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# Sensitization by Formate Ions Doped at Different Depths in Silver Bromide Microcrystals

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**Abstract.** *In a double-jet apparatus controlled by a microcomputer, a series of formate doping emulsions of cubic AgBr grains in which formate ions were doped at different sites were prepared when a certain volume of sodium formate solution was injected into the emulsifying solution at different time intervals after the beginning of precipitation at a constant* pAg. *The sensitometric results from these formate doped emulsions showed: (1) that there were great differences in sensitivity between the emulsions that the same quantity of formate ions were doped at different sites of grains; (2) that relative sensitivity of doping emulsions to the corresponding undoping ones monotonically increased as the formate ions were moved closer to surface of grains; (3) that a cooperative sensitization by doping formate ions,* S+Au *and dye could be carried out to make a higher level of sensitivity possible without a significant increase in fog density; (4) that the formate ions doped inside AgBr grains were able to trap holes produced in dye aggregates adsorbed on the surface of grains, moreover, the closer to surface the doping ions were, the greater a sensitivity gain was. © 2006 Society for Imaging Science and Technology.*
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## INTRODUCTION

In 1998–2003 Belloni et al.[1–4] first and subsequently reported that formate ions doped in AgBr grains could remarkably sensitize the emulsion and they also proposed a mechanism for the sensitization by formate doping, that was

$$\mathrm{HCO_2^-} + h^+ \rightarrow \cdot\mathrm{CO_2^-} + \mathrm{H}^+, \tag{1}$$

$$\cdot\mathrm{CO_2^-} + \mathrm{Ag}_n^+ \rightarrow \mathrm{Ag}_n + \mathrm{CO_2}. \tag{2}$$

After then, Guo et al.,[5] using the electron spin resonance (ESR) technique, gave indirect evidence for the existence of reaction (1), i.e., an intensified ESR signal of $\cdot\mathrm{CO_2^-}$ was clearly detected from a dispersion of AgBr grains in a saturated solution of formate under illumination. Nevertheless, Hailstone[6] expressed questions, particularly about the effectiveness of the sensitization of the formate doped emulsions sensitized spectrally by sensitizing dyes. It is a justified question because there is no knowledge about the interaction between formate ions doped in grains and positive holes photogenerated from dye adsorbed on the surface of grains. In the present paper, sensitization by formate ions doped at different depths of cubic AgBr grains that were unsensitized, and grains that were sensitized chemically and spectrally on the surface was investigated

## EXPERIMENT

### *Preparation of an Emulsion of Cubic AgBr Grains in Which Formate Ions Were Doped at Different Sites*

A computerized double-jet apparatus was used to control all parameters of emulsifying process. In the first 10 min, $\mathrm{AgNO_3}$ and KBr solutions of 2.0 mol/L were continuously added, respectively at a constant flow rate of 2.0 and 1.2 ml/min to an agitating gelatin solution 12 g/600 ml $\mathrm{H_2O}$ at 50 °C and *p*Ag was kept at 7.4. Then *p*Ag was adjusted to 3.6 and the flow rates of the solutions were linearly increased by 0.2 and 0.19 ml/min for about 24 min when, in different time intervals, a specific amount of sodium formate ($1\times10^{-4}$ mol/mol Ag) in solution was injected to the emulsifying vessel. After than, *p*Ag was adjusted back to 7.4 and the precipitation was going on for a couple of minutes until terminated. Post-treatment of the prepared emulsions was just as usual and *p*H and *p*Ag of the emulsions were adjusted respectively to 5.5 and 7.2 for storage.

### *Sulfur-Plus-Gold Sensitization*

$\mathrm{Na_2S_2O_3}$ solution (0.5 ml, 0.1%) and 0.05 ml of a mixture of $\mathrm{AuCl_3}$ (0.02%) and $\mathrm{NH_4SCN}$ (0.2%) solutions in equal volume were added in turn to 50 g emulsions. Then the emulsions were digested at 50 °C for 60 min and then 0.5 ml of TAI solution (2%) was added.

