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Original Paper

Sensitization of ultra-fine-grain photographic emulsions (II): Combination of chemical sensitization and halogen acceptors

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Abstract: Sensitization methods including chemical sensitization and halogen acceptors (HA) for ultra-fine-grain (UFG) emulsions with different grain sizes and crystal habits were investigated and the desensitizing factors peculiar to UFG emulsions were analyzed. Sulfur-gold sensitization or HA alone gave a small sensitivity increase but the combination of both gave the maximum effect; reduction sensitization alone had a large effect but the combination with HA decreased the sensitivity from this level. Rehalogenation was suggested to be an important factor in the desensitization of UFG emulsions. Sensitization effects with exposure intensities and crystal habits were qualitatively similar between low and high intensities, and {111} and {100} faces, but the former cases showed larger effects than the latter cases. The sensitivity after sensitizing treatments was proportional to the higher power than the third one of grain size. The sensitivity of the unsensitized UFG emulsion was also in this proportional relationship, but was much lower than that of the sensitized emulsions.

Key words: Silver-salt photographic material, Ultra-fine-grain emulsion, Chemical sensitization, Halogen acceptor, Rehalogenation

1. Introduction

Silver halide photographic materials with ultra-fine-grain (UFG) emulsions are used for high-resolution recordings such as holograms[1)]. Nowadays, they are also used to record ultra-fine radiation tracks as they provide high resolution[2)]. Even though UFG emulsions are important for fine-recordings, the photographic characteristics of UFG emulsions are still not understood. For example, the photographic responses to high-intensity (HI) and low-intensity (LI) exposures are significantly different. Radiation exposure is similar to HI exposure[3)] while holograms are recorded with long-period exposure due to the low sensitivity of UFG emulsions. The former exposure often causes the dispersion of latent image specks (LIS), which is one factor decreasing sensitivity[4, 5)]. The dispersion of LIS is affected by chemical sensitization[6~11)], and these sensitizations are also affected by the crystal habits of the emulsion grains[12~15)]. These must be considered when designing photosensitive materials using UFG emulsions, but their characteristics are still not understood well.

It is known that photographic sensitivity to light is proportional to the volume of silver halide grains or proportional to the third power of the grain size[5)]. It was also reported that the sensitivity to radiation was proportional to the 1.5th power of the projected area of the grains[16)]. On the other hand, there are reports that the sensitivity is proportional to higher than the third power of the grain size in the size region including ultra-fine grains[17,18)]. This suggests that there are some desensitizing factors that enhance the sensitivity decrease, particularly in UFG emulsions.

To increase the intrinsic sensitivity of photographic materials, some chemical sensitization methods are usually applied[19, 20)]. Among these methods, sulfur-gold (SG) sensitization has high sensitivity and effectively recovers the sensitivity loss due to the dispersion of LIS and HI exposure[4,21~23)]. Previously, we investigated the sensitivity increase of UFG emulsions by SG sensitization and the halogen acceptor (HA) of sodium nitrite; we found that the halogen acceptor gave a large sensitivity-increase for UFG emulsions especially at LI exposure, while the SG sensitization did not[18)]. It is known that HAs are effective in removing rehalogenation[24~28)]. A hole arriving at the surface turns to an adsorbed halogen atom and this attacks a silver atom in the LIS to cause rehalogenation. In UFG emulsions, holes will easily turn to halogen atoms due to the large surface-volume ratio, and rehalogenation proceeds rapidly. Therefore, reduction (R) sensitization can also restrain rehalogenation, as already reported[14, 19, 20, 29)]. Moreover, there is a patent that R sensitization is useful to increase in the sensitivity of UFG emulsion for hologram[30)], although the mechanism of sensitization is not discussed. However, we did not try the R sensitization in UFG emulsions at that time.

Following the previous investigations[18)] we tried to expand the methods to increase the sensitivity of UFG emulsions. We used both R and SG sensitizations, and also used acetone semicarbazone and sodium nitrite as HAs. We then compared the effects by these methods and investigated the additivity of these methods. We also analyzed the difference with low and high intensities, the size-de-

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pendence, and the effect of crystal habit of the grains to clarify the desensitizing factors peculiar to UFG emulsions.

