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Sensitization of Ultra-Fine-Grain Photographic Emulsions

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Abstract. *The sensitivity of ultra-fine-grain (UFG) emulsions (minimum size 35 nm) was studied and was found to be proportional to the fourth and fifth powers of the grain size. The sensitivity decreased more than expected from the decrease in the absorption of light. A desensitizing factor peculiar to UFG emulsions was suggested. A large increase in the sensitivity was observed for low-intensity light exposure when a coated film was immersed in a sodium nitrite solution before exposure. Under these conditions, sensitivity became proportional to the third power of the grain size. Rehalogenation is the desensitizing factor in the UFG emulsion and the sodium nitrite solution functions as a halogen acceptor. Rehalogenation proceeds markedly in UFG emulsions because silver atoms and halogen atoms/molecules are formed nearby and could therefore react easily with each other. The sensitivity increase of the UFG emulsion due to sulfur-gold sensitization was smaller than that due to immersion in the sodium nitrite solution; both increases were additive for low-intensity exposure. In contrast, the sensitivity increases were inversely related (and not additive) for high-intensity exposure. © 2009 Society for Imaging Science and Technology.*

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INTRODUCTION

Silver halide photographic materials have numerous advantages. One of them is the high image resolution that they provide. A maximum resolution of 10,000 lines/mm is claimed for the photographic material used for hologram recording.[1] Such a high resolution cannot be obtained with current digital photographic systems. Photographic materials that provide such high resolution use ultra-fine-grain (UFG) emulsions, which consist of grains that are less than 100 nm in diameter. In general, photographic sensitivity is proportional to the volume of the silver halide grains, and this dependence is consistent with the fact that the number of photons absorbed is proportional to the grain volume.[2] It therefore follows that the sensitivity of UFG emulsions is low because the volumes of individual grains are small.

Thus far, there have been few studies conducted on UFG emulsions. Some of these studies describe the preparation methods for UFG emulsions, such as one method utilizing fish gelatin,[3–6] or another utilizing poly(vinyl alcohol) as protective colloid.[7,8] Reports on the photosensitive mechanism of UFG emulsions are also limited,[9–13] and it is still not well understood compared with that of normal emulsions with submicrometer-scale grain sizes. It also has not been confirmed whether or not the sensitivity of a UFG emulsion is proportional to the grain volume. Zou investigated the size dependence of the sensitivity for grains of sizes ranging from 55 to 450 nm and found that the sensitivity was proportional to the 5.2 power of the grain size.[9]

Furthermore, although effective sensitization is indispensable for a UFG emulsion, reports describing suitable sensitization methods are limited. In this study, we investigate whether the sensitivity of UFG emulsions is proportional to the volume. We also describe efforts to identify effective sensitization methods.

EXPERIMENT

Two types of gelatino-silver hallide emulsions were used. The first was a series of emulsions with $AgBr_{0.98}I_{0.02}$ monodisperse cubic grains prepared at $pAg=8.3$ and $pH=5.8$ in 2.5% gelatin solution by a standard double-jet technique. These emulsions were used in our previous studies on photothermography.[10,12,13] The grains were observed by electron microscopy, and the edge length and the coefficient of variation of each emulsion were obtained as 35 nm, 13%; 43 nm, 13%; 80 nm, 10%; 92 nm, 13%; 124 nm, 13%; and 148 nm, 11%. They were machine-coated at 50 mg_{Ag}/dm^2. They are represented as Em_{A35}, Em_{A43}, etc., where the subscript designates the central tendency of the grain size distribution.

