Latent-image formation in tabular AgBr grains: experimental studies

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Latent-image formation in tabular AgBr grains: experimental studies

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Abstract: Five tabular-grain AgBr emulsions of varying grain thickness were studied. Two were chemically sensitized in the presence of a blue spectral sensitizing dye, whereas the other three were chemically sensitized in the presence of a green spectral sensitizing dye. A companion set of emulsions chemically sensitized in the absence of dye was also prepared. Internal image development of the unsensitized emulsions showed substantial internal image in one emulsion, but minor amounts in the other emulsions. After chemical sensitization, there was no detectable internal image in any of the emulsions. Reciprocity failure data from $10^{-4}$ to $10^3$ s showed that the emulsions sensitized in the presence of dye had little if any high-irradiance reciprocity failure, suggesting the minimum developable size of the latent image was three atoms for the development conditions used. Low-irradiance reciprocity failure commenced at 0.1–1 s. Long wavelength sensitivity studies showed that the chemical sensitization generally enhanced the sensitivity of three spectral regions in the emulsions sensitized in the absence of dye—550, 650 and 750 nm. These spectral regions are suggested to coincide with three distinct states of the sensitizer centres. Data for the emulsions chemically sensitized in the presence of dye were limited owing to the interference by dye absorption. The temperature dependence of the long wavelength sensitivity showed the activation energy for this process increased as the wavelength increased. Quantum sensitivity measurements were also made at the midpoint of the $D$–$\log E$ curve using 0.1 s exposures. Neglecting the polydisperse nature of these emulsions, values were 10–19 absorbed photons/grain for 400-nm exposures and 13–27 absorbed photons/grain for spectral exposures. An energy-level diagram was constructed for the emulsions sensitized in the absence of dye using their measured activation energies and the photon energies of the three spectral regions. The 550 centre is most likely a single-sulphide or single-selenide centre, with an unknown gold content and provides a shallow electron trap (0.1 eV maximum depth). The compositions of the 650 and 750 centres are most likely multiple sulphide or selenide or sulphide–selenide with unknown gold content. They provide deeper electron traps of depth 0.225–0.425 eV (650 centre) and 0.45–0.65 (750 centre), with the 650 centre probably the dominant of the two in terms of concentration.

Keywords: AgBr, tabular grain, chemical sensitization, long wavelength sensitivity, quantum sensitivity

1 INTRODUCTION

High-aspect-ratio tabular grains have many imaging advantages over three-dimensional grains. However, the sensitivity advantages can only be achieved if the imaging efficiency of tabular grains is at least as high as that of three-dimensional grains. The extensive use of these emulsions in current image capture systems suggests such comparable efficiency has been achieved, although quantitative assessments of the imaging efficiency have not received much attention in the published literature. In addition, very little has
been published regarding the relationship between the physical properties of tabular grains and their latent-image formation efficiencies.\textsuperscript{5,3} The present work reports the electronic properties of AgBr tabular grain emulsions, along with estimates of their imaging efficiency.

The purpose of the research was primarily to support the computer simulation studies of these emulsions, both in terms of validation of the results and as input parameter values. The computer simulation results are communicated in a companion paper.\textsuperscript{4} One of the main thrusts of both the experimental and simulation work is to assess the effect of tabular grain thickness on latent-image formation. The photographic advantages of very thin tabular grains (average thickness $<70$ nm) have recently been reported.\textsuperscript{5} Such grains are claimed to give very favourable speed–granularity relationships in colour systems, provided they incorporate an iodide gradient increasing toward the grain edges and a silver salt epitaxy. In addition, very thin grains have desirable optical properties for constructing colour photographic multilayers.

The present work focused on a set of five different emulsions (two chemically sensitized in the presence of a blue dye and three chemically sensitized in the presence of a green dye). For comparison purposes, these same five emulsions were also chemically sensitized in the absence of dye. The experimental techniques applied include internal versus surface image evaluation, reciprocity failure, long wavelength sensitivity and its temperature dependence, and quantum sensitivity (QS) measurements. The internal/surface, reciprocity failure and QS data serve to validate the correctness of the computer simulation results. The long wavelength sensitivity and its temperature dependence allow an estimation of the trap depths provided by the chemical sensitization, and thereby provide input data to the computer simulations.

The next section summarizes the experimental procedures. Then the internal image forming tendencies of the emulsions, their reciprocity characteristics, their long wavelength sensitivity and its temperature dependence, and the estimated QSs are described. Next, an energy-level diagram for the traps produced by chemical sensitization, a discussion of the properties of the centres produced by chemical sensitization, the effect of dye on chemical sensitization, the limitations of the estimated QSs and, finally, the conclusions of the study are presented.

