Factors influencing the rate of sensitization and maximum sensitivity of an iridium (III) surface sensitized silver bromide emulsion

Nimrod Natan
FACTORS INFLUENCING THE RATE OF SENSITIZATION AND MAXIMUM SENSITIVITY OF AN IRIDIUM (III) SURFACE SENSITIZED SILVER BROMIDE EMULSION

by
Nimrod Natan
B.S. Washington College
(1985)

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Center for Imaging Science in the College of Graphic Arts and Photography of the Rochester Institute of Technology

September 1987

Signature of the Author

Nimrod Natan

Accepted by
Coordinator, M.S. Degree Program
The M.S. Degree Thesis of Nimrod Natan has been examined and approved by the thesis committee as satisfactory for the thesis requirements for the Master of Science degree.

Mr. Harry E. Roberts, Thesis Advisor

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Mr. Juan A. Zuleta

10-31-87

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ABSTRACT

A monodisperse silver bromide emulsion was surface sensitized with potassium hexachloroiridate (III). The rate of sensitization and maximum photographic sensitivity were determined at different sensitization conditions. The effects of silver ion concentration (pAg), length of sensitization, and the presence of the thiocyanate anion during sensitization were defined. The highest gain of sensitivity of an iridium sensitized emulsion over an unsensitized emulsion was 0.43 log H units at pAg 9 after 30 minutes of after-ripening at 70° C. The highest gain of
sensitivity of an iridium + thiocyanate sensitized emulsion over an unsensitized emulsion was 0.55 log H units at pAg 9 after minimal after-ripening. The experimental results were used to confirm an existing theory for the action of thiocyanate in iridium sensitization, as well as to optimize the system.
ACKNOWLEDGMENTS

The author wishes to acknowledge Mr. Harry E. Roberts from RIT, Dr. Jerry LeBlanc from the Eastman Kodak Research Laboratories, and Mr. Dave Burski from the Eastman Kodak Research Laboratories for their assistance in the project.

To the late Dr. Ron "Doc" Francis from RIT for his teachings.

This research would not have been possible without the involvement, teaching, and friendship of Mr. Juan A. Zuleta.
To my father, Yzchak Natan.
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INTRODUCTION

Increasing the photographic speed of silver halide emulsions has always been a central objective in photographic science. Chemical sensitization does just that. Chemical sensitization includes three major types: sulfur sensitization, reduction sensitization, and noble-metal sensitization. Noble metal sensitization usually involves the use of gold salts. However, group VIII metals have been gaining more recognition in the past four decades. Iridium is one of the more interesting members of the group VIII metals since it produces a larger increase in photographic speed and contrast than rhodium and palladium, without increasing the fog level.

Iridium salts were mentioned as chemical sensitizers as early as 1896. Schonfelder and Kehle were probably the first to recognize the sensitizing qualities of iridium\(^1\). Not until the early 1950's, was much time spent studying the mechanisms and applications associated with iridium sensitization. In 1951, Trivelli and Smith were awarded patents describing the use of group VIII metal salts as photographic fog inhibitors\(^2,3,4,5\). In 1955, Work was awarded a patent that included the use of iridium salt in the production of a direct-positive emulsion\(^6\). Mitchel, Evans, and Hedge were the first to publish a paper trying to
explain the mechanism of iridium sensitization\textsuperscript{7}. In 1959, West and Saunders studied the action of iridium salt using thin sheet crystals\textsuperscript{8}. They concluded that the iridite ion acted as a positive hole trap.

In 1968, Bahnmuller attempted to settle some of the contradictions found in earlier publications and patents\textsuperscript{9}. In his paper, Bahnmuller examined some of the parameters influencing iridium sensitization, and supported the hole-trapping mechanism of iridium (III) suggested by West and Saunders. During the same year, Sakai and Baba studied the behavior of an iridium sensitized silver halide system using different levels of exposure\textsuperscript{10}. Like Banmuller, they attributed the sensitization to hole-trapping. Sakai and Baba also found that iridium (IV) is reduced to iridium (III) in the presence of excess silver ions. Pouradier showed iridium (IV) is reduced to iridium (III) by gelatin\textsuperscript{11}.