Experimental

Two types of photographic emulsions were used. The first was a series of emulsions with $AgBr_{0.98}I_{0.02}$ monodisperse cubic grains, hereafter called Em_A. These emulsions were used in our previous studies[18, 31, 32]. The edge lengths of these grains were 35, 43, 80, 92, 124, and 148 nm, and we compared the grain-size effect using these emulsions. The second emulsion consisted of nearly spherical AgBr0.98I0.02 grains and the grain diameter was approximately 40–50 nm. This emulsion, identified as Em_B, was also used in our previous studies[18,33].

We subjected these emulsions to SG sensitization or R sensitization. A gold thiosulfate complex $\{Na_3Au(S_2O_3)_2\}$ was used as the sensitizer for the former[18, 34] and its quantity was varied from 1 to 15 mmol/molAg. A thioureadioxide $\{(NH_2)(NH)CSO_2H\}$ was used as the sensitizer for the latter and its quantity was varied from 0.1 to 30 mmol/molAg. The emulsions were treated at 60 °C for 60 min during both sensitization treatments. These emulsions were coated on a poly(ethylene terephthalate) (PET) base by hand, hence the thickness of coated films had some irregularity.

These unsensitized and sensitized emulsions were treated with HAs. Sodium nitrite (NO; $NaNO_2$) and acetone semicarbazone $\{ASC; (CH_3)_2C{=}NNHCONH_2\}$ were used as HAs. This treatment was performed using two methods. The first method involved the addition of the HA to the emulsion just before coating. In the second method, the coated film was immersed in the HA solution before exposure. In the former case, 0.35 $mmol/mol_{Ag}$ of NO was added to the Em_A emulsions, and 0.3-1.2 $mmol/mol_{Ag}$ of NO or 0.35 $mmol/mol_{Ag}$ of ASC was added to the Em_B emulsion. In the latter case, a coated film was immersed in the HA solution with a concentration of 0.1 mol/L NO (or ASC) 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 the LI white light exposure (duration 100 s). The intensity in front of the step wedge was 539 lx and the exposure value was represented with H (lx s). For the HI exposure (duration 10^{-6} s), a xenon flash lamp was installed in the sensitometer. As the intensity of the HI exposure was not measured and the exposure value was represented as a relative value (rel. E), exposure values of H for the LI exposure and of rel. E for the HI exposure were not identical.

The exposed films were developed using a D72 developer diluted 1:4. The development temperature was 20 °C and the development time was 5 min. Normal stop, fixation, and washing treatments were performed after development. The optical densities (OD) of the developed films were measured with a photographic densitometer and photographic characteristic curves were obtained. Because the thickness of coated films had some irregularity due to the hand-coating, the measured OD values sometimes varied widely. Therefore, we measured the OD at several points and treated the data statistically. The sensitivity was compared with the reciprocal of the exposure value that gave OD of 0.1 above fog on a characteristic curve. We set this small value of 0.1 for the sensitivity measurement because the sensitivity of the UFG emulsions was very low and near the limit of measurement. However, this brought about some uncertainty in sensitivity.

Experimental Results

Characteristic curves of the set of Em_A emulsions with grains of different edge lengths with LI exposure are shown in Fig. 1. They were treated with SG sensitization (5 $mmol/mol_{Ag}$) and/or immersion in an NO solution (0.1 mol/L). Sensitivity decreased with decrease in grain size, especially that of the unsensitized emulsion with the smallest grain decreased drastically to reach the limit of measurement. SG sensitization alone was significantly effective in increasing sensitivity in larger-grain emulsions, while it was not so in smaller-grain ones. HA alone was not very effective, but increased the maximum density and contrast. A combination of both gave a large increase in sensitivity, even for the smaller-grain emulsions.

