) = e^{-v} \bullet v^n / n!$, which was the probability of grains each having n developed clusters. To compare the distribution of $f(n)$ we calculated s = standard deviation of the distribution of $f(n)$ and $d_s = s^2/v$.

The last value d_s is useful as an index of the width of distribution as suggested by Hailstone.[5] When the dis-

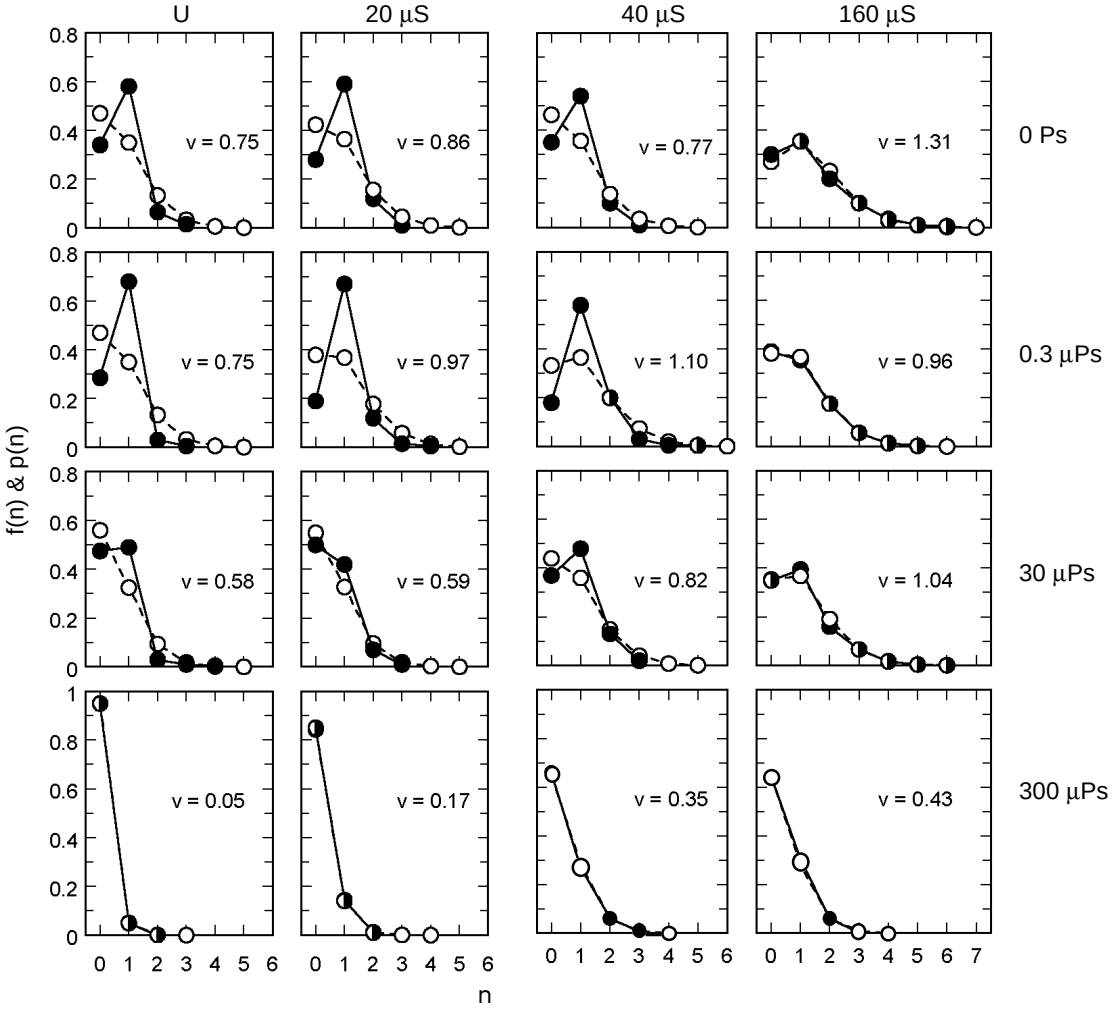

Figure 2. Distribution of the number of small developed silver clusters in a grain for the sulfur-sensitized and phenosafranine-added emulsions exposed in room air.

tribution of *f(n)* is the narrow one-cluster-per-grain (OCPG) type, d_s is smaller than unity, and when it is equivalent to the Poisson distribution, d_s is equal to unity.