### *Spectral Sensitization by Dye*

A green sensitizing dye, a red sensitizing dye, and a blue sensitizing dye as shown in Figs. 1(a)–1(c) were used, respectively, for the spectral sensitization of the emulsions. The maximum of sensitization of these dyes was at 550, 640, or 460 nm, respectively, 2.5 ml of the dye methanol solution (0.1%) was added to 50 g of the chemically sensitized emulsion, which was agitated at 40 °C for 5 min. The emulsions were kept still for 20 min and then coated on a triacetate film base.

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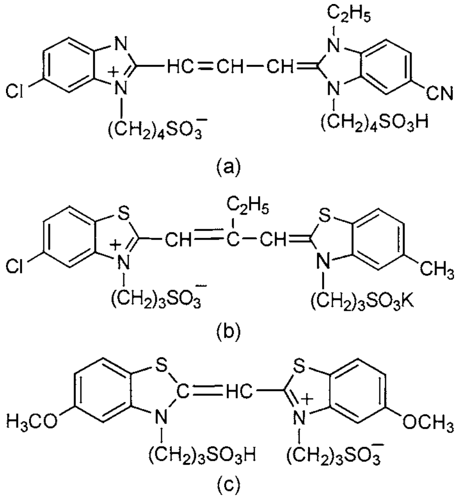

Figure 1. Structures of sensitizing dyes: (a) green sensitizing dye; (b) red sensitizing dye; and (c) blue sensitizing dye.

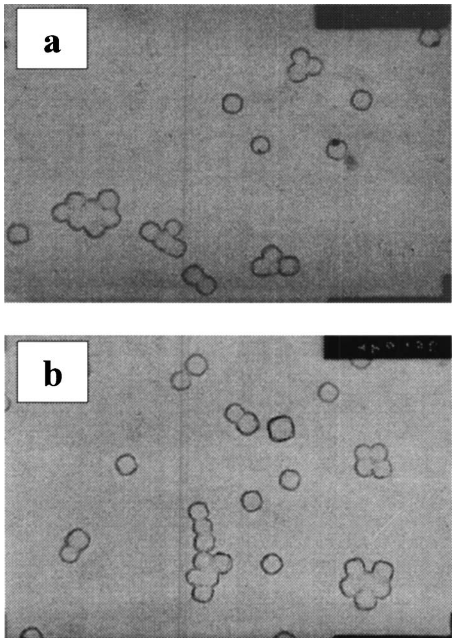

Figure 2. TEM micrographs of two cubic AgBr emulsions, grain sizes of which were: (a) 170 nm for the undoped one; and (b) 180 nm for the dopes one with formate ions at 0.59 away from the center of grains.

### *Sensitometry*

The coated emulsion layers were exposed to white light with color temperature 5500 K or to monochromatic light (red, green, or blue) via a filter with a maximum transmittance at the central wavelength 650, 550, or 430 nm for 1 s in a CGG sensitometer. The exposed emulsion layers were developed in a MAA-1 surface developer at 20 °C for 10 min. The optical densities were evaluated by Macbeth 903 densitometer. The sensitivity was given by the reciprocal of the exposure required to give an optical density of 0.1 above fog density. Sensitivity of the formate undoped primitive emulsion was taken to be 100 for calculation of relative sensitivities.

### *Observation and Measurement of Silver Bromide Grains*

A JEM-100CX transmission electron microscope (TEM) was used for observation and measurement of the cubic grain sizes. Seven samples of emulsion grains were observed and two of them, one undoped and another doped at 0.59 of the relative edge length from the center of grains, are shown in Figs. 2(a) and 2(b). It can be seen from Fig. 2 that the edges and corners of cubic grains were not as sharp as the cubic grains prepared in the conventional way, which may arise from a *p*Ag drop (from 7.4 to 3.6) for doping. On the other hand, no overly fine grains were found in the micrographs of all samples, which means that no new nuclei were formed in the process of growth and formate doping of grains.