Characteristic curves for the set of Em_A emulsions treated with R

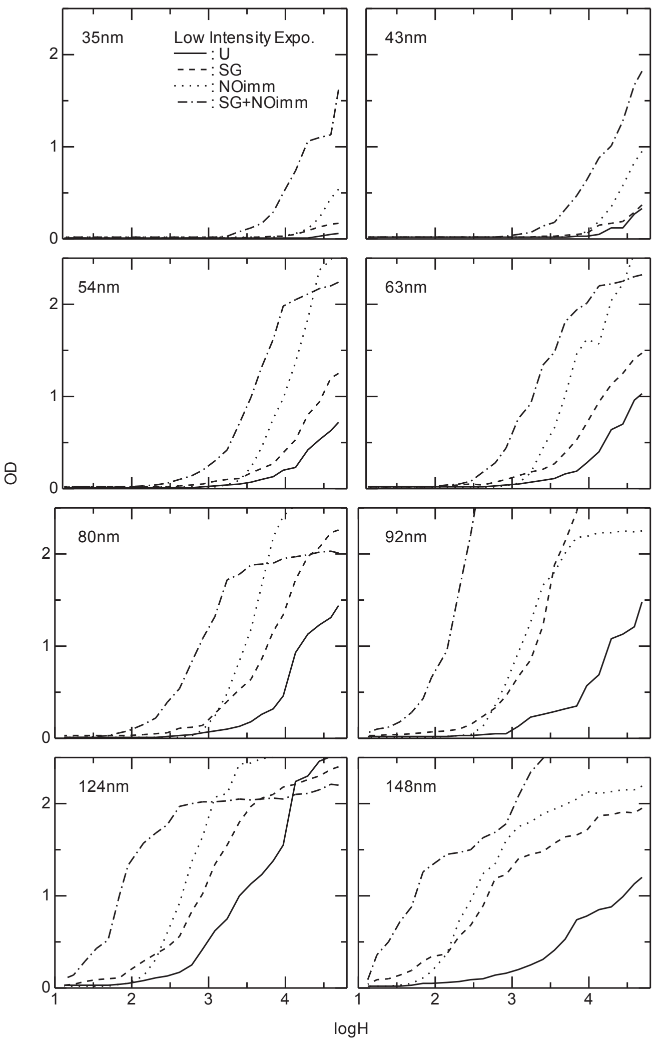

Fig. 1 Characteristic curves of Em_A emulsions with cubic grains of different edge lengths treated for SG sensitization and/or immersion in sodium nitrite solution (NO) at low-intensity (100 s) exposure.
— : Unsensitization, ---- : SG sensitization, *** : Immersion in NO, : SG sensitization and immersion in NO.

sensitization (3 mmol/mol_{Ag}) and/or immersion in the NO solution are shown in Fig. 2 with LI exposure. In the larger-grain emulsions, fog appeared with R sensitization treatment and we could not obtain characteristic curves. R sensitization alone gave high sensitivity and increase in contrast, while the combination of HA and R sensitization decreased the sensitivity from that of R sensitization alone.

Characteristic curves for the set of Em_A emulsions treated with the same protocol as in Fig. 1 are shown in Fig. 3 for HI exposure. Sensitivities of the unsensitized emulsions with smaller grains were beyond the measurement limit. Although it is known that SG sensitization is effective for HI exposure, the effect was definitive with the smaller-grain emulsions. The effect of HA alone was small.

Characteristic curves for the set of Em_A emulsions treated with the same protocol as in Fig. 2 are shown in Fig. 4 for HI exposure. R sensitization alone had high sensitivity. The combination with HA decreased the sensitivity from this level, similar to the observations with LI exposure. Behaviors with HI and LI exposures were qualitatively similar, but the sensitivity increase by these methods with HI exposure was not as drastic as with LI exposure.

The relationships between the edge length and sensitivity for LI exposure are represented on a logarithmic scale for Em_A emulsions with SG sensitization and/or immersion in NO solution on the left side of Fig. 5, and those with R sensitization and/or NO immersion on the right side. Points for these relationships lay mostly on a straight line with similar slope. However, the sensitivity of the unsensitized emulsion with the smallest grains decreased drastically and large desensitization appeared, as shown by the deviation from the straight line. The slopes of each sensitization method are represented in the lower right of the figures, and they were all larger than three. These suggested that there were some desensitizing factors in smaller-grain emulsions and these factors worked drastically on the unsensitized emulsion.

The relationships between the edge length and sensitivity for HI exposure are represented in Fig. 6 in the same way as in Fig. 5. The points for each sensitization method were on a straight line, but the slopes were all larger than three. The sensitivities for unsensitized emulsions with smaller grains under HI exposure were very low, and there was no point at these sizes. These sensitivities were lower than those expected from extrapolation of this line. These suggest that a desensitization route peculiar to the UFG emulsion also exists with HI exposure.