Eachus and Graves used electron paramagnetic resonance (EPR) to study single crystals of iridium (III) sensitized silver bromide and silver chloride, and concluded that the trivalent iridium acted as an electron trap\textsuperscript{12}.

In 1980, Carroll reviewed major publications and patents dealing with the use of iridium as a photographic sensitizing agent\textsuperscript{13}. He suggested iridium may act as either a hole trap (in the case of iridium III) or an electron trap (iridium IV). Carroll, like Banmuller, also
concludes iridium must be built into the silver halide crystal for an efficient sensitization.

The International Congress of Photographic Science held at the University of Cambridge, England, in 1982 included a large number of papers dealing with iridium sensitization. Eachus extended his EPR studies to iridium sensitized silver bromide and silver chloride colloidal solutions and emulsions, and concluded that "the trivalent iridium ion behaved as a deep transient electron trap at room temperature"14. Gilman used silver halide internally sensitized with iridium to study the mechanism of spectral sensitization15, and concluded that iridium sensitized emulsions offered an ideal model for the study of spectral sensitization, and more relevant to this study, that "iridium ions incorporated in the interior of a 0.2 μm cubic AgBrI emulsion trap electrons more effectively than a surface sulphur-gold sensitization or the strongest electron-trapping dyes studied to date". Leubner studied iridium sensitization using sensitizing dyes16. In his paper, he rejected both the hole trapping and the electron trapping mechanisms, and introduced a new model whereby sensitization is explained by "transient electron trapping by not or partially vacancy-neutralized iridium centers without direct electron or hole trapping by the iridium ions". Other related papers in the 1982 ICPS included the study of iridium-doped silver bromide using luminescence spectroscopy17, location of the latent image in iridium sensitized emulsion using Malinowski's etch-develop
technique\textsuperscript{18}, and the development of iridium doped silver bromide emulsions\textsuperscript{19}.

In 1985, Zwicky's research supported the view that iridium (IV) was an electron trap, while iridium (III) acted as a positive hole trap\textsuperscript{20}. Zwicky also suggested that iridium increased the sensitivity of a photographic emulsion by enhancing the developability of the latent image after exposure. In 1986, Zuleta presented data supporting the view that iridium must be incorporated in the silver halide crystal for an efficient sensitization\textsuperscript{21}, by showing how different silver halide solvents significantly improved the efficiency of surface sensitization with iridium. His data also supported an electron trapping mechanism for the sensitization.

The number of applications of iridium salts in the photographic field is surprisingly high when one considers the relatively small number of publications dealing with the mechanism of iridium sensitization. According to the patent literature, iridium is used in direct positive systems both as the sensitizer in a core/shell emulsion\textsuperscript{22}, and in combination with a reducing agent acting as a fogging agent\textsuperscript{23}. Iridium is also used as an anti-kinking agent in direct positive systems\textsuperscript{24}. Iridium is reported to be included in a print-out\textsuperscript{25} and x-ray\textsuperscript{26} emulsions. There are also the patents specifying iridium as a "general" chemical sensitizer\textsuperscript{27,28,29}. Iridium is mentioned in connection with the reduction
of high intensity reciprocity law failure\textsuperscript{30}, and as an antifoggent and a stabilizer\textsuperscript{31}.

Despite the contradictions found in the literature concerning the mechanism of iridium sensitization, it is agreed almost by all that in order for the iridium salt to produce an efficient sensitization, it must be built into the silver halide crystal. Most researchers used an internally sensitized emulsions, thus creating the traps in the interior of the grain. Kawijara and co-workers produced a sub-surface sensitization by adding the iridium salt during the end of the precipitation\textsuperscript{32}. Zuleta explored a novel way to achieve the desired sub-surface images\textsuperscript{21}. Using silver halide solvents to etch the grain and place the iridium where it is most effective as a sensitizing agent, in the sub-surface region, Zuleta produced a significant increase of photographic sensitivity.