The arithmetical average size and the corresponding standard deviation (SD) of grains in all seven emulsions, including undoped and six doped ones, are listed in Table I. The standard deviations of grain size were all within 0.01, which indicated that the grain monodispersity of each emulsion was quite good. The average size and the SD of grains for all seven emulsions were $0.18 \pm 0.02\ \mu$m.

## RESULTS AND DISCUSSION

### *Relative Depth or Position of the Formate Ions Doped in the Cubic Grains*

The depth or position of the doped formate ions in the cubic grains is based on the following assumptions: (1) during the precipitation of AgBr, all additions of dopant (formate) are at the stage of grain growth when no new nuclei are formed, thus the number of grains remains a constant; (2) that the additional dopant is rapidly adsorbed on the surface of growing grains at a specific *p*Ag for a couple of minutes; (3) the distribution of grain sizes is quite uniform. The first assumption was based on a mathematic model by Jagannathan et al.,[7] which was adopted to calculate some operating parameters, such as flow rates of the reactant solutions, etc., to control the growth of grains without formation of new nuclei. The data on average grain sizes and their corresponding SD's of the prepared seven emulsions, as given in Table I, showed the monodispersity of grain size each emulsion was quite good, even though the fluctuation of average sizes between different emulsions was slightly greater; $\mathrm{SD} = \pm 0.02\ \mu$m as given above, was slightly greater than that of any single emulsion ($\mathrm{SD} = \pm 0.01\ \mu$m). Nevertheless it could be consistent with the third assumption. The second assumption should be considered only as a sort of hypothesis with which the adsorption rate of formate ions was assumed to be proportional to the square of edge length of a growing grain at a constant *p*Ag, so it should be more consistent with the condition described in assumption (2) when the growing grain sizes were bigger than when smaller. For this reason, some deviation from assumption (2) might exist in the doping positions closer to the center of grains to create a gap between the actual doping position and the calculated one. For the sake of simplification, this deviation will be neglected. Based on the above three assumptions, each doping position could be approximately calculated as follows.

The relative positions of the dopant in a cubic grain can be easily calculated by $L_r(t) = [M(t)/M]^{1/3}$, where $L_r(t)$ de-

**Table I.** Grain sizes and sites of formate ions doped in grains of emulsions prepared.

| No. of emulsions | 0 (undoped) | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| Grain size[a] ($\mu$m) | 0.17 ±0.01 | 0.18 ±0.01 | 0.17 ±0.01 | 0.17 ±0.01 | 0.20 ±0.01 | 0.17 ±0.01 | 0.20 ±0.01 |
| $M(t)/M$ | - | 0.20 | 0.40 | 0.60 | 0.80 | 0.85 | 0.90 |
| $L_r(t)$ | - | 0.59 | 0.74 | 0.84 | 0.93 | 0.95 | 0.97 |
| $l_a$ (nm)[b] | - | 53 | 67 | 76 | 84 | 86 | 87 |
| $D_r(t)$ | - | 0.41 | 0.26 | 0.16 | 0.07 | 0.05 | 0.03 |
| $d_a$ (nm)[b] | - | 37 | 23 | 14 | 6 | 4 | 3 |

[a] The average grain size of all seven emulsions was $0.18 \pm 0.02$ $\mu$m.

[b] $l_a$ and $d_a$ were absolute length from the center and depth from the surface, at which the doping layer was located. They were given by products of the average half edge length of grains ($l_h = 90$ nm) multiplied by $L_r(t)$ and $D_r(t)$.

notes a relative length from the center to the doped layer, ranging from 0 to 1 relative to the half of edge length of a cubic grain, and was a function of time $t$ when the dopant was injected into the emulsifying reactor; $M(t)$ an additional accumulative amount of $Ag^+$ at the time $t$; $M$ the total additional amount of $Ag^+$ at the ending of precipitation. The relative depth, away from the surface of grains, is given by $D_r(t) = 1 - L_r(t)$. A schematic diagram for the positions of dopant in a cubic grain was shown in Fig. 3. $M$ and $M(t)$'s were given, so the sites of doped formate ions in the cubic grains of emulsion could be calculated as listed in Table I.