## 2 EXPERIMENTAL

### 2.1 Emulsions and coatings

Five AgBr tabular-grain emulsions were prepared by the usual double-jet technique. Table 1 summarizes the characteristics of these emulsions. The emulsions were optimally chemically sensitized in the presence of spectral sensitizing dye. The quantities of reagent used are summarized in Table 2. All emulsions had a stabilizing package added, the dominant reagent being tetrazaindene. In addition to the optimal sensitization condition, each emulsion was also chemically sensitized with the same reagents and concentrations, but without the spectral sensitizing present. The structures of the blue and green spectral sensitizing dye are given in Fig. 1.

The emulsions were coated on a clear base at a silver laydown to achieve $D_{\text{max}} = 1$. The aim of $D_{\text{max}} = 1$ is a compromise in silver coverage between that required to achieve reasonably uniform light absorption

<table>
<thead>
<tr>
<th>Type</th>
<th>Thickness (nm)</th>
<th>Volume*</th>
<th>$\sigma^t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>220</td>
<td>0.377</td>
<td>0.14</td>
</tr>
<tr>
<td>Blue</td>
<td>107</td>
<td>0.377\textsuperscript{t}</td>
<td>–</td>
</tr>
<tr>
<td>Green</td>
<td>220</td>
<td>0.166</td>
<td>0.03</td>
</tr>
<tr>
<td>Green</td>
<td>160</td>
<td>0.070</td>
<td>0.21</td>
</tr>
<tr>
<td>Green</td>
<td>90</td>
<td>0.101</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\*Number weighted. Obtained from electrolytic measurements.
\textsuperscript{t}Standard deviation of grain volume distribution.

This emulsion has a bimodal size distribution. The grain volume given is an estimate for the broad component. There is a very narrow size class at very small volume, presumably three-dimensional fine grains.

### 2.2 Sensitizing reagents

Table 2 Chemical sensitization details

<table>
<thead>
<tr>
<th>Reagent*</th>
<th>Reagent concentration, µmoles/mole Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Blue</td>
</tr>
<tr>
<td>S\textsuperscript{t}</td>
<td>5.1</td>
</tr>
<tr>
<td>Se\textsuperscript{t}</td>
<td>3.4</td>
</tr>
<tr>
<td>Au\textsuperscript{t}</td>
<td>3.4</td>
</tr>
<tr>
<td>Dye, % 80</td>
<td>90</td>
</tr>
<tr>
<td>monolayer</td>
<td>100</td>
</tr>
</tbody>
</table>

*All sensitizations include KSCN at 1 mmole/mole Ag.
\textsuperscript{t}Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}·5H\textsubscript{2}O.
\textsuperscript{t}Triphenylphosphine selenide.
\textsuperscript{t}HAuCl\textsubscript{4}.
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depthwise in the coating for the QS studies and that required to minimize densitometry-induced errors.

For each emulsion, four coating variants were made:
1. unsensitized
2. unsensitized plus the concentration of dye that would be used in the chemical sensitization
3. optimum S/Se/Au/KSCN levels plus the optimum dye level
4. S/Se/Au/KSCN levels as in number 3, but no dye.

2.2 Internal/surface image

Internal image was detected by first subjecting the exposed coating to a bleach treatment of 5 min in a ferricyanide solution which also contained pheno-safranine dye to minimize bleach-enhanced internal fog. The coatings were then washed in running water for 5 min, soaked for 5 min in a 1 g KBr/L bath to restore the pAg, and then developed in D19 plus 0.1 g KI/L for 10 min. Omitting the bleach step (plus the subsequent washings) allowed a measure of total image. Surface image was detected with 20-min EAA-1 development. All development and pretreatments were done at 20°C with nitrogen-burst agitation.

2.3 Reciprocity failure measurements

Reciprocity failure data were obtained by combining the sensitometry obtained from two sensitometers—an EG&G Mark VII for the $10^{-4}$–$10^{-2}$ s exposures and a more conventional sensitometer with a tungsten-halogen light source for the 0.1–1000 s exposures. For each sensitometer, appropriate neutral density filters were used to achieve approximate equal energy exposures, with suitable correction values used in the final speed calculation. In addition, a crossover experiment allowed the data from the QS studies to be combined into one continuous reciprocity failure curve. In the case of the blue-sensitized emulsions, a 10-nm half bandwidth 400-nm interference filter was used and, in the case of the green-sensitized emulsions, a broadband blue filter was used with a long wavelength cut-off of 450 nm. Thus, all the reciprocity data pertain to intrinsic absorption.