Characteristic curves for the Em_B emulsion treated with SG or R sensitization or the addition of NO before coating, where the amount of sensitizer or additive was altered gradually, are shown in Fig. 7 for LI exposure. We could not obtain the sensitivity for the

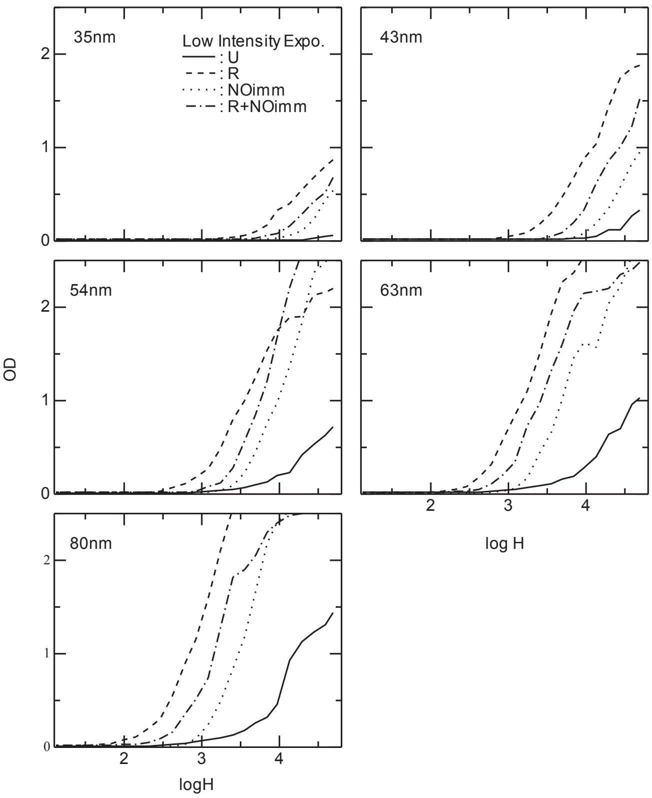

Fig. 2 Characteristic curves of Em_A emulsions with cubic grains of different edge lengths treated for R sensitization and/or immersion in NO solution at low-intensity (100 s) exposure.
— : Unsensitization, ---- : R sensitization, *** : Immersion in NO, : R sensitization and immersion in NO.