Despite the numerous publications and patents concerning iridium sensitization, much is left unexplained. Up to Zuleta's work, there was very little reason to select iridium as a sensitizer over other group VIII metals. His work suggests iridium is a practical sensitizer, but many more sensitization parameters are needed before the metal can be used in a commercial photographic emulsion.

This work will examine some of the important parameters of iridium
and iridium/thiocyanate sensitization. The emulsion to be used is a monodisperse, fine-grain, octahedral silver bromide emulsion. The emulsion will be surface sensitized with potassium hexachloroiridate (III) salt and potassium thiocyanate (hereafter referred to as "iridium" and "thiocyanate") during the afterripening stage. The parameters studied are silver ion concentration (pAg) during sensitization and time of sensitization. The quantization of these two factors is essential for emulsion making. Both will affect important characteristics such as photographic speed, fog level, and contrast. The results will be used to optimize the specific system for maximum photographic speed. The study will also help explaining the function of the thiocyanate anion in iridium sensitization.
EQUIPMENT

Lauda constant temperature bath, model RC20
Orion pH and mv meter, model 701
EG & G sensitometer, Mark VII
Cole Parmer pumps Masterflex, 7013 pump heads
Orion multiple electrode switch box, model 605
Macbeth densitometer
Film hand coater
METHODS

The experimental procedure for this thesis was divided into three general steps: emulsion precipitation, sensitization, and exposure and processing.

Emulsion Precipitation

A monodisperse, pure silver bromide, octahedral emulsion was chosen for this study. A double-jet delivery system was used, as shown in Figure 1. Solutions of 1.0 M silver nitrate and 1.0 M potassium bromide were simultaneously added to a 0.01 M potassium bromide solution containing 40.0 g phthaloylated gelatin. Delivery rate of silver solution was 20 ml/min, that of the bromide pump was 20.2 ml/min. Precipitation time was 30 minutes at 65°C. Nucleation was achieved at a delivery rate of 2.5 ml/min, and the rate was increased to the values shown above over a period of 10 minutes. Silver ion concentration was monitored during precipitation using a silver bar electrode and a Ag/AgCl as the reference electrode. A 0.1M potassium nitrate salt bridge was used as shown in Figure 2. A pH electrode was also connected to the potentiometer to allow a simultaneous pH and vAg (electrochemical potential) readings. Constant pAg value of 8.45 was maintained by slight adjustment to the rate of delivery of the bromide solution. Foaming was limited by spraying a mixture of secondary and tertiary butyl alcohols.
Most precipitation parameters, including the electrochemical potential value (vAg) corresponding to the desired silver ion concentration value (pAg) for the octahedral crystal habit were obtained using a computer program utilizing the following equations:

**pAg to vAg Conversion**\(^{21}\)

\[ vAg = EAg - E_{ref} \]

\[ E_0 = 799 - 0.1(t - 25) \]

\[ E_{Ag} = 799 - 0.1(t - 25) - 0.1984(t + 273.15) - pAg \]

\[ pAg = pKsp - pBr \text{ and } pBr = -\log(aBr^-[Br^-]) \]

\[ pKsp = -(12.126 - 5868/T - 0.015953T) \]

\[ \ln aBr^- = ( -A * i^{1/2} ) / (1 + i^{1/2}) + 0.22(i) \]

\[ A = 1.327 + 1.50563 \times 10^{-8}t + 1.16836 \times 10^{-5}t^2 \]

\[ A = \text{Debye-Huckel constant} \]

\[ i = \text{ionic strength} \]

\[ aBr^- = \text{bromide ion activity} \]

\[ E_{ref} = 197 \text{ mV} \]
\[ T = \text{absolute temperature} \]
\[ t = \text{temperature in celsius} \]