2.4 Long wavelength sensitivity

These measurements were done with a special sensitometer which allowed evacuation of the coatings. Details of the sensitometer can be found elsewhere. Following overnight evacuation, the coatings were exposed either at 400 nm (10-nm half bandwidth interference filter) or at selected longer wavelengths (25-nm or 70-nm half bandwidth interference filters) for various times to achieve a density suitable for measuring speed (0.15 above fog). The measured speeds were corrected for differences in exposure time and irradiance in order to achieve an equal incident photon comparison. Further corrections were done for differences in intrinsic speed between the five emulsions in order to achieve a comparison at equal efficiency of usage of the injected electrons. After applying these corrections, any differences at different wavelengths are due to differences in either absorption and/or energetics.

The temperature dependence of the long wavelength sensitivity was done in a similar manner, except the temperature of the film was adjusted by flowing He gas across the film. The He gas was first cooled to liquid nitrogen temperature and then warmed to the desired sample temperature by passing the He flow across a set of heaters whose duty cycle was controlled by the output of the temperature controller. Temperature control was better than ±1°C and the temperature gradient across the film was generally <1°C. The measured 400-nm activation energies were corrected for the temperature dependence of absorption at 400 nm (estimated as 20 meV). This corrected activation energy was then subtracted from the activation energy measured at long wavelengths in order to achieve the activation energy associated only with the initial charge transfer following light absorption.

1 Structures for blue and green dyes
2.5 Quantum sensitivity

These measurements were made using the same sensitometer as that used for the long wavelength studies. Exposures were made at 0.12 s with 10-nm half bandwidth interference filters, which had been checked for blockage (<0.01% transmission) outside the bandpass region. Calibration of the light source was done with a calibrated silicon photodetector with a calibration traceable to the National Institute of Science and Technology (NIST). The output of the detector was read with a Hewlett-Packard digital ammeter and the value converted to W/cm² using the detector calibration curve.

Additional information needed for the QS calculation is absorbance, which was obtained by subtracting the measured diffuse transmittance and diffuse reflectance data from unity, silver coverage from X-ray fluorescence measurements, exposure time from the shutter calibration, and grain volume from Table 1.

3 RESULTS

3.1 Internal/surface image

Internal image could be detected in the unsensitized emulsions to varying degrees. The $D - \log E$ curves are given in Appendix A. The emulsion with the highest degree of internal image was the B220 emulsion, where the internal image was faster than the surface image. For the other four emulsions, the degree of internal image was relatively low. The location of the internal image is not known, but presumably it is forming at defects associated with the twin planes.

Problems were encountered during the application of these techniques to the chemically sensitized emulsions. First, the ferricyanide bleach could not remove the surface image, even at higher ferricyanide concentrations and longer bleach times. Secondly, the surface image could be bleached by an acid-dichromate bleach, but this bleach generated significant internal fog, presumably through a bleach-enhanced fogging process, because the phenosafranine dye was not present as it was in the ferricyanide bleaching.

One final technique was to compare the high-irradiance and low-irradiance $D_{\text{max}}$ produced by surface development with EAA-1. Previous experimental and simulation work have shown this technique to be an alternative way of detecting the sensitometric influences of internal competition on surface latent-image formation. If the internal electron trapping and any subsequent processes are influencing surface latent-image formation, this should be observable from a decrease in the low-irradiance $D_{\text{max}}$ relative to that for a high-irradiance exposure. Applying this technique resulted in no irradiance-dependent difference in $D_{\text{max}}$ for any of the five sensitized emulsions, as shown in Table 3.

To check this technique, it was also applied to the unsensitized emulsions for which there are internal image data as a comparison. These data are also given in Table 3. For the B107 and the three green-dyed emulsions, no real difference in $D_{\text{max}}$ is found, as would be expected from their low degree of internal image (see Appendix A). Likewise, a clear decrease in $D_{\text{max}}$ is seen for the B220, which also shows a higher internal speed than surface speed in the internal/surface development study. These results validate the technique and support the conclusion that surface latent-image formation in the sensitized emulsions should not suffer competition effects from any internal latent-image formation.

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>$D_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sensitized</td>
</tr>
<tr>
<td></td>
<td>High irradiance</td>
</tr>
<tr>
<td>B220</td>
<td>0.72</td>
</tr>
<tr>
<td>B107</td>
<td>0.94</td>
</tr>
<tr>
<td>O220</td>
<td>0.80</td>
</tr>
<tr>
<td>O160</td>
<td>0.84</td>
</tr>
<tr>
<td>O90</td>
<td>0.78</td>
</tr>
</tbody>
</table>

3.2 Reciprocity failure

Reciprocity failure data are given in Fig. 2 for the two blue-sensitized emulsions and in Fig. 3 for the three green-sensitized emulsions. For all five emulsions, total development (D19 + KI) was used for the unsensitized and unsensitized plus dye samples, and EAA-1 development for the sensitized versions.