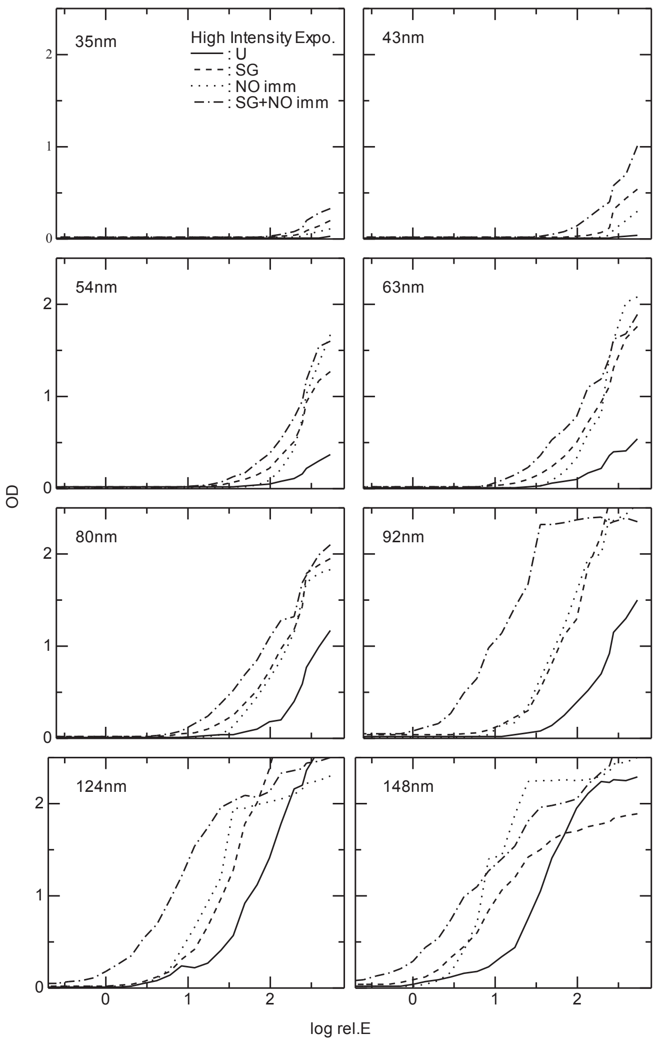

Fig. 3 Characteristic curves of Em_A emulsions with cubic grains of different edge lengths treated for SG sensitization and/or immersion in NO solution at high-intensity (10^{-6} s) exposure.
— : Unsensitization, ---- : SG sensitization, *** : Immersion in NO, : SG sensitization and immersion in NO.

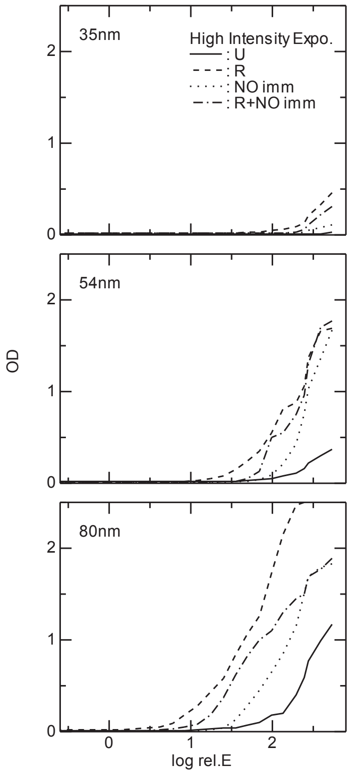

Fig. 4 Characteristic curves of Em_A emulsions with cubic grains of different edge lengths treated for R sensitization and/or immersion in NO solution at high-intensity (10^{-6} s) exposure.
— : Unsensitization, ---- : R sensitization, *** : Immersion in NO, : R sensitization and immersion in NO.

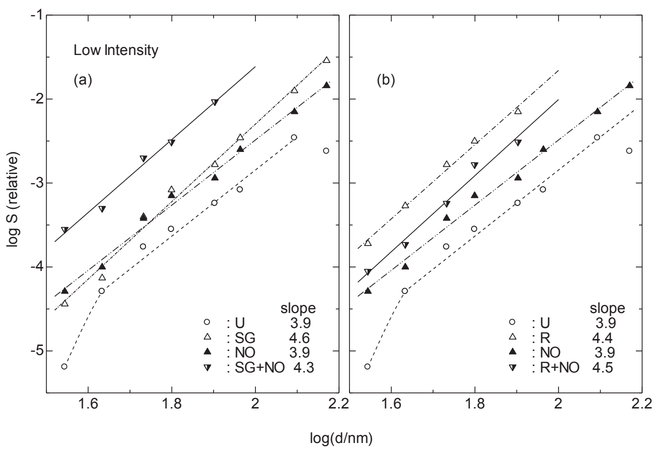

Fig. 5 Logarithmic plot of the edge length of cubic grains in Em_A emulsions versus sensitivity for low-intensity (100 s) exposure with each sensitization method. Slope is the inclination of the straight line through the plotted points.
U: Unsensitization, SG: SG sensitization, R: R sensitization, NO: immersion in NO solution.

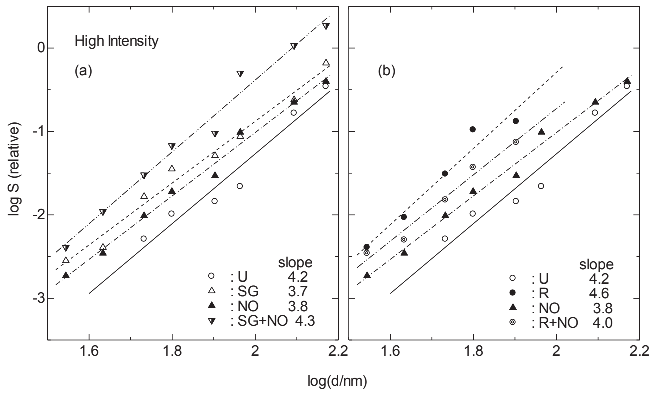

Fig. 6 Logarithmic plot of the edge length of cubic grains in Em_A emulsions versus sensitivity for high-intensity (10^{-6} s) exposure with each sensitization method. Slope is the inclination of the straight line through the plotted points.
U: Unsensitization, SG: SG sensitization, R: R sensitization, NO: immersion in NO solution.