**Pump Delivery Rates:**

\[ C = C_i = \frac{\# \text{ of moles of Br}^-}{\text{total solution volume}} \]

\[ C = \frac{(X_i + X_b - X_a)}{(V_i + V_b + V_a)} \]
\[ = \frac{(X_i + V_b C_b - X_a)}{(V_i + V_b + V_a)} \]

\[ V_b = \frac{(C_i V_a + X_a)}{(C_b - C_i)} \]

\[ R_b = \frac{V_b}{t} \]

\[ V_i = \text{initial volume of bromide and gel solution} \]
\[ C_i = \text{concentration of initial sln} \]
\[ X_i = \# \text{ moles of bromide in initial sln} \]
\[ V_b = \text{volume of bromide sln added} \]
\[ X_b = \# \text{ moles of bromide added} \]
\[ V_a = \text{volume of silver sln added} \]
\[ X_a = \# \text{ moles of silver added} \]
\[ C_b = \text{concentration of bromide jet} \]
\[ t = \text{length of precipitation} \]
The actual program used is included as Appendix 1.

The emulsion obtained by the procedure indicated was a highly monodisperse, fine grain, octahedral emulsion. Particle size distribution data was obtained by using electronic image analysis. It was determined that 81% of the grains were 0.25 μm in diameter and 19% were 0.23 μm in diameter. Figure 3 shows the grain size distribution of the emulsion. Figure 4 is an electron micrograph of the emulsion magnified 3000 times. Transmission electron micrography (TEM) and the electronic image analysis were performed by staff at the Eastman Kodak Company.
Figure 1. Precipitation vessel
Figure 2. Electrode and salt bridge apparatus
### Figure 3. Grain size distribution of the emulsion
Figure 4. Electron micrograph of emulsion. X3000
Normal emulsion preparation steps followed the emulsion precipitation: pH was reduced to 3.6 with sulfuric acid, vessel was cooled in an ice bath, liquid was decanted, emulsion washed with distilled water, pH raised to 6.0 with sodium hydroxide, and lowered to 4.2 for storage.

**Sensitization**

To study the effects of silver ion concentration during sensitization, length of sensitization, and any interaction between them, the following experimental design was utilized:

<table>
<thead>
<tr>
<th>Factor</th>
<th>Range</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>pAg</td>
<td>7 - 10</td>
<td>7, 8, 9, &amp; 10</td>
</tr>
<tr>
<td>[SCN^-]</td>
<td>0 - 500 mg/mol</td>
<td>0 &amp; 500 mg/mol</td>
</tr>
<tr>
<td>Sens. time</td>
<td>0 - 60 min.</td>
<td>0, 5, 10, 30, &amp; 60 min.</td>
</tr>
</tbody>
</table>

Appendix 2 includes more details concerning the experimental design.

The emulsion was redispersed, pAg set at 8, and pH set at 6.5.

The bulk emulsion was divided into four containers. pAg's were adjusted to 7, 8, 9 and 10 using 0.1 M solutions of potassium bromide and silver nitrate. pAg to vAg conversions were performed using the program
The sample having a pAg 7 was further divided into two beakers. A 0.016 moles samples were taken from each beaker, and designated "7b" (for "pAg 7, blank"). The samples were placed in an ice bath after 16 ml of distilled water were added to it. The first beaker was sensitized with 50 mg iridium salt/mole AgBr, and the second beaker with 50 mg iridium salt, 500 mg potassium thiocyanate/mole AgBr\textsuperscript{33}. The amounts were selected from Zuleta's study which optimized the amounts of iridium and iridium and thiocyanate for a similar emulsion\textsuperscript{33}. All iridium solutions (16.00 mg iridium salt/25 ml solution) were prepared shortly before use. The iridium and iridium/thiocyanate (38.14 mg thiocyanate/5 ml solution) solutions were added to the emulsions at 40°C. The sensitized emulsions were stirred for 3 minutes, and transferred to a 70°C thermostated water bath. Samples were not covered, and stirred for 30 sec. every 5 min. The second 0.016 moles samples were withdrawn immediately following the transfer. Sixteen milliliters of distilled water were added to each sample, and they were then placed in an ice bath. The procedure was repeated after 5, 10, 30, and 60 minutes. The samples were remelted at 40°C, and hand coated onto a clear Estar support. A milliliter each of saponin (wetting agent) and mucochloric acid (hardener) were added to the emulsion just before coating. The films were dried overnight and then cut into 10 cm strips.
The procedure was repeated with the emulsions with pAg's 8, 9 and 10. All experimental parameters were kept the same as much as possible to assure the significance and validity of the comparisons.