The second type of gelatino-AgX emulsion consisted of nearly spherical $AgBr_{0.98}I_{0.02}$ grains prepared at $pAg=8.3$ and $pH=5.6-5.8$. The grain diameter was approximately 40–50 nm. This emulsion was hand-coated; thus, the silver coverage was not uniform. This emulsion, identified as Em_B, was used in our previous studies on holography.[14]

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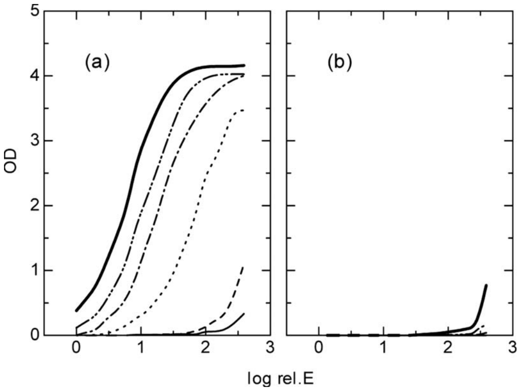

Figure 1. Characteristic curves of Em_A emulsions with grains of different edge lengths: (a) high-intensity (10^{-6} s) exposure, (b) low-intensity (100 s) exposure. Development period=24 min. Edge length: –=35 nm, ---=43 nm, ···=80 nm, –·–=92 nm, –··–=124 nm, ━=148 nm.

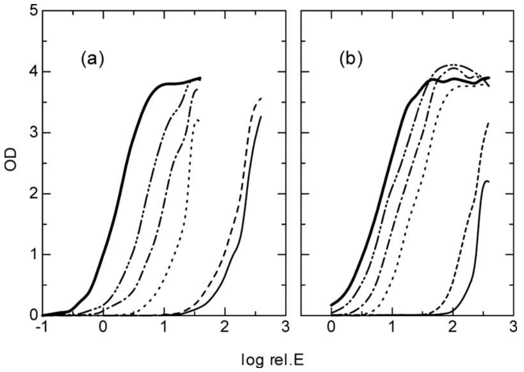

Figure 2. Characteristic curves of Em_A emulsion with grains of different edge lengths immersed in a sodium nitrite solution before exposure: (a) high-intensity (10^{-6} s) exposure, (b) low-intensity (100 s) exposure. Development period=24 min. Edge length: –=35 nm, ---=43 nm, ···=80 nm, –·–=92 nm, –··–=124 nm, ━=148 nm.

We subjected the Em_B emulsion to sulfur-gold sensitization. A gold thiosulfate complex ($Na_3Au(S_2O_3)_2$) was used as sensitizer,[15] and its quantity was varied from 1 to 15 mmol/mol_{Ag}. The emulsion was treated at 60°C for 60 min without any *p*Ag and *p*H adjustments. The sensitization level is expressed in "m SG."

Some of the emulsions were treated with a halogen acceptor to prevent rehalogenatio; sodium nitrite ($NaNO_2$) was used as the halogen acceptor.[16–20] This treatment was performed using two methods. The first method involved the addition of sodium nitrite to the emulsion before coating. In the second method, the coated film was immersed in the sodium nitrite solution before exposure. In the former case, 1 to 10 mmol/mol_{Ag} of sodium nitrite was added to the emulsion. In the latter case, a coated film was immersed in the sodium nitrite solution at a concentration of 0.1 mol/L at 20°C for 3 min.

Sensitivity was measured using a JIS III sensitometer. The original tungsten filament lamp in the sensitometer was used for a low-intensity (LI) white light exposure of 100 s. The intensity in front of the step wedge was 539 lx. For a high-intensity (HI) exposure of 10^{-6} s, a xenon flash lamp was installed in the sensitometer, but the intensity was not measured. As the exposure values were represented as relative values, they were not identical with either of the intensities. The exposed films were developed using a D72 developer diluted to 1:4. The developer temperature was 20°C, and the development time was 1, 8, 12, 18, and 24 min. Normal stop, fixation, and washing treatments were performed after development. The sensitivity was compared with the reciprocal of the exposure value that gave 0.1 optical density above fog on a characteristic curve.