We conducted sensitometry on the thick layer coating in room air condition with a JIS III type sensitometer. The exposed films were developed with M-AA-1 surface developer for 5 min at 20°C. We also used this sensitometer for the arrested development technique with exposure in room air.

Experimental Results

Sensitivity changes with the amount of **Ps**, M_{Ps}, at each sensitization level, exposed in room air are shown in Fig. 1. The ordinate represents the sensitivity as the relative exposure value, log rel. $E_{0.5}$, which gave the optical density of half of the maximum density for each sample, and the abscissa represents M_{Ps}. The sensitivity decreased remarkably with M_{Ps} for the unsensitized emulsion. This desensitization decreased with the increase of sulfur sensitization level.

The distributions of *f(n)* and *p(n)* for the exposure in room air are shown in Fig. 2. Not all results are shown. Open circles with a solid line and closed circles with a dashed line represent the results as *f(n)* and *p(n)* respectively. There was only one cluster and the plots of *f(n)* and *p(n)* did not overlap for the unsensitized and the weakly sensitized samples. The distribution type was OCPG. The number of clusters increased and the plots of *f(n)* and *p(n)* overlapped for the strongly sensitized 160 μ mol S sample. The distribution type shifted to the Poisson distribution. At the same time, d_s increased and approached unity, which leads to the same conclusion.

Those behaviors were not affected by the addition of **Ps**. Both *f(n)* and *p(n)* overlapped and d_s approached unity at the highest level of 300 μ mol **Ps** sample. But this does not mean a change in the distribution type. As Hailstone suggested,[5] we must compare those results at a similar v value, because the value d_s always approaches unity at low v values. As the v value of th 300 μ mol **Ps** sample was considerably lower than the other samples due to the low sensitivity, we could not compare it at a similar v value.

The sensitivity changes with the amount of **Ps** at each sensitization level, exposed in vacuum, are shown in Fig. 3. The upper and lower figures are the results with no storage and with 10 min storage in vacuum after exposure respectively. Both indicate that the sensitivity decreases only slightly with M_{Ps} even for the unsensitized emulsion. The vacuum condition depresses the desensitization strongly.

The distributions of *f(n)* and *p(n)* for the exposure in a vacuum are shown in Fig. 4. Not all results are shown. The figure pairs represent the results with no storage and with 10 min storage, respectively. We obtained the distributions at several exposure values and took the one for which the p value was the closest to 0.5 without the storage.

We also got the relationships of exposure to p, v and d_s. Those for the 40 μ S 30 μ **Ps** sample are shown in Fig. 5 as an example. Open circles with a solid line and closed circles with a dashed line represent the results with no storage and with 10 min storage respectively. The relationships to p and to v are alike. Both show that p and v increase with the storage owing to the delayed formation of latent image specks. Values of d_s are lower than unity. This suggests that the distribution of *f(n)* is narrower than the Poisson distribution *p(n)*.

The relationships of M_{Ps} to d_s at each sensitization level are shown in Fig. 6. The upper and lower figures