**Exposure and Processing**

The strips were exposed using an EG&G Mark VII sensitometer and a 21-step step tablet. Exposure was 52 lux-sec for 10^-2 seconds. The strips were developed fifteen to thirty minutes following exposure in a low solvent developer, Kodak D-72 developer, for 2 minutes at 24°C. They were then put through the standard processing steps: acidic stop bath for 30 seconds, rapid fix bath for 4 minutes, and wash bath for 5 minutes.

Density measurements were done on a Macbeth densitometer. D log H curves were constructed, and exposure points at density of 0.95 above base + fog determined.

Several film samples from the pAg 8 and pAg 10 emulsions were exposed as described and developed using an internal developer described in Appendix 3, and Kodak D-76 developer.
RESULTS

The following characteristic curves were constructed from the data:

![Graph showing characteristic curves for different pAg values.]

Figure 5. D log H curves for the unsensitized emulsion.

Figure 5. compares the characteristic curves of the unsensitized emulsions at different pAg's. As expected, the sensitivity of the silver bromide decreased with decreasing silver ion concentration (or increasing pAg). The well known effect was established by Sheppard and Wightman\(^34\) in 1931, and later studied by Matejec and Mayer\(^35\), Leubner\(^36\), and more. It is attributed to the effect of pAg on the efficiency of halogen acceptance and the number of available interstitial silver ions.

Figures 6, 7, 8 and 9 compare the characteristic curves of the
sensitized emulsions. Maximum sensitivity within our parameters was used to pick the sensitization time for each pAg. One can observe an increase of sensitivity due to iridium sensitization ranging from $\Delta S$ of 0.15 to 0.43 log units, as well as the further increase in sensitivity when iridium is used in combination with thiocyanate as described earlier by Zuleta$^{33}$ (ranging from $\Delta S$ of 0.23 to 0.55 log units).

Figure 6. D log H curve for pAg 7. Maximum sensitivity within our parameters was used to pick the sensitization time for each pAg.
Figure 7. D log H curve for pAg B.
Figure 8. D log H curve for pAg 9.

Figure 9. D log H curve for pAg 10.
The exposure levels in relative log units were found for a density of 0.95 above base + fog. The values for each of the curves are tabulated in Table 1. and graphed in Figure 10 (the emulsion of pAg 9 and with thiocyanate having the lowest value thus the higher sensitivity). The graph plots the speed points in log H units from the characteristic curves against pAg.

<table>
<thead>
<tr>
<th></th>
<th>pAg 7</th>
<th>pAg 8</th>
<th>pAg 9</th>
<th>pAg 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>1.25</td>
<td>1.28</td>
<td>1.38</td>
<td>1.60</td>
</tr>
<tr>
<td>Ir</td>
<td>1.10</td>
<td>1.05</td>
<td>0.95</td>
<td>1.42</td>
</tr>
<tr>
<td>Ir + SCN⁻</td>
<td>0.94</td>
<td>0.94</td>
<td>0.83</td>
<td>1.37</td>
</tr>
</tbody>
</table>

Table 1. Exposure levels (in relative log units) at 0.95 density units above base + fog.
Figure 10. Sensitivity of unsensitized control, iridium sensitized, and iridium + thiocyanate sensitized emulsions as a function of pAg. Maximum sensitivity within our parameters was as the sensitization time for each pAg.

The speed of the unsensitized emulsion is subtracted from the Table 1. and Figure 10. to determine the change in sensitivity due only to iridium sensitization. Table 2. was arrived at by subtracting the exposure level at the speed point of the unsensitized emulsion from the sensitized samples. Figure 11. illustrates the effect.
<table>
<thead>
<tr>
<th>pAg</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>0.15</th>
<th>0.21</th>
<th>0.43</th>
<th>0.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir + SCN^-</td>
<td>0.31</td>
<td>0.34</td>
<td>0.55</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 2. Increase of photographic sensitivity from unsensitized emulsion (blank) due to iridium and iridium/thiocyanate at 0.95 density units above base + fog.