The data for the two blue-sensitized emulsions look quite similar. As expected, the S/Se/Au plus dye versions show the highest speed, but low-irradiance reciprocity failure (LIRF) is noticeable beginning at
0.1 s. There is no high-irradiance reciprocity failure (HIRF) over the time range studied, suggesting the development conditions are detecting a minimum developable size of three atoms. This would be expected for sulphur-plus-gold sensitization and should also hold true for the S/Se/Au sensitization of these emulsions. Somewhat surprisingly, the speed increase over the unsensitized emulsion is only about 0.8 log $E$ for the B220 emulsion, perhaps because of the total development conditions used to obtain the sensitometry of the unsensitized emulsion. For the B107 emulsion, the speed increase is about 1.2 log $E$, more in line with what would be expected for S/Se/Au sensitization.

The behaviour of the G220 emulsion is quite similar to that of the B220 emulsion, although the speed increase in the optimum sensitization over the unsensitized emulsion is somewhat greater (about...
1.3 log $E$). The thinner green-sensitized emulsions tend to show some slight HIRF for the optimally sensitized versions, although differentiating from noise is difficult. Speed gains over the unsensitized emulsion for these two thinner versions tend to be smaller than the G220 (0.8–1.0 log $E$). The speeds of the G160 sensitized with and without dye tend to be similar except at low irradiance.

3.3 Long wavelength sensitivity

Of most interest is how the chemical sensitization affects the inherent long wavelength sensitivity of the emulsion. Therefore, $\Delta$Speed versus wavelength plots will be examined. These are constructed by subtracting the long wavelength sensitivity of a reference emulsion from that of the sample of interest. Since the dye itself affects the long wavelength sensitivity of the unsensitized emulsion, one has two references. For the emulsion with S/Se/Au only, the unsensitized emulsion is used as reference. For the emulsion sensitized with S/Se/Au plus dye, the unsensitized-plus-dye emulsion is used as reference.

One possible complication in using the dyed, unsensitized emulsion as a reference is the state of the blue dye. The absorptance spectra of the dyed emulsion depends on the temperature history of the dye—added at 40°C and then coated or experiencing the same temperature cycle as during chemical sensitization. Thus, the dye may be in a different state in the latter case, which may affect the long wavelength sensitivity. Dye adsorption experiments on the B107 emulsion showed a significantly more prominent J-aggregate absorption for the emulsion that had experienced the chemical sensitization heat cycle. The green dye showed a slight red shift in its J-aggregate peak wavelength in a similar comparison.

Similar to the reciprocity failure measurements, total development is used for the unsensitized and unsensitized-plus-dye emulsions. This was particularly important for these measurements in order to be able to detect all the electrons made available for latent-image formation. For the sensitized emulsions, EAA-1 development is used, as there is no internal image in these emulsions.

Figure 4 shows the $\Delta$Speed versus wavelength response for the two blue-sensitized emulsions. Although the plots have the appearance of absorption spectra, they should not be interpreted as such. Their only use is to help define where the sensitization-induced changes are occurring relative to the sensitivity of the reference emulsion. Comparing peak heights at different wavelengths or between two samples at the same wavelength is not valid because the response is due to a photographic process whose energetics may be different at different wavelengths or in different samples.

Within the resolution limits imposed by the filters, whose maximum transmission wavelengths vary in 50-nm increments, the emulsions sensitized in the absence of dye generally show three prominent regions in the plots of Fig. 4: 550, 650 and 750 nm. For the B107 emulsion, the regions of prominence change when the dye is present: 700 nm rather 650 and 750 nm as in the B220 case. As might be expected from its effect on speed (see Fig. 2), the presence of the adsorbed dye in both emulsions influences the final state of the sensitizer-site distribution.

Figure 5 shows the $\Delta$Speed versus wavelength plots for the green-sensitized emulsions. Of course, in this case when the green dye is present, one is limited to

![Speed versus wavelength for two blue-sensitized emulsions with (solid) and without (dashed) dye; labels give sensitization conditions](image_url)
650 nm and longer wavelengths because of absorption by the dye. The data for the emulsions sensitized in the absence of dye show general features similar to the blue-sensitized emulsions: regions of prominence at 550, 650 and 750 nm. In the case of the G90 emulsion, the 650-nm region is no longer prominent, and the prominent longest wavelength region is uncertain. For the case when the dye is present during chemical sensitization, the data are too limited to draw conclusions regarding the regions of prominence. The results for the undyed emulsions are summarized in Table 4.