RESULTS

Characteristic curves of the set of untreated emulsions with grains of different edge lengths and unsensitized Em_A are shown in Figure 1 for the HI and LI exposures. The exposure values are not identical between the two intensities. The results for the longest development time of 24 min are shown in the figure. For LI exposure, little darkening was observed and then only for large-grain emulsions with the longest development time. This darkening scarcely increased even when the exposure time for the same intensity was prolonged; therefore, severe low-intensity reciprocity failure was observed in these emulsions. In contrast, for HI exposure, we obtained significant density and could record a characteristic curve. We also observed that the sensitivity decreased with grain edge length.

The characteristic curves of the Em_A films immersed in the sodium nitrite solution before exposure are shown in Figure 2 for both intensity exposures. The developing time was the same, i.e., 24 min. The sensitivity increased drastically for LI exposure. The figure shows an increase of two orders of magnitude or more in the sensitivity of the Em_{A148} film. Significant darkening was obtained even for the Em_{A35} film with the smallest grains. Such a large increase in the sensitivity was not observed for HI exposure. In addition, the increase in the sensitivity of large-grain emulsions was small, while that of small-grain emulsions was significant.

The development rates of the Em_{A35}, Em_{A80}, and Em_{A148} films with and without immersion in the sodium nitrite solution are shown in Figure. 3 for HI exposure and several exposure values. Darkening proceeded rapidly in the initial stage of the development; therefore, the variation in the induction period of the development on each grain was not large. Further, there is almost no difference between the films that were immersed and those that were not immersed.

The relationship between the edge length and sensitivity for Em_A films is represented on a logarithmic scale in Figure 4 for HI exposure and in Figure 5 for LI exposure for each development time. White circles correspond to the result for the immersed films, and black circles correspond to that for the films that were not immersed. Both sets of circles follow nearly straight lines. For films that were HI-exposed without immersion, the slope of the straight line R is approximately 4.4–4.8. The value of R would be 3 if the sensitivity were proportional to the grain volume, i.e., if the sensitivity were proportional to the number of photons absorbed in a grain.[2] Consequently, a decrease in sensitivity for the UFG emulsion

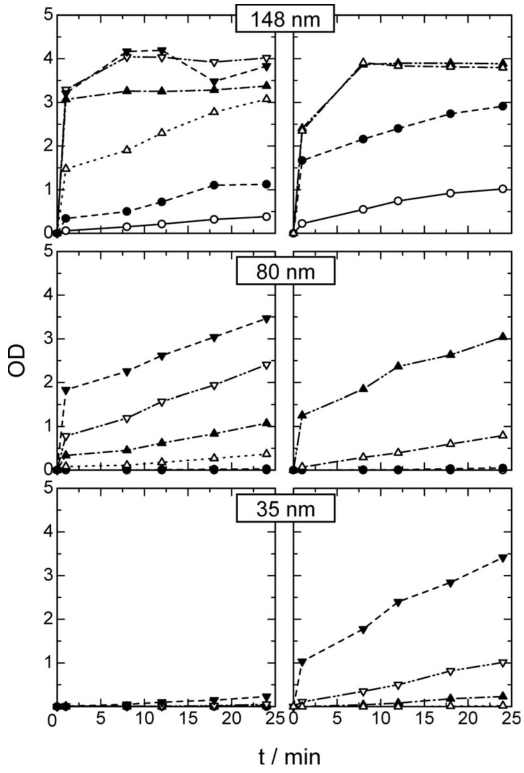

Figure 3. Rate of development of Em_A emulsions with grains of different edge lengths for a high-intensity (10^{-6} s) exposure. Left: no immersion in a sodium nitrite solution before exposure. Right: with immersion. Exposure value as log rel. E: ○=0, ●=0.46, △=1.08, ▲=1.55, ▽=1.99, ▼=2.44.