![Graph showing change in photographic sensitivity due to iridium and iridium + thiocyanate as a function of pAg.](image)

Figure 11. Change in photographic sensitivity due to iridium and iridium + thiocyanate as a function of pAg.

The data indicates that maximum sensitivity of the silver bromide emulsion is reached when iridium + thiocyanate is used at a pAg 9.0. It
can be also observed that the effect of thiocyanate on iridium sensitization diminishes as pAg increases. Table 3. and Figure 12 were obtained by subtracting the exposure level at the speed point of the emulsion without thiocyanate from the emulsion with thiocyanate.

<table>
<thead>
<tr>
<th>pAg</th>
<th>ΔS</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.16</td>
</tr>
<tr>
<td>8</td>
<td>0.13</td>
</tr>
<tr>
<td>9</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3. Effect of thiocyanate on the photographic sensitivity of an iridium (III) surface-sensitized AgBr emulsion.

Figure 12. Change in effect of thiocyanate on iridium sensitization as a function of pAg.
The optimum sensitization used above was reached at different sensitization times. The effect of pAg on optimum sensitization time is shown in Table 4, Table 5., and Figure 13.

<table>
<thead>
<tr>
<th>Sens. Time, min.</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>30</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion (pAg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 Ir</td>
<td>1.23</td>
<td>1.20</td>
<td>1.17</td>
<td>1.14</td>
<td>1.10</td>
</tr>
<tr>
<td>7 Ir + SCN⁻</td>
<td>1.02</td>
<td>1.00</td>
<td>0.94</td>
<td>0.97</td>
<td>1.00</td>
</tr>
<tr>
<td>8 Ir</td>
<td>1.12</td>
<td>1.10</td>
<td>1.08</td>
<td>1.07</td>
<td>1.05</td>
</tr>
<tr>
<td>8 Ir + SCN⁻</td>
<td>0.97</td>
<td>0.96</td>
<td>0.95</td>
<td>0.96</td>
<td>1.01</td>
</tr>
<tr>
<td>9 Ir</td>
<td>1.10</td>
<td>1.08</td>
<td>0.98</td>
<td>0.95</td>
<td>1.00</td>
</tr>
<tr>
<td>9 Ir + SCN⁻</td>
<td>0.83</td>
<td>0.83</td>
<td>0.84</td>
<td>0.84</td>
<td>0.87</td>
</tr>
<tr>
<td>10 Ir</td>
<td>1.46</td>
<td>1.45</td>
<td>1.42</td>
<td>1.42</td>
<td>1.42</td>
</tr>
<tr>
<td>10 Ir + SCN⁻</td>
<td>1.37</td>
<td>1.37</td>
<td>1.40</td>
<td>1.42</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Table 4. Exposure levels (in relative log units) at 0.95 density units above base + fog as a function of sensitization time.
Table 5. Time (min.) to reach maximum sensitivity within our parameters.

<table>
<thead>
<tr>
<th>pAg</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir+SCN⁻</td>
<td>10</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ir</td>
<td>≥60</td>
<td>≥60</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 13. Effect of pAg on time of sensitization required to reach maximum sensitivity.

The time for maximum sensitization for the emulsions in which no thiocyanate was used with the iridium showed a significant dependency.
on pAg. At pAg's 7 and 8, it took at least 60 minutes to reach maximum sensitivity. Since there is no data for the sensitization at times longer than 60 minutes, one cannot be sure whether sensitization was completed. At pAg 10 it took 10 minutes to reach maximum sensitivity. In emulsions in which thiocyanate was used with iridium, less dependency was seen. At low pAg, it took only 10 minutes to reach maximum sensitivity. At higher pAg's, maximum sensitivity was reached at "0" minutes (which is actually 3 minutes at 40°C).