### 3.4 Temperature dependence of long wavelength sensitivity

The Arrhenius plots of the temperature dependence of long wavelength sensitivity all showed linear behaviour, as is typical in these kinds of measurements. Thus, an activation energy can be obtained. Some of the prominent regions observed in Figs 4 and 5 for those emulsions sensitized without dye (see Table 4) were chosen for exposure wavelengths. However, exposure times at 750 nm would have been too long to be practical, so for this case a cut-on filter was used with 1%T at 700 nm, 40%T at 750 nm and 80%T at 765 nm and longer wavelengths (LL750 filter). The activation energies will be used to construct energy-level diagrams in the Discussion (Section 5).

The corrected activation energies (see Experimental, Section 2) are summarized in Table 5 for the blue-sensitized emulsions. The values are quite similar for both emulsions. Without the dye, the activation energies tend to be lower. Activation energies for the green-sensitized emulsions are given in Table 6. As with the blue emulsions, the absence of dye lowers the activation energy, particularly for the G90 emulsion.

### Table 4 Wavelength of prominence in long wavelength sensitivity results for emulsions sensitized in absence of adsorbed dye

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>550</td>
</tr>
<tr>
<td>B220</td>
<td>Yes</td>
</tr>
<tr>
<td>B107</td>
<td>?</td>
</tr>
<tr>
<td>G220</td>
<td>Yes</td>
</tr>
<tr>
<td>G160</td>
<td>Yes</td>
</tr>
<tr>
<td>G90</td>
<td>Yes</td>
</tr>
</tbody>
</table>
A general trend for both the dyed and undyed emulsions is an activation energy increase with increasing wavelength.

### 3.5 Quantum sensitivity

In these measurements, it is assumed that the emulsions are monodisperse, speed is measured at a density midway between $D_{\text{max}}$ and $D_{\text{min}}$, and the following equation is used to calculate $QS$:

$$QS = \frac{(E_c/E_s) A I TV}{SW 10^{-4}}$$

where $E$ is the exposure required to achieve 50% maximum density, after correction for fog, $E_c$ is the exposure at the clear step of the step tablet (the point of maximum exposure), $A$ is the absorbance of the coating, $I$ is the irradiance, $T$ is the exposure time, $V$ is the grain volume, $q$ is the density of silver halide, $S$ is the silver coverage, $W$ is the weight factor for converting from AgNO$_3$ coating weight to AgBr coating weight, and $10^{-4}$ is a units conversion factor.

There is a problem in using the absorbance data in calculating $QS$ at 400 nm. Because the coating base and gel can absorb at this wavelength, it is not strictly correct to subtract the absorption at 400 nm of a fixed-out coating from that for the coating itself, because scattering by the grains can enhance the base plus gel absorption. But, there is no way of measuring this effect in the current coatings, so one is forced to use the simple subtraction, which must be done in the Beer’s Law sense using optical densities.

A second problem also has to do with absorbance. Strictly speaking, the irradiance at each wavelength should be multiplied by the absorbance at that wavelength, and then summed over all wavelengths to get the total number of photons absorbed. Unfortunately, this requires spectral irradiance data, which are not available for our light source. The integrated irradiance passing through the interference filters is simply measured. Experience has shown that this approximation is good for 400-nm exposures because the increasing light absorption from, say, 420 to 380 nm by the AgBr is compensated for by the decreasing output from our tungsten–halogen light source. In this case, the difference between the convolved data and that obtained by considering all photons to be at 400 nm is negligibly small. But this difference cannot be ignored in the spectral region, particularly when J-aggregates are present. Here, a mismatch between the peak of the filter transmittance and the peak absorption by the adsorbed dye can introduce some error.

Of course, these errors pale in comparison to the main error of these measurements. Equation (1) is strictly valid for monodisperse emulsions coated thin enough so that all the grains have equal access to the incoming photons. These tabular grain emulsions are far from monodisperse, so the calculated numbers have only qualitative value. Furthermore, because the degree of polydispersity varies among the five emulsions, comparisons between the different emulsions are difficult. If the grain size class corresponding to the mean volume in Table 1 were to become half developable at the midway reference density used in these calculations, there would be some usefulness in these numbers. Such a situation seems highly fortuitous. Nevertheless, these are all the data available at the present time.