### *Relative Sensitivities of Primitive, Chemically, and Spectrally Sensitized Emulsions in Which the Formate Ions Were Doped at Different Sites of Cubic AgBr Grains*

Comparing with the sensitivity of the undoped primitive emulsion as a control, the relative sensitivities for all other emulsions exposed to a source of light with 5500 K, including those undoped and doped with formate ions at different sites, as well as unsensitized (primitive) and sensitized by S+Au and dye ($G$) or dye ($R$), i.e., green or red sensitive, are given in Table II and Fig. 4. These data and curves indicated some interesting results as follows.

(1) Changes of the relative sensitivity with the doping sites may be separated into two regions. In the first region, at $0.6 \leqslant L_r(t) \leqslant 0.95$, relative sensitivity increases gradually as the doping sites are moved toward the surface; however, in the second region, where $L_r(t)$ was above 0.95 and closer to the surface, sensitivity of the doped emulsions abruptly increases. It indicates a significant effect of the doping site on the sensitization, particularly for the doped emulsions sensitized by both dye ($G$) and dye ($R$). The closer to the surface of the grains the formate-doping layer is, the better or the more effective to the sensitization. These results were essentially consistent with what Belloni et al.[3] reported. In the present study, however, the maximal sensitivity gain (MSG) for the S+Au+dye ($G$) emulsion doped at $L_r(t) = 0.97$ was only about 2.5 times higher than that for the corresponding undoped emulsion, which was much lower than ten times as reported by Belloni and co-workers. The difference may arise from two main reasons: (1) that we did not find any significant effect of the delayed latent image formation in our experiments, which was said to double the sensitivity gain; (2) that the region close to the surface of the grains is so sensitive to sensitization, as illustrated in Fig. 4, that any slight change in the doping site may give rise to a great change in sensitivity. For this reason, the doping site at $L_r(t) = 0.97$ where the maximal sensitivity was obtained from our experiments may not be a real optimal site at which the MSG could be obtained. It might be better if the site were extended even further toward the surface. On the other hand, it has been noticed that desensitization of some doped emulsions took place at $0.6 \leqslant L_r(t) \leqslant 0.85$ which has never been reported before, and which could not be accounted for at present. It will be studied further in the future.

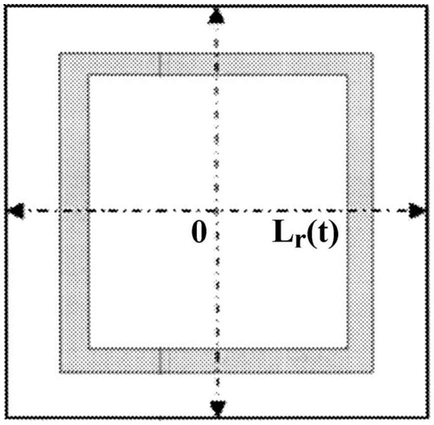

Figure 3. Schematic for position of dopant located in gray zone.

(2) The conventional sensitizations, such as by S+Au and dye, were still applied to the formate doped emulsions without any unwanted effect, which meant that the sensitization caused by the doped formate ions was compatible

**Table II.** Relative sensitivities and fog densities of the emulsions that formate ions were doped at different sites of grains and exposed to white light (5500 K). Note: (1) the sensitivity of undoping primitive emulsion was taken as 100 and (2) the data in parentheses were fog densities.

| No. of emulsions | Sites of dopant $L_r(t)$ | Sr ($D_0$) for primitive | Sr ($D_0$) for S+Au sensitized | Sr ($D_0$) for S+Au +dye (*G*) | Sr ($D_0$) for S+Au +dye (*R*) |
|---|---|---|---|---|---|
| 0 | No dopant | 100(0.01) | 177(0.02) | 1076(0.01) | 1154(0.04) |
| 1 | 0.59 | 62(0.01) | 129(0.01) | 577(0.02) | 373(0.04) |
| 2 | 0.74 | 212(0.01) | 231(0.01) | 865(0.03) | 615(0.05) |
| 3 | 0.84 | 192(0.02) | 339(0.01) | 1154(0.04) | 1000(0.04) |
| 4 | 0.93 | 173(0.02) | 346(0.01) | 1385(0.02) | 1115(0.02) |
| 5 | 0.95 | 169(0.00) | 339(0.03) | 1462(0.02) | 1308(0.02) |
| 6 | 0.97 | 423(0.02) | 673(0.03) | 2692(0.05) | 2885(0.05) |

with the conventional ones to make a cooperative sensitization possible. It might be attributed to independent sensitizing mechanisms, hole trapping, and electron concentrating, in the process of latent image formation.