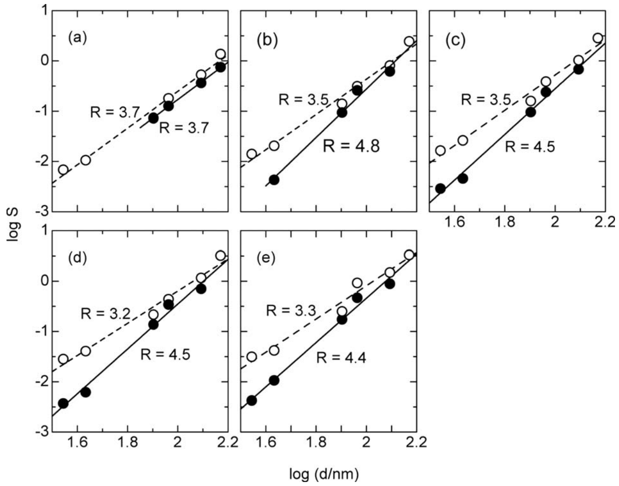

Figure 4. Logarithmic plot of the edge length of grains in Em_A emulsions versus sensitivity for high-intensity (10^{-6} s) exposure with different development times. (a) 1 min, (b) 8 min, (c) 12 min, (d) 18 min, (e) 24 min. Open circles+dashed line: without immersion in a sodium nitrite solution before exposure. Closed circles+solid line: after immersion. R=slope of the straight line through the plotted points.

is more than that expected from a decrease in the absorption of photons with decreasing grain size. On the other hand, the value of R for the films that were immersed and subsequently HI-exposed is 3.3–3.5, close to the expected value of 3. For LI exposure, the sensitivity was considerably lower; hence, its dependence on the grain size could not be ascer-

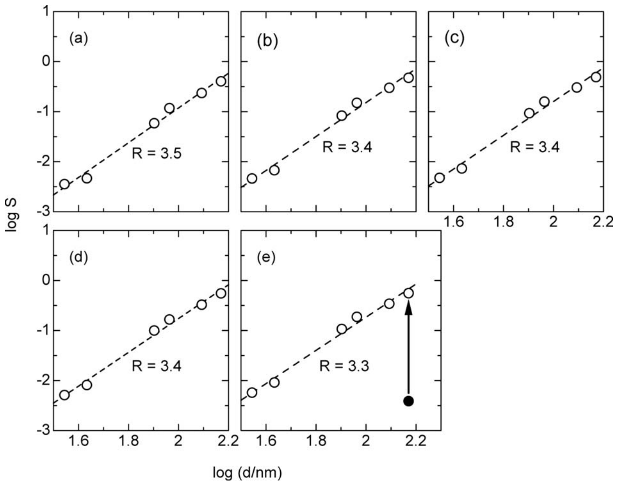

Figure 5. Logarithmic plot of the edge length of the grains in Em_A emulsions versus sensitivity for low-intensity (100 s) exposure with different development times. (a) 1 min, (b) 8 min, (c) 12 min, (d) 18 min, (e) 24 min. Open circles+dashed line: without immersion in the sodium nitrite solution before exposure. Closed circles+solid line: after immersion. R=slope of the straight line through the plotted points.

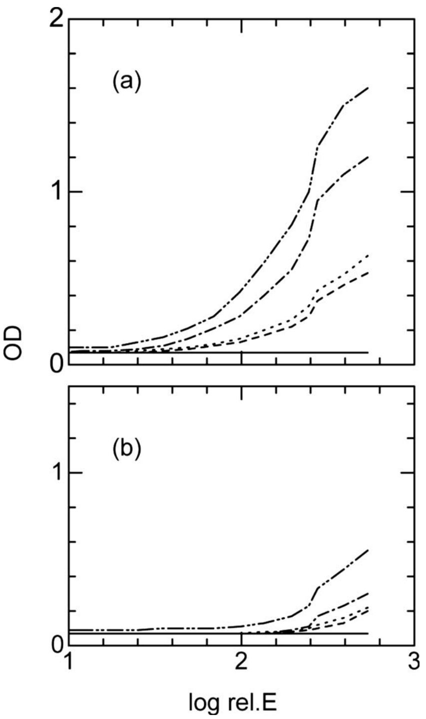

Figure 6. Characteristic curves of Em_B emulsion for different sensitization levels when subjected to sulfur-gold sensitization (SG). (a) high-intensity (10^{-6} s) exposure, (b) low intensity (100 s) exposure. Sensitization level: −=U, - - -=1 m SG, ⋯=3 m SG, −·−=5 m SG, −··−=10 m SG.

tained for films that were not immersed. However, the immersed films exhibited a noticeable increase in the sensitivity, as shown by the arrow in Fig. 5(e), and this increase was sufficient to allow measurement of grain size dependence. The values of the slopes were in the range of 3.3–3.4, which is similar to the values obtained for HI exposure.