The $QS$ data are summarized in Table 7. The $QS$ values for 400-nm exposures range between 10 and 19 absorbed photons/grain; those for spectral exposures range from 13 to 27 absorbed photons/grain. For the blue-sensitized emulsions, a decrease in efficiency with decreasing thickness is seen, whereas for the green-sensitized emulsions, there does not appear to be any particular trend with grain thickness. Presumably, other emulsion factors are influencing the $QS$. Because data are available for both intrinsic and spectral exposures, the RQE can be calculated by dividing the

---

**Table 5** Corrected activation energies for blue-sensitized emulsions

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\Delta E_{\text{act}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B220</td>
</tr>
<tr>
<td>dye no dye</td>
<td>50 ± 28</td>
</tr>
<tr>
<td>dye no dye</td>
<td>145 ± 25</td>
</tr>
<tr>
<td>dye no dye</td>
<td>77 ± 36</td>
</tr>
</tbody>
</table>

**Table 6** Corrected activation energies for green-sensitized emulsions

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\Delta E_{\text{act}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G220</td>
</tr>
<tr>
<td>dye no dye</td>
<td>41 ± 28</td>
</tr>
<tr>
<td>dye no dye</td>
<td>169 ± 35</td>
</tr>
<tr>
<td>dye no dye</td>
<td>191 ± 43</td>
</tr>
</tbody>
</table>

Strictly speaking, the irradiance at each wavelength must be multiplied by the absorbance at that wavelength, and then summed over all wavelengths to get the total number of photons absorbed. Unfortunately, this requires spectral irradiance data, which are not available for our light source. The integrated irradiance passing through the interference filters is simply measured. Experience has shown that this approximation is good for 400-nm exposures because the increasing light absorption from, say, 420 to 380 nm by the AgBr is compensated for by the decreasing output from our tungsten–halogen light source. In this case, the difference between the convolved data and that obtained by considering all photons to be at 400 nm is negligibly small. But this difference cannot be ignored in the spectral region, particularly when J-aggregates are present. Here, a mismatch between the peak of the filter transmittance and the peak absorption by the adsorbed dye can introduce some error.

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5 DISCUSSION

5.1 Energy-level diagram

The interpretation of the long wavelength sensitivity has been discussed elsewhere.\textsuperscript{13–15} Briefly, the activation energy is thought to be associated with the transfer of a hole from an excited sensitizer centre to the valence band. This creates an anion radical of the sensitizer centre. It is reasonable to expect the lowest vacant level of the unexcited centre (now a singly occupied molecular orbital) to shift upwards after the hole transfer. This shift is estimated to be 0.2–0.4 eV.\textsuperscript{13–15} The sensitizer centre now has the characteristics it would have if it simply captured an electron from the conduction band. That is, it is the trapped-electron state which is of interest as input to the computer simulations.

Knowledge of the activation energy, the photon energy and the assumed 0.2–0.4 eV shift allows one to create the energy-level diagram shown in Fig. 6. As with other studies of energy levels within crystalline solids, entropy effects can be ignored in developing this energy-level diagram.\textsuperscript{16} In constructing this energy-level scheme, the three regions of greatest change in the \textit{Δ}Speed versus wavelength plots were chosen for the emulsions sensitized in the absence of

\begin{center}
\textbf{Table 7} Quantum sensitivity and RQE data
\end{center}

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>QS (mean absorbed photons/grain)*</th>
<th>RQE†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 nm</td>
<td>470 nm</td>
</tr>
<tr>
<td>B220</td>
<td>11 ± 2</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>B107</td>
<td>17 ± 3 †</td>
<td>23 ± 5 ‡</td>
</tr>
<tr>
<td>G220</td>
<td>19 ± 4</td>
<td>–</td>
</tr>
<tr>
<td>G160</td>
<td>11 ± 2</td>
<td>–</td>
</tr>
<tr>
<td>G90</td>
<td>10 ± 2</td>
<td>–</td>
</tr>
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*At halfway between minimum and maximum density.
†0.12 s exposure; estimated uncertainty ± 30%.
‡Grain volume uncertain. Calculated values assume the grain volume is the same as the B220.

4 SUMMARY OF EXPERIMENTAL DATA

1. Internal competition does not appear to be a problem for the chemically sensitized emulsions.
2. Reciprocity data show little if any HIRF, indicating the developer is detecting a minimum developable size of three atoms. LIRF begins at 0.1–1 s exposure.
3. Long wavelength sensitivity data for the emulsions sensitized without adsorbed dye generally show three spectral regions affected by chemical sensitization: 550 nm, 650 nm and 750 nm. Similar data could not be obtained for the emulsions sensitized in the presence of adsorbed dye. Chemical sensitization in the absence of dye generally produces larger changes in long wavelength sensitivity relative to the reference emulsion.
4. The temperature dependence of long wavelength sensitivity shows Arrhenius behaviour from which activation energies can be calculated. The corrected activation energies in the spectral regions where the chemical sensitization has its greatest effect are somewhat larger when the dye is present during the chemical sensitization. Generally, the activation energy increased with increasing wavelength.
5. Quantum sensitivities were in the 10–30 photons/grain range, with values for the spectral region being somewhat higher than those for intrinsic exposures. RQEs for spectral sensitization were in the 0.6–0.8 range.