(3) One of advantages for the formate doping of emulsions is a lower level of fog density ($\leq 0.05$) regardless of chemically or/and spectrally sensitization. It makes them superior to silver dimer ($Ag_2$) doped emulsions, even though $Ag_2$ is thought to possess the same function as a hole scavenger.[8,9]

### *Sensitization of the Formate Doped Emulsions Sensitized by* S+Au+Dye *(R, G, or B) Exposed to the Corresponding Monochromatic Light (R, G, or B)*

It is known for dye sensitized emulsions that photogenerated holes produced as a result of dye photoexcited by corresponding monochromatic light sensitive are located in the highest occupied molecular orbital (HOMO) of the dye *J*-aggregate adsorbed on surface of Ag*X* grains.[10,11] When the dye ($G,R$) sensitized emulsions are exposed to white light as with 5500 K, however, the photogenerated holes are possibly produced from two different places: at the valence band (VD) in the interior of grains by the absorbed blue light, i.e., inherently sensitivity of Ag*X* grains, or in the HOMO of the dye aggregates on the surface of grains, respectively by light absorbed by the sensitizer. So the sensitivity gains of formate doping emulsions, as given in Table II, may come from two contributions: one made by an interaction of the doped formate ions with the internal holes at VD of the grains and another by that with holes in surface dye aggregates. In order to get rid of the first effect and separately to observe the second one, it was necessary to make doped emulsions sensitized by S+Au+dye ($R$) or S+Au+dye ($G$), respectively, to be exposed to red light or green light instead of white light. The curve delineating a change in relative sensitivity versus doping sites for the doped emulsions illuminated by red light or green light was separately plotted in Figs. 5(a) and 5(b).

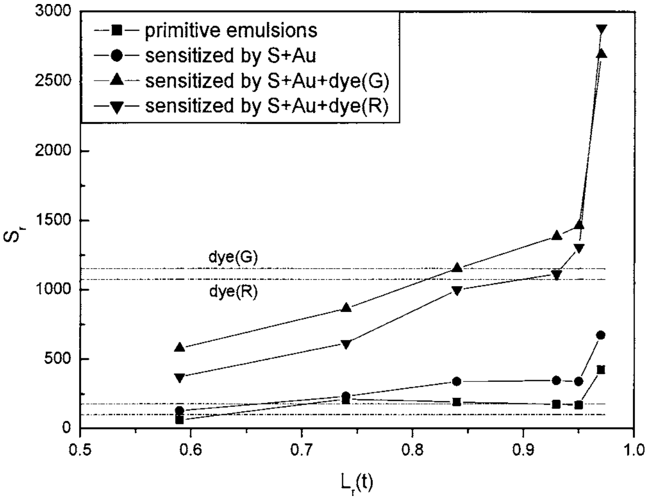

Figure 4. Relative sensitivities of doped emulsions in which formate ions were at different sites exposed to white light. The parallel dash-dotted lines denote sensitivity levels ($S_0$) of the corresponding undoped emulsions.