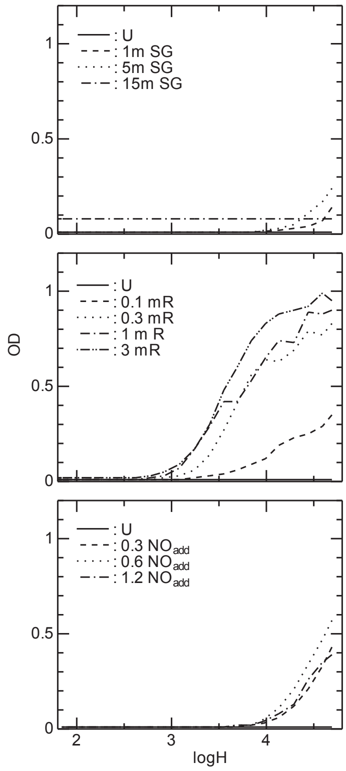

Fig. 7 Characteristic curves of Em_B emulsions with octahedral grains after different sensitization methods at different levels and at low intensity (100 s) exposure.
Top: SG sensitization, center: R sensitization, bottom: addition of NO solution before coating.

unsensitized emulsion, due to its low sensitivity. SG sensitization showed a small increase in sensitivity; increase in the amount of sensitizer caused significant fog. R sensitization showed a large effect of sensitization with an increase in the amount of sensitizer. Addition of NO showed a larger increase in sensitivity than SG sensitization, but did not reach the level of R sensitization. Increase in the amount of NO did not cause a significant increase in sensitivity. The effect of R sensitization on the Em_B emulsion was much larger than that on the Em_A emulsions with similar grain size.

We added NO or ASC to the Em_B emulsions treated with SG or R sensitization before coating or immersed the coated films in solutions containing them to investigate the combined effects. Characteristic curves of these materials with LI exposure are shown in Fig. 8. The figure on the left shows the results of SG sensitization and the figure on the right shows the results of R sensitization. As with the Em_A emulsions with small grains, sensitization effects by SG sensitization or HA alone were not large but the combination of both gave the largest effect. Immersion treatment gave a larger effect than

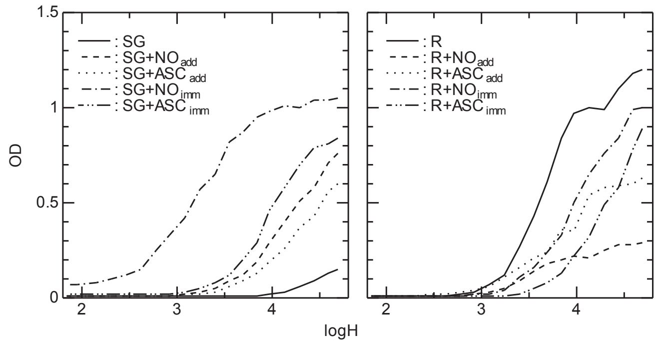

Fig. 8 Characteristic curves of Em_B emulsion with octahedral grains after different sensitization methods and combination of them at low intensity (100 s) exposure.
Left: SG sensitization, right: R sensitization.
NO: sodium nitrite, ASC: acetonsemicarbazone, add: addition of HA solution before coating, imm: immersion of coated film in HA solution.

addition. This increased amount of sensitivity was much larger than that in the Em_A emulsions. R sensitization alone also showed a large effect, even though this did not reach the level with combined SG sensitization and NO; the combination with R sensitization and HA decreased the sensitivity, as with the Em_A emulsions. Generally the effect of sensitization method on the Em_B emulsion was similar to that on the Em_A emulsions but quantitatively larger; this was one main difference between the Em_B and Em_A emulsions.