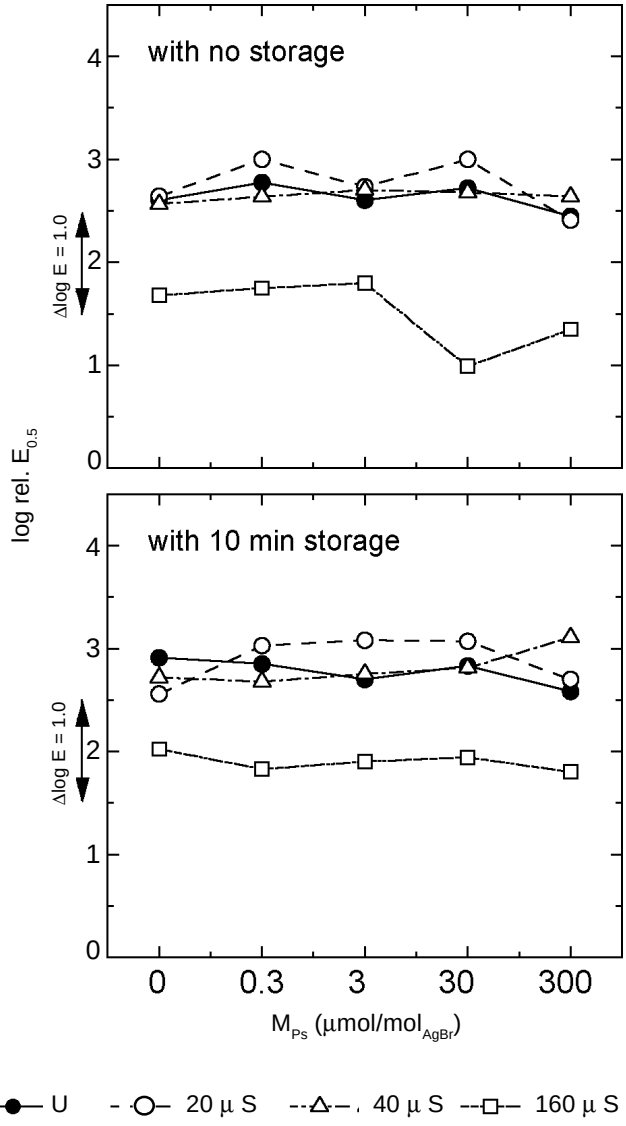

Figure 3. Relative sensitivity of the sulfur-sensitized and phenosafranine-added emulsions exposed in a vacuum. Top figure : with no storage in a vacuum after exposure, bottom figure : with 10 min storage.

are the results with no storage and with 10 min storage respectively. Every d_s value was taken at the exposure value of p = 0.5 with no storage. Each d_s value at the 160 μ mol S sample approaches to unity and this indicates that the sulfur sensitization enhances the dispersion of latent image specks. On the other hand, **Ps** did not affect the d_s value and so the dispersion in the vacuum condition.

The relationships of M_{Ps} to Δp and Δv at each sensitization level are shown in Fig. 7. Every value was taken at the exposure value of p = 0.5 with no storage. Both values without **Ps** decreased at the low sensitization level and then increased again with the sensitization level. This behavior is similar to the previous papers.[2,6]

Moreover, both Δp and Δv decreased at the small amount of **Ps** and then increased again with the amount of **Ps**, although there was some scattering, especially in Δp. Small amount of **Ps** decreased both values and depressed the delayed formation even at the high sulfur-sensitization level. On the contrary, a large amount