From Figs. 5(a) and 5(b) some interesting results were shown: (1) that shape and trend of two curves for $S_r$ as a function of $L_r(t)$ for the doped emulsions exposed to the corresponding actinic light were quite similar to each other, i.e., in both cases $S_r$ increases monotonically as the doping layer moves toward the surface and reaches a maximum at $L_r(t)=0.97$, close to the surface; (2) that the sensitivity gains may be supposed to be a result of an interaction between the internal doping formate ions and the positive holes primarily produced from the HOMO of dye aggregate on the surface of the grains; (3) that such an interaction may take place when holes were transferred across the interface into the valence band of a grain and trapped by doping ions that were considered to be still at their doping sites and immabile. So the closer the distance between these two species is,

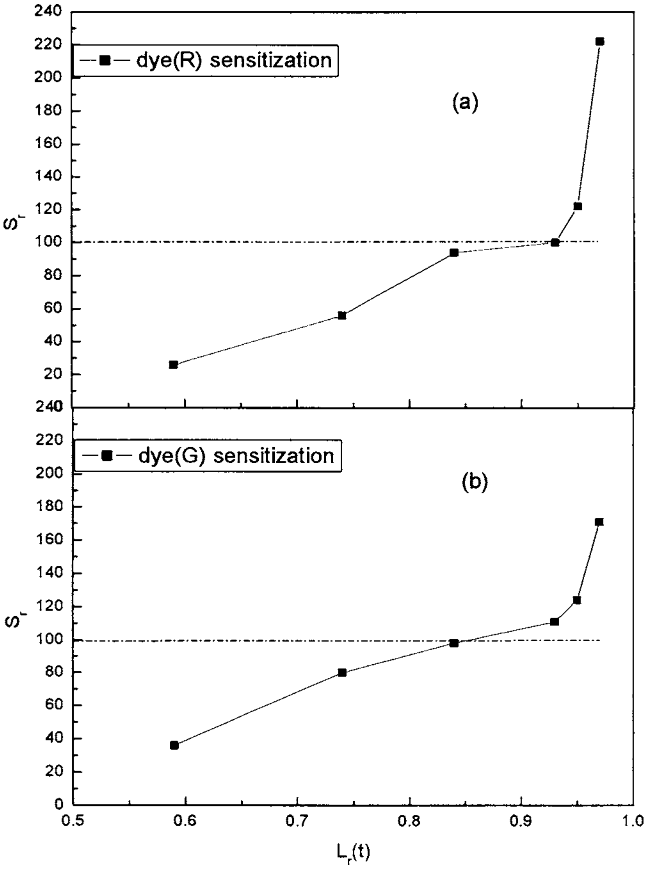

Figure 5. Relative sensitivity vs $L_r(t)$ for emulsions in which formate ions were doped at different sites of grains: (a) for the doped emulsions sensitized by S+Au+dye (*R*) exposed to red light; (b) for those sensitized by S+Au+dye (*G*) exposed to green light. The parallel dash-dotted line denotes a sensitivity level ($S_0$) of an undoped emulsion.

the greater the probability for their interaction is, thus, the more beneficial to an increase in the sensitivity gain.

As far as the sensitization of formate doped at different sites of AgBr grains is concerned, obviously, the site at which the value of MSG ($S_{max}/S_0$) emerges, i.e., $L_r(t)=0.97$ in the present study, is the most important. Thus, all MSG data, including those obtained from the primitive, S+Au and dye (*R*, *G*, or *B*) sensitized doping emulsions that exposed to either white light or sensitive monochromatic light, were listed in Table III for the sake of comparison. From the MSG data in Table III it can be found: (1) that the MSG values for undyed primitive and S+Au sensitized emulsions exposed to white light, both are 4.0, the greatest, because most of holes trapped by doping ions were generated from the VB of grains, thus trapped more efficiently: (2) that the MSG values for dyed emulsions exposed to white light are greater than those for the corresponding one exposed to, respectively, sensitive light, except for dyed (*B*) emulsions where MSG values are nearly equal (3.3 and 3.2), because the holes trapped by doping ions could be generated in both VD and surface dye, respectively, by blue and a blue component in white light, whereas the holes generated in surface dye when dyed ($R,G$) emulsion is exposed to the corresponding actinic light have to be transferred into VD and then are trapped by the doping ions, so it is less effective; (3) that there exists a difference in MSG values of three different dyed emulsions exposed to the corresponding actinic light, i.e., 2.2, 1.7, and 3.2, respectively, for dyed (*R*), dyed (*G*), and dyed (*B*) ones. This difference may be ascribed to different efficiencies with which the holes are trapped. There may be many factors to influence the hole trapping efficiency, such as different energy barriers that holes must overcome when transferred to VD of grains, etc., and which need to be studied further in the future.