Samples developed with the total developer and with Kodak D-76 developer showed no increase in photographic speed over samples developed with Kodak D-72 developer.
DISCUSSION

The unsensitized emulsion samples behaved as expected. As demonstrated in Figure 10, the sensitivity of the silver bromide material decreased as silver ion concentration decreased (pAg increased). Many references attempt to explain the phenomenon. Matejec and Meyer\textsuperscript{35} claimed changing pAg affects the space-charge layer in the silver halide crystal. According to their model, light induced electrons would travel to the grain surface at low pAg, and be available for latent image formation, thus increasing the sensitivity. Leubner\textsuperscript{36}, through his studies with sensitizing dyes, attributes the effect to the reduction of silver ion at low pAg. Gelatin's role in halide removal is also a factor\textsuperscript{37-39}. At high pAg's, high concentration of bromide ions will decrease the gelatin's ability to trap positive holes produced by light, thus decreasing the material's sensitivity.

The data produced by this project shows that this effect is partially reversed, possibly due to the iridium and iridium and thiocyanate sensitization for pAg's 7 through 10. The highest degree of sensitization was reached at pAg 9. This effect cannot be explained using the empirical chemical reaction between the iridium salt and the silver bromide crystal since the reaction for the formation of the iridium sensitivity centers,
would predict that the sensitivity of the silver bromide material will **decrease** as pAg is raised. The explanation for the effect is related to Banmuller's conclusion (which was later reinforced by Carroll\textsuperscript{13} and Zuleta\textsuperscript{21}) that iridium must be built into the grain to produce an efficient sensitization\textsuperscript{9}.

As pAg increases, the solubility of silver bromide increases (Figure 14), and the iridium could be incorporated into the silver bromide crystal lattice at a greater rate and higher efficiency. At the extreme pAg 10, the iridium, though built into the silver bromide crystal, is not sufficient to overcome the desensitizing effects of the excess bromide ion surrounding the grain and the low concentration of the free silver ion; sensitivity sharply decreases. It is also possible that the desensitization at the higher pAg is due to the effect of bromide ion concentration on the formation of the iridium sensitization centers (iridium center is simply not built at high pAg). A combination of both factors is also conceivable. However, since the samples were coated at different pAg's, our data does not allow us to distinguish between the two effects.

Since no additional sensitivity was gained when an total developer was used for developing the emulsion sensitized at pAg 10, it is unlikely...
that the decrease in sensitivity is due to burying the iridium too deep for the low-solvent developer to reach the center.

![Graph](image_url)


The rest of the data produced by this project supports the importance of the role of silver bromide solubility due to higher pAg's. Thiocyanate increases the efficiency of iridium sensitization by etching the silver bromide grain and allowing the iridium to be incorporated in the crystal lattice\(^2\). As pAg increases, the importance of the thiocyanate diminishes since the higher solubility of the grain allows the iridium to
be built into the grain without the aid of the silver halide solvent. At pAg 10, there is no significant difference between the maximum sensitivity of the iridium sensitized silver bromide with or without the thiocyanate.

The results from the rate of sensitization studies for iridium and iridium and thiocyanate (Figure 13) provide more evidence for the proposed mechanism. When iridium is used by itself, as pAg increases, so does the rate of sensitization. At least sixty minutes were required to reach maximum sensitivity at pAg 7, only 10 minutes at pAg 10. The same pattern was observed when thiocyanate was used with the iridium salt. Once again, as pAg increases, solubility of silver bromide increases, and iridium can be easily built into the crystal lattice and act as an efficient sensitizer.
CONCLUSIONS

The data produced by this research project provides sensitization optimization for the system studied. For a fine grain, monodisperse, octahedral silver bromide emulsion, maximum sensitivity can be reached by surface sensitization of iridium (III) and thiocyanate at pAg 9 for 5 minutes. The sensitivity achieved is not as high as sulfur + gold sensitization\textsuperscript{21}, but some of its characteristics may be quite useful for different applications such as graphic arts materials.