6 Energy-level diagram for sensitizer centres in S/Se/Au/SCN sensitized tabular grains (without dye); three centres correspond to three regions of \textit{Δ}Speed versus wavelength plots (see Figs 4 and 5 and Table 4); all numbers have units of eV; numbers near VB level are averaged corrected activation energies from Tables 5 and 6 for no dye case; shaded rectangles indicate range of calculated trap depth energies
adsorbed dye: 550 nm, 650 nm and 750 nm. Note that the average of the activation energy data over all emulsions was estimated and then the value rounded. These three wavelength regions are believed to correspond to three distinct types of sensitizer centres (see below). It can be seen that the shortest wavelength site (550 nm) produces a very shallow ‘trapping level’. The two remaining sensitizer sites with the absorptions at 650 nm and 750 nm produce trapping levels of 0.225–0.425 eV and 0.45–0.65 eV, respectively. These centres, which will be denoted as the ‘550’, ‘650’ and ‘750 centres’ hereafter, are the ones controlling the sensitometry of the sensitized emulsions.

5.2 Nature of sensitizer centres

In earlier work with sulphur-sensitized AgBr octahedra, the authors observed 550 and 650–700 centres.14,15 The former shows a first-order dependence on thiosulphate concentration, indicating it is a single-sulphide centre. The latter centre shows a higher-order dependence on thiosulphate concentration but, because its activation energy also varies with thiosulphate concentration, its composition is somewhat uncertain.15 But, it is unlikely to consist of single sulphides, and it is referred to as a multiple-sulphide centre. At low thiosulphate concentrations, only the single-sulphide centre is observed, yet some speed increase in the unsensitized emulsion is seen, suggesting that the single sulphides have some electron-trapping ability. This is consistent with the energy-level scheme shown in Fig. 6. However, only optimum speed is seen in these octahedra when the multiple sulphides, with their deeper trapping level, form.

The assignment of single-sulphide centres as electron-trapping is different from that of others which have suggested that single-sulphide centres are hole-trapping.17–19 The effect of these single-sulphide centres on reciprocity failure is more consistent with an electron-trapping function.14,15 As indicated in Fig. 6, all three sites have hole-trapping possibilities. But, if we assume they form near regions with excess positive charge, such as positive kink or kink-like sites, one would expect them to be electron traps. This is more consistent with their sensitometric effects.

A further feature of importance in the present discussion is the role of thiocyanate (SCN) in affecting the electronic properties of the sensitizer centres. It has been found that the SCN has its greatest effect on the multiple-sulphide centres in AgBr octahedra.20 The long wavelength sensitivity of such centres is enhanced and the activation energy decreased, along with an increase in light absorption. The data suggest that the SCN increases the electron trap depth.

Work with sulphur-sensitized and selenium-sensitized AgIBr cubes shows 550 nm and 800 nm centres (for both sulphur and selenium),21,22 a 700 nm centre (sulphur),21 and a 650 nm centre (selenium).22 The 550 nm centre shows a first-order dependence on the sensitizer concentration and is assigned to single chalconide centres. The longer wavelength absorptions are more difficult to characterize. As with the AgBr octahedra, they are assigned to multiple chalconides.

Thus, it seems that in the S/Se/Au/SCN sensitized tabular grains of the present study, a combination is seen of what was observed in cubes and octahedra. This conclusion is for the case in which the emulsions are sensitized in the absence of adsorbed dye. Since the earlier work did not include gold as part of the sensitization, this suggestion assumes that the incorporation of gold does not change the absorption wavelength of the centre. Work with sulphur-plus-gold sensitized AgIBr cubes supports this assumption.23 It is likely that the 550-centre is a single sulphide or selenium, but the gold content is unknown. These centres, however, probably lead to only a modest improvement in the efficiency of the emulsion over that of the unsensitized condition. The 650 and 750 centres probably contain more than one chalconide plus an unknown amount of gold. It is likely that these latter centres are critical to achieving high efficiency.