It may be useful to make an estimate for effective acting distance and optimal acting distance between the doping layer and the dye adsorbed on the surface of grains, if the effective acting distance is defined as a critical distance beyond which the sensitization caused by the formate doping ions will disappear and the optimal acting distance is defined as a distance within which a maximum sensitivity gain is obtainable. The effective acting distance and the optimal act-

**Table III.** MSGs of the doping emulsions sensitized by dyes ($R,G,B$) and exposed to different light sources.

| Status of emulsions | Light source (light absorbed) | Site of holes generated | $S_{max}/S_0$ |
|---|---|---|---|
| Primitive | White (blue component) | Inside grains | 4.0 |
| S+Au | White (blue component) | Inside grains | 4.0 |
| S+Au+dye (*R*) | White (blue+red component) | Inside grain and in surface dye | 2.5 |
| S+Au+dye (*R*) | Red (red only) | On surface only | 2.2 |
| S+Au+dye (*G*) | White (blue+green component) | Inside grain and in surface dye | 2.5 |
| S+Au+dye (*G*) | Green (green only) | On surface only | 1.7 |
| S+Au+dye (*B*) | White (blue component) | Inside grain and in surface dye | 3.3 |
| S+Au+dye (*B*) | Blue (blue only) | Inside grain and in surface dye | 3.2 |

ing distance for dyed doping emulsions could be easily obtained via some simple calculations based on the data in Table I and Fig. 5. If a series of doped emulsions sensitized by dye ($G$) is taken as an example, we can find an intersection point of the curve and the parallel line denoting a sensitivity level of the corresponding undoping emulsion in Fig. 5(b), at $L_{\mathrm{r}}(t)=0.85$ or $D_{\mathrm{r}}(t)=0.15$, then the absolute depth from the surface $d_a=l_h\times D_{\mathrm{r}}(t)=13.5$ nm (where $l_h=90$ nm is average half edge length of grains). The absolute depth, $d_a=13.5$ nm, namely the effective acting distance equivalent to about 23 cell layers of silver bromide where the cell constant is 0.577 nm.

As for the optimal acting distance, the absolute depth, $d_a=3$ nm, equivalent to five cell layers could be obtained by the same calculation as long as $L_{\mathrm{r}}(t)=0.97$ or $D_{\mathrm{r}}(t)=0.03$ in Table I is taken, corresponding to the maximum sensitivity gain. A depth of five cell layers is just in the range of the subsurface layer of a grain. As is well known, the subsurface layer is situated in a susceptible space charge region in which a slight change may cause a significant change in physicochemical properties of the emulsion, particularly in latent image formation, which makes the mechanism of the sensitization caused by formate doping ions more complicated. It is necessary to clarify what is the real reason to effect the significant sensitization, to a change in the space charge layer caused by the formate ions, or more effective hole trapping, as proposed by Belloni and co-workers. To sum up, this is an important and interesting question worth further studies.

Finally, it has to be emphasized that the above results were obtained only from doped cubic emulsions with an average grain size of about 0.2 $\mu$m. It does not mean that these results could be generalized to other doped emulsions with different grain sizes and crystal habits, such as octahedral or tabular emulsions which we have not yet investigated so far.

## CONCLUSIONS

1. There are great differences in sensitivity between cubic emulsions with the same quantities of formate ions are doped at different sites in AgBr grains.
2. The relative sensitivity of doped emulsions to the corresponding undoped ones monotonically increases as the formate ions are moved closer to surface of grains.
3. A cooperative sensitization by doped formate ions, sulfer, gold, and dye could be carried out to make a higher level of sensitization possible without any significant increase in the fog level.
4. The formate ions doped inside grains are still able to trap the holes produced in dye aggregates adsorbed on the surface of grains to sensitize the dyed emulsions, moreover, the closer to the surface of grains the formate ions are, the greater the sensitivity gain is.

## ACKNOWLEDGMENT

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