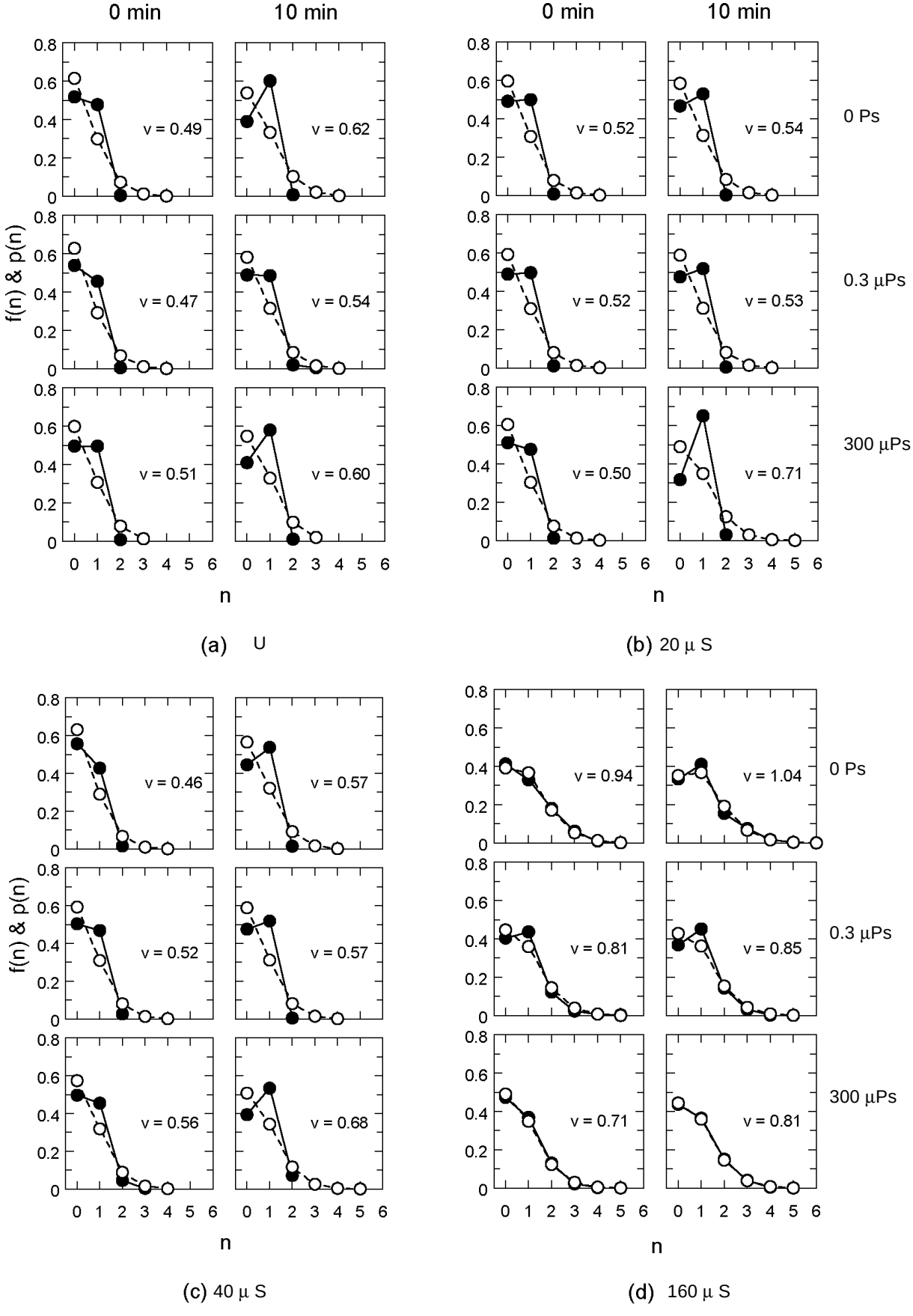

Figure 4. Distribution of the number of small developed silver clusters in a grain for the sulfur-sensitized and phenosafranine-added emulsions exposed in a vacuum. Left side : with no storage in a vacuum after exposure, right side : with 10 min storage. (a) U, (b) 20 μ S, (c) 40 μ S, (d) 160 μ S.