The characteristic curves of the Em_B emulsion with sulfur-gold sensitization are shown in Figure 6, where the

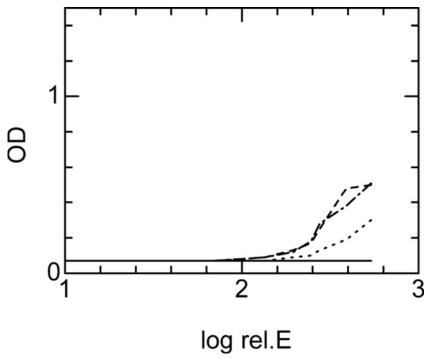

Figure 7. Characteristic curves of Em_B emulsions to which sodium nitrite (HA) of different levels is added before coating. High-intensity (10^{-6} s) exposure. Addition level: –=0, ---=1 m HA, ⋯=3 m HA, –·–=10 m HA.

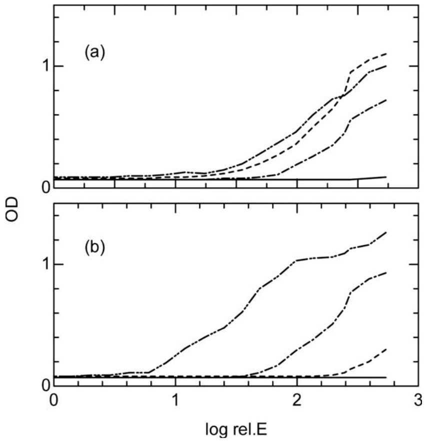

Figure 8. Characteristic curves of E_B emulsion for sulfur-gold sensitization and immersion in the sodium nitrite solution (HA) before exposure: (a) High-intensity (10^{-6} s) exposure, (b) low-intensity (100 s) exposure. Sensitization level=5 mmol sensitizer/mol_{Ag}. –=U, ---=SG, –·–=U+HA, –··–=SG+HA

top and bottom figures show the curves for HI and LI exposures, respectively. The unsensitized Em_B emulsions did not exhibit any darkening for both intensities; however, sensitivity was observed after sulfur-gold sensitization had been performed.

The characteristic curves for the unsensitized Em_B emulsions to which a certain amount of sodium nitrite was added before coating are shown in Figure 7 for HI exposure. An increase in the sensitivity was observed for HI exposure, although it was smaller than that obtained with sulfur-gold sensitization. The emulsions to which sodium nitrite was added did not show any darkening for LI exposure.

Since sodium nitrite is a reducing agent, it cannot be simultaneously added to the sulfur-gold sensitizer, which contains unstable gold ions. We therefore investigated a combined system in which the coated film with sulfur-gold-sensitized emulsion was immersed in the sodium nitrite solution. The characteristic curves of this sample are shown in Figure 8 for HI and LI exposures. Even though the addition of sodium nitrite did not show any darkening for LI exposure, significant darkening was observed after immersion. It was possible to obtain a large increase in the sensitivity compared with that obtained by sulfur-gold sensitization.

The increases in the sensitivity by immersion in sodium nitrite and by sulfur-gold sensitization for LI exposure occurred individually and separately. Both effects are additive. In contrast, for HI exposure, the sensitivity increase by sulfur-gold sensitization was greater than that obtained by immersion in sodium nitrite. The total increase in the sensitivity when both treatments were performed was small compared with the sum of the sensitivity increases obtained from individual treatments; the two treatments did not produce an additive result for HI exposure.