Discussion

Previously we reported that there was intense desensitization on UFG emulsions due to rehalogenation. HA gave a large sensitivity increase, especially at LI exposure due to the restraint of rehalogenation while the SG sensitization did not[18]. This tendency was also observed in this investigation. Moreover, the maximum density and contrast due to SG sensitization alone were still low. These suggest that SG sensitization is not enough to restrain the rehalogenation of UFG emulsions. It is known that the increase in sensitivity by SG sensitization is due to the increase in the formation efficiency of LIS and to the induction of developability in smaller sub-image specks[19,21]. Therefore, SG sensitization is also effective at HI exposure[4, 21–23], which causes the dispersion of LIS where many small and undevelopable sub-image specks were formed. However, the small specks formed under SG sensitization may be rehalogenated easily in the UFG emulsion by halogen atoms generated simultaneously; this causes the small sensitization effect. On the other hand, combination of SG sensitization and HA gave the maximum sensitization effect in the previous report[18] and in this investigation. Therefore, when HA restrains rehalogenation, small specks formed on SG-sensitized emulsion survive and become developable to cause a large increase in sensitivity.

It is considered that R sensitization acts as hole traps[4, 35] and removes holes on the surface, which has the same matter to adsorbed halide atoms. Because the ratio of holes on the surface increased with smaller grains, it restrains both recombination and rehalogenation, causing large sensitization effects in the UFG emulsions. However, the sensitivity could not reach the level of SG sensitization plus HA, because R sensitization cannot make smaller sub-image specks developable. The sensitization effects were not additive when both R sensitization and HA were used together. Maybe both had the same function of removing halogen atoms, and HA treatment decreased the high sensitivity caused by R sensitization. One possibility is that the adsorption of HA on the R sensitization centers would disturb their action and decrease the sensitivity from the level of R sensitization alone.

The Em_A emulsions consist of cubic grains with {100} faces while Em_B consists of spherical grains, which will be regarded as grains with {111} faces. The effect of sensitization of the Em_B emulsion was generally larger than those of Em_A. There was a remarkable difference between the Em_B and Em_A emulsions with SG sensitization plus HA and R sensitization, while SG sensitization alone did not show a remarkable difference. Birch reported that halogen atoms were preferentially evolved at {111} faces on cubo-octahedral grains[14]. Because this evolution would decrease the number of holes inside a grain and decrease recombination, the effective removal of halogen atoms on the surface by HA or R sensitization would increase the sensitivity of the Em_B emulsion.

Increase in the amount of R-sensitizer was effective in increasing the sensitivity, while that of HA was not. HAs are only adsorbed on the surface and do not form sensitization centers by decomposing the sensitizer as do SG or R sensitizations. The number of adsorbed HA will be saturated at adsorption equilibrium and the effect becomes constant thereafter. Consequently, smaller molecules of HA (such as NO) will be favorable for UFG emulsions, as shown in the results combining SG sensitization and HA in Fig. 8.

Relationships between logarithmic scales of grain size and sensitivity were almost on a straight line, as shown in Figs. 5 and 6. However, this relationship deviated significantly to the lower-sensitivity side at the unsensitized emulsion. This suggests strong desensitization on UFG emulsions, and this desensitization would be due to rehalogenation[18]. This deviation was recovered by some sensitization treatments and these treatments would relieve the desensitizing factors working on the unsensitized emulsion. As the slopes of these straight lines were all still larger than three, these treatments could not remove the desensitizing factors with UFG emulsions completely.

Multi-scattering is generally strong at large grains, but weak at fine grains. This causes increase in the absorption of light at larger grains and this is one possible reason why the slopes were larger than three. In this case, however, the plotted points will not be on a straight line because the points with larger grains are on the straight line of slope three and the ones with smaller grains deviate from this line. Moreover, this change would occur with all types of sensitization method because the grain shape itself is not affected by these methods. Though the accuracy of the sensitivity measurement was insufficient, bending of the line was observed only for the unsensitized emulsion and not others. Consequently, this scattering effect would not be significant.

We obtained a large sensitivity increase in the UFG emulsion by combining several sensitization methods. The combination of SG sensitization and HA revealed the largest sensitivity, although the sensitivity was still proportional to the higher power than the third one of grain size. It was confirmed again that the removal of halogen atoms is effective in UFG emulsions, and rehalogenation is an important factor causing desensitization.

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