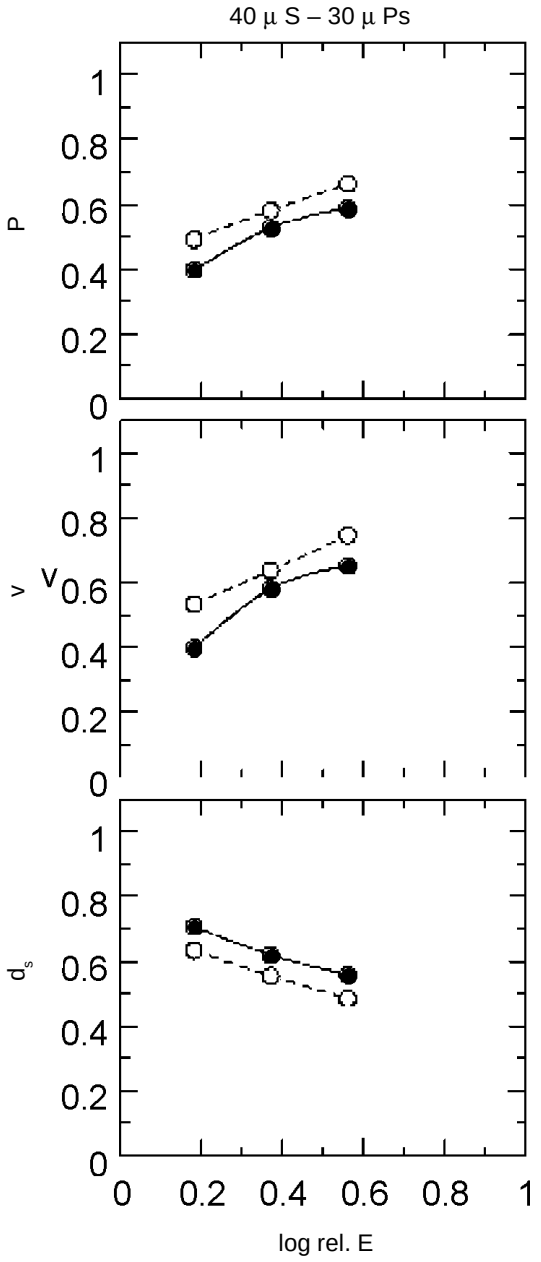

Figure 5. Relationships of log rel. E versus p, v and d_s for the Oct (40 μ mol S - 30 μ mol **Ps**) sample exposed in a vacuum. Open circles with a solid line : with no storage in a vacuum after exposure, closed circles with a dashed line : with 10 min storage. Top figure : p, middle figure : v, bottom figure : d_s.

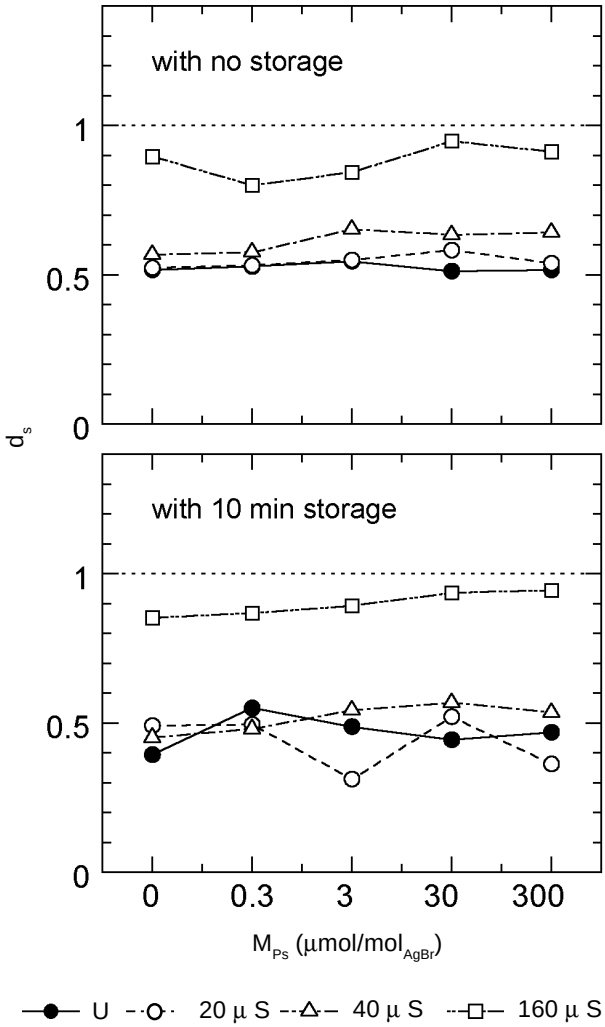

Figure 6. Relationships of d_s to the amount of phenosafranine M_{Ps} for the sulfur-sensitized emulsions exposed in a vacuum. Top figure : with no storage in a vacuum after exposure, bottom figure : with 10 min storage.

of **Ps** increased the values and enhanced it even at the low sensitization level. **Ps** has a more dominant effect on the delayed formation than the sulfur sensitization.