For the tabular grains sensitized in the presence of dye, there appear to be some differences from the above conclusions. When sensitized in the presence of the blue dye, the B220 emulsion follows the trend seen for the undyed emulsions. But, this was not the case for the B107 emulsion. Here, the wavelength region of prominence shifted such that the 650 nm region now appeared at 700 nm and the 750 nm region may have also shifted to longer wavelengths. For the green-dyed emulsions, the absorption by the dye severely limited the usable data. Regions of prominence could not be determined.

5.3 Location and concentration of sensitizer centres

For the purposes of the companion computer simulation work, it would be helpful to know where these centres are located and how many of them there are.
The first attribute could be determined by looking at grains in the electron microscope that have been subjected to exposure and arrested development. It is likely that the development centres form at multiple-chalconide centres. Alternatively, a physical development technique without exposure could be used, which may reveal more of the centres.

The second attribute is more difficult to satisfy, particularly in an absolute sense. In a relative sense, diffuse reflectance spectroscopy (DRS) data can be used. Although no such data are available for the emulsions used in this study, DRS data for octahedra and cubes can be referred to in order to get a qualitative idea. A general rule is that absorption decreases as the wavelength increases. So, unless there is a difference in the absorption coefficients, the 650 centres should have a higher concentration than the 750 centres.

Achieving absolute concentrations requires additional data. The conversion of thiosulphate to adsorbed sulphide, of the gold reagent to adsorbed gold, and of the selenium reagent to adsorbed selenide would be needed. This would give the amount of material able to form the sensitizer centres. But, an appreciable amount may not be active. This conclusion comes from comparing DRS data with long wavelength sensitivity data. The DRS data routinely show a major absorption around 480 nm but, typically, very little change is seen in the long wavelength sensitivity at this wavelength, suggesting that the material contributing to this absorption is not photographically active. Deconvoluting the DRS data with peak wavelengths observed in the long wavelength experiment would enable active material to be distinguished from inactive material.

5.4 Effect of dye

Because the activation energies are higher for the centres formed in the presence of dye, an energy-level scheme constructed as shown in Fig. 6 would lead to traps that are somewhat shallower than when the centres are formed in the absence of dye. The deeper traps for the undyed emulsions could provide an explanation for their poor efficiency—the deeper traps lead to an oversensitization condition. Oversensitization often leads to a shift in the onset of LIRF towards longer times. Such behaviour can be seen in Fig. 2 for the blue-sensitized emulsions, but is not apparent in Fig. 3 for the green-sensitized emulsions.

5.5 QS measurements

The QS measurements suggest that the optimally sensitized tabular-grain emulsions are reasonably efficient at forming latent image. However, because the measurements do not take into account the polydisperse nature of the grain-size distributions for these emulsions, the measurements must be considered qualitative. Furthermore, because the polydispersity varies between the five emulsions, even relative efficiency comparisons are qualitative.

A further problem with these measurements is that the absorbance used in the QS calculations is taken from the absorptance spectra at the peak transmission of the interference filter for that particular wavelength. This procedure works well for the 400 nm filter but, for the 470 and 540 filters where J-aggregate absorption is occurring, any mismatch between the filter transmittance band and the J-aggregate absorption band can cause errors in the calculated absorption. These calculations should really use a convolution of the filter transmittance with the J-aggregate absorption across the passband of the filter. However, given the qualitative nature of the QS measurement, this additional source of error probably is minor.

6 CONCLUSIONS

This work was the present authors’ first attempt to apply long wavelength sensitivity techniques to tabular grains. It was demonstrated that it is feasible to do so, although interference of spectral sensitizing dyes is a problem in its general application. In the present case, the technique led to the identification of three types of centres produced by the chemical sensitization in the absence of dye. These centres are similar to those previously observed on octahedra and cubes, suggesting some generality in the type of centre produced by chemical sensitization. Activation energies were used to construct an energy-level scheme that will be utilized in the computer simulation phase of the project. For those cases where adsorbed dye was present during chemical sensitization, the data were generally inconclusive regarding what type of centres were formed by chemical sensitization.

Internal latent-image formation was found to be an insignificant factor in the sensitized emulsions. Reciprocity failure data and QS values were obtained for use in validating the computer simulation results.
There was no clear trend in the effect of grain thickness on latent-image forming efficiency. The green-dyed emulsions showed improved efficiency, whereas the blue-dyed emulsions showed poorer efficiency with decreasing thickness.

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REFERENCES

APPENDIX A

The $D$–log $E$ curves for total, internal and surface image at $10^{-2}$ s exposure are shown in Fig. A1.

A1 $D$–log $E$ curves for total, internal and surface image for blue-sensitized and green-sensitized emulsions