DISCUSSION

The sensitivity is proportional to the third power of the edge length or the grain volume when it is proportional to the number of photons absorbed in a grain.[2] However, the sensitivity in the absence of immersion for HI exposure was proportional to the 4.4–4.8 power of the edge length. Zou investigated the size dependence of the sensitivity for grains with 55−450 nm edge length and 0.2 s exposure, and the sensitivity was proportional to the 5.2 power of the edge length.[9] These results reveal that the sensitivity decrease of UFG emulsions is significantly larger than the expected decrease due to the absorption of photons. Accordingly, there should be a factor peculiar to the UFG emulsions that causes a size-dependent decrease in sensitivity.

We previously analyzed the formation of photolytic silver clusters by diffuse reflectance spectroscopy for the same emulsions with a different grain size.[10] Although the amount of coated silver per unit area was the same, the absorption by silver clusters increased for larger grains. This result suggested that formation efficiency of photolytic silver clusters decreases with grain volume, which is in agreement with the sensitivity decreases peculiar to UFG emulsions obtained in this study. The factors causing these phenomena appear to be the same.

Severe low-intensity reciprocity failure occurring in UFG emulsions would be a possible factor. However, the sensitivity for HI exposure also decreased beyond the expected proportional decrease due to the grain volume and, therefore, low-intensity reciprocity failure was not the sole factor.

Immersion of a film in the sodium nitrite solution increased its sensitivity. For HI exposure, the increase was observed only for small-grain emulsions. The sensitivity of large-grain emulsions was almost identical, independent of sodium nitrite immersion. Thus, the size dependence of films that were immersed is close to the third power of the grain size.

The effect of immersion was more remarkable for LI exposure. The sensitivity increased by more than 2 orders of magnitude, even for the large-grain emulsion. At the same time, the observed sensitivity was also nearly proportional to the grain volume, similar to that observed for HI exposure. This result suggests that the sensitivity decrease peculiar to UFG emulsions disappears, and that the sensitivity becomes proportional to the number of photons absorbed in a grain as a consequencc of immersion of a film in the sodium nitrite solution.

Sodium nitrite is known to be a halogen acceptor that prevents rehalogenation.[16–20] Therefore, we propose that rehaloganation is a significant factor causing the decrease in sensitivity peculiar to UFG emulsions. Sodium nitrite removes halogen atoms/molecules rapidly to prevent silver clusters from being attacked.

Severe low-intensity reciprocity failure occurs in UFG emulsions. According to the latent image formation process with the step-by-step mechanism based on the Gurney–Mott theory,[21] low-intensity reciprocity failure is due to the instability of the minute silver clusters formed at the first stage of the process. Although processes such as thermal decay and an oxidative reaction involving oxygen and moisture can be considered with regard to the process that make minute silver clusters disappear,[21,22] the marked recovery of the sensitivity for immersion in sodium nitrite suggests that rehalogenation is also the main cause for low-intensity reciprocity failure in UFG emulsions. Halogen atoms/molecules would readily attack the unstable silver clusters in a UFG emulsion.

In general, a decrease in the sensitivity due to rehalogenation in emulsions with submicrometer-scale grains is not significant for high-intensity exposures.[16] This may be because both silver and halogen atoms are formed separately, and the halogen atoms/molecules are removed by certain processes. Such a removal would be facilitated by separating photoelectrons and holes. One possible process is the separation of holes to surface and of electrons to bulk in the grain due to the surface space charge layer. As the thickness of the space charge layer is several tens of nm,[23] the layer does not form in nanometer-scale grains which brings about incomplete separation. Another separation process relates to the difference in diffusion coefficients between an electron and a hole. The diffusion coefficient for electrons is much larger than that for holes, which causes the Dember effect. Absence of the Dember effect in an emulsion with small grain size suggests that electrons and holes remain confined within a small area. Thus, silver and halogen atoms are formed close to each other in a UFG emulsion grain. A halogen atom/molecule can attack a nearby silver cluster before it is removed and, therefore, rehalogenation proceeds more readily in UFG emulsions. The process proceeds more rapidly for LI exposure because silver clusters grow slowly and small clusters can be more readily attacked.