Discussion

The result with sulfur-sensitized emulsions without **Ps** was similar to the previous study, where we accounted for those results.[2,6] The number of SSAS decreased nearly to zero in the weakly sensitized emulsion. In the strongly sensitized emulsion the number of LIS was increased, and there we suggested that the number of SSAS increased further. However, the reason was not clarified at that time. We would like to explain this behavior using the concept of domain for the delayed formation suggested in the previous study.[7]

This domain is the region where SSAS can migrate towards a silver speck within its lifetime. Even a small grain may comprise several domains. If LSIS forms in the domain, delayed formation would take place and, if the domain lacked LSIS, it would not.

Here, we consider again the effect of sulfur sensitization. At the weak sensitization level the number of SSAS decreases and this makes it less probable that LSIS forms in the domain. At the strong sensitization level the number of SSAS is not yet so many, but the number of LSIS increases owing to the dispersion effect. As the probability of forming LSIS in the domain increases, delayed formation again takes place.

Next, we consider the effects of **Ps**. **Ps** decreased the sensitivity in room air conditions, and this desensitization was depressed by eliminating oxygen and moisture. **Ps** did not affect d_s, while sulfur sensitization increased it. Therefore, **Ps** did not affect the dispersion both in room air and under vacuum, although we could not judge it from the d_s value in room air. On the contrary, **Ps** affected the delayed formation strongly. Low amount of **Ps** depressed the delayed formation. High amounts of

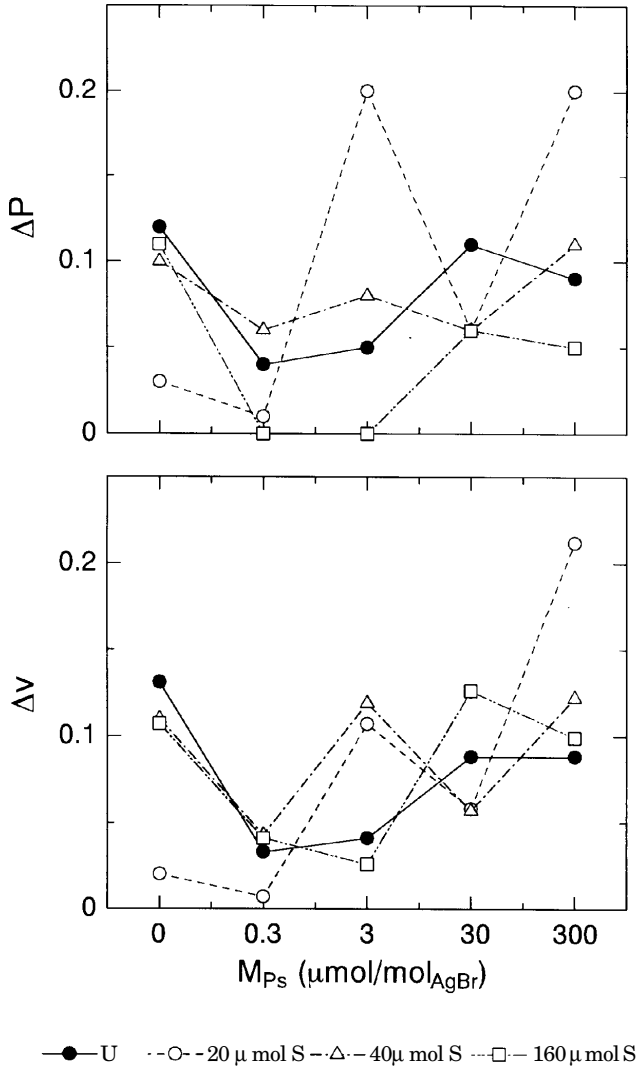

Figure 7. Relationships of Δp and Δv to the amount of phenosafranine M_{Ps} for the sulfur-sensitized emulsions exposed in a vacuum. Top figure : Δp, bottom figure : Δv.

Ps restored the delayed formation even in the weakly sulfur-sensitized emulsion. The effect of **Ps** to the delayed formation changed with the amount of **Ps** and **Ps** has a more dominant effect than the sulfur sensitization.

Those results suggest that **Ps** does not affect the formation of latent image specks but does affect SSAS. The formation of SSAS was depressed at low amounts of **Ps**. We have no extinct explanation now why the low amount of **Ps** depresses the formation of SSAS. On the other hand, high amounts of **Ps** enhanced the delayed formation. This suggests that the number of SSAS would increase and **Ps** would enhance the formation of SSAS.

Ps acts as a desensitizer in room air. **Ps** traps electrons temporarily and mediates the recombination in cooperation with oxygen and moisture. **Ps** also traps electrons in a vacuum. However, as there is no oxygen or moisture, the recombination would not proceed and most of the trapped electrons return to the conduction band of AgBr. At the same time, some SSAS would form from some of the electrons trapped at **Ps**.

Moreover, this will explain the second step of the delayed formation at the **Ps**-added emulsion. We sometimes observed a second increase of sensitivity, first, in the cubic grain emulsion with **Ps**[3] and second, in the octahedral grain emulsion without **Ps**.[7] We explained the mechanism of this second increase in the octahedral grain emulsion in our recent paper as follows.[7] When the number of SSAS increases, the probability of another SSAS forming in the domain increases. If there is a smaller LSIS of Ag_{n-2} type and two or more SSAS in the same domain, this LSIS absorbs two SSAS successively, as described in Eq. 2 and 3.

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

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

The same thing happens at the highly **Ps**-added cubic grain emulsion as **Ps** increases the number of SSAS.

SSAS have a unique character which is different from so-called latent image specks. Previously we suggested that SSAS did not grow to a larger silver atom speck.[7] There will be two types of single atom species forming on exposure. One is a precursor of LIS which can grow to a larger silver speck by trapping an electron. The other cannot grow larger as it cannot trap an electron. With the multiflash method Kawasaki measured the lifetime of unstable silver atom species as ca.1 s.[8] The species measured there was the precursor because the multiflash response would be due to the competition of photoelectron-trapping between the species. SSAS are the other type of single atom species. Insofar as it cannot trap electrons, it may be difficult to detect SSAS.

It is well recognized that there are two kinds of reduction sensitization centers, that is, R-centers and P-centers.[9–14] Both centers were considered to be two atom specks, but the P-centers can trap an electron and grow into larger latent image specks, while R-centers cannot trap an electron.

Therefore, there are two kinds of small silver atom specks which include not only two atom specks but also single atom species. The difference is that the R-centers form only by chemical reduction because SSAS do not grow to the two or more atom specks, while SSAS form on exposure.

The only way for SSAS to grow to larger specks would be through some aggregation processes. The delayed formation is a kind of aggregation process, although the latent image specks forming through those processes may be not so numerous.

Conclusions

1. **Ps** desensitized in room air especially in unsensitized emulsion, though it did not desensitize in a vacuum.
2. **Ps** did not affect the dispersion of latent image specks either in room air or in a vacuum.
3. High amounts of **Ps** enhanced the delayed formation of latent image specks in a vacuum, while low amounts of **Ps** depressed it. The high amount of **Ps** in a vacuum would promote the formation of SSAS.
4. An emulsion grain is divided into several domains. A domain is the region where SSAS can migrate towards the silver speck within its lifetime. If LSIS forms in the domain, delayed formation can proceed.
5. There are two types of single silver atom species. One is an electron trap as a precursor of the latent image speck. The other is not an electron trap, and does not grow larger on exposure. SSAS discussed here belong to the latter class. They can only grow through some aggregation process, such as delayed formation. ▲

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