The development rates shown in Fig. 3 indicate that variations in the induction periods were small regardless of whether or not the film was immersed in the sodium nitrite solution. It is known that statistical fluctuations cause large variations in the induction periods when the latent image specks are of the minimum developable size.[24] This effect is often observed when the dispersion of latent image specks occurs because multiple specks compete with each other in capturing photoelectrons; therefore, most of them are of the minimum developable size.[25,26] Consequently, the latent image specks in UFG emulsions have a sufficient size for development. It is probable that dispersion of latent image specks does not occur even for HI exposure, and there is only one latent image speck per grain in a UFG emulsion. Almost all specks can grow to a sufficient size. Attacks by halogen atoms/molecules cause a decrease in the size of the latent image specks. Large specks will change to the minimum developable size, while specks of the minimum size will lose their developability. Consequently, the size distribution shifts to smaller sizes. The development rate does not change, however, irrespective of immersion in sodium nitrite.

Sulfur-gold sensitization was effective for sensitizing UFG emulsions, as shown in Fig. 6. However, a substantial amount of sensitizer was necessary to obtain optimum sensitivity in comparison with the large-grain emulsion.[15] This may be because sensitization centers have to be formed on each grain, and the large number of grains in a UFG emulsion requires a large amount of sensitizer.

The addition of sodium nitrite to a UFG emulsion was ineffective, as shown in Fig. 7. One explanation for this observation is that the sodium nitrite was decomposed due to the high temperature in the emulsion to be added. On the other hand, the increase in sensitivity was significant when a coated film was immersed in the sodium nitrite solution. This sensitivity increase was especially notable for LI exposure, where the sensitivity increase was five times or more compared with that obtained using sulfur-gold sensitization. Moreover, the increase in the sensitivity was greater when a film with sulfur-gold sensitization was immersed in a sodium nitrite solution. The effects of sulfur-gold sensitization and immersion are additive. In contrast, for HI exposure, the increase in the sensitivity due to sulfur-gold sensitization was larger than that due to immersion, and additivity was not observed.

Sulfur-gold sensitization increases sensitivity by increasing the formation efficiency of the latent image specks and by decreasing the minimum developable size.[17,27] These effects are remarkable for HI exposure, which shows that higher sensitivity is obtained by sulfur-gold sensitization compared with that by immersion in a sodium nitrite solution.

Sulfur-gold sensitization also moderates rehaloganation, but not to the extent achieved by using a sodium nitrite solution. This moderation may be due to the sulfide monomers that function not only as hole traps but also as halogen acceptors.[28,29] Sodium nitrite functions as an effective halogen scavenger and prevents rehaloganation more efficiently than sulfur-gold sensitization. The result is a large increase in sensitivity for LI exposure.

CONCLUSIONS

1. The sensitivity of UFG emulsions increases when their films are immersed in a sodium nitrite solution before exposure. This increase was remarkable for LI exposure.
2. The sensitivity increased in proportion to the fourth and fifth powers of the grain size when the emulsion

was not immersed in a sodium nitrite solution. However, sensitivity increased with the third power of the grain size when the film was immersed. This suggests that there is a size-dependent, sensitivity-decreasing factor peculiar to UFG emulsions.

3. Rehalogenation proceeds readily in a UFG emulsion because silver clusters and halogen atoms/molecules are formed close to each other. This we propose is the main cause of the sensitivity decrease peculiar to UFG emulsions.
4. Sulfur-gold sensitization also increases the sensitivity of a UFG emulsion. Immersion in a sodium nitrite solution was more effective than the sulfur-gold sensitization method for LI exposure, although this result was reversed for HI exposure. Increases owing to each process were additive for LI exposure but not for HI exposure.

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