A more significant conclusion of this thesis is the verification of the mechanism proposed by Zuleta for the role of thiocyanate in iridium sensitization\textsuperscript{21}. The data supports the view that thiocyanate acts as a silver halide solvent for the silver bromide crystal and facilitates the incorporation of iridium where it is at a more effective level within the crystal. This is due to both an increase in the rate of sensitization and an increase in the magnitude of the increase in sensitivity.

The importance of the solubility of the silver bromide in iridium sensitization is also suggested. For pAg's 7, 8, and 9, the increasing solubility of the silver bromide during sensitization may affect the ease of iridium center incorporation, thus increasing the sensitivity of the material. This conclusion is also supported by the decreasing effect of the thiocyanate and the increasing rate of sensitization at higher pAg's.
The decrease of sensitivity at pAg 10 can be attributed to coating effects, no incorporation of iridium center in the crystal lattice, or both.

Much needs to be further studied about iridium and iridium and thiocyanate sensitization. A similar experiment which contains data for emulsions coated at the same pAg will be able to further explain the desensitization of the iridium sensitized emulsion at pAg 10. The absence of fog in all samples studied may be useful in some applications, the high contrast in others. Many graphic arts materials that are currently using rhodium may benefit from the advantages of iridium. The effect of pAg on gold + thiocyanate sensitization should be studied. A determination of the location of the iridium center would either support or dispute the theory dealing with the role of thiocyanate in iridium sensitization. And finally, the experimental procedure utilized for this experiment should be used with other group VIII metals.
APPENDIX 1

EMULSION LAB COMPUTER PROGRAM

10 REM "emull"
20 REM "***************************************************************************"
30 REM "PROGRAM TO CALCULATE THE PUMP RATES, pAg, vAg, AND pBr FOR"
40 REM "A DOUBLE JET SILVER BROMIDE EMULSION CONTROLLING CRYSTAL HABIT"
50 REM "***************************************************************************"
60 PRINT;PRINT;PRINT
70 PRINT "WELCOME TO EMULSION 1."
80 PRINT;PRINT
90 PRINT "[B] This program enables you to calculate the flow rate of the bromide"
100 PRINT "pump to keep the excess bromide constant throughout precipitation, given"
110 PRINT "the initial bromide concentration, the silver pump rate, and the"
120 PRINT "concentrations of the silver and bromide jets.
"
130 PRINT "It also calculates the pAg and vAg from your bromide concentration.
"
140 PRINT;PRINT
150 PRINT "[H] This program gives you the required initial bromide concentration
"
160 PRINT "and the control limits at the chosen "
170 PRINT "crystal habit and temperature."
180 PRINT;PRINT
190 PRINT "[P] This program will calculate the initial bromide concentration,"
200 PRINT "pump rates and vAg for a certain pAg and temperature"
210 PRINT;PRINT
220 INPUT "Which program do you want to use? [B, H, P]; M"
230 IF M="B" OR M="H" THEN 270
240 IF M="P" OR M="b" THEN 2100
250 IF M="h" OR M="p" THEN 910
260 PRINT;PRINT
270 PRINT;"NOTE: YOUR BROMIDE JET CONCENTRATION SHOULD BE AT LEAST ONE ORDER OF"
280 PRINT;"MAGNITUDE LARGER THAN YOUR INITIAL CONCENTRATION"
290 PRINT;PRINT
300 INPUT "What is the initial volume of solution (in ml); M VI
310 PRINT
320 INPUT "What is the initial bromide concentration; M CI
330 PRINT
340 INPUT "What is the silver pump rate (in ml/min); M RAG
350 PRINT
360 INPUT "What is the silver jet concentration; M CAG
370 PRINT
380 INPUT "What is the bromide jet concentration; M CBR
390 PRINT
400 INPUT "What is the precipitation time (in min); M TIME
410 PRINT
420 INPUT "What is the temperature in Celsius; M T
430 PRINT
440 Q=LOG(10)
450 RATE= (1000/TIME)*(CI*RAG*TIME+RAG*TIME*CAG)/(1000*CBR- CI)
460 EO=799-.1*(T-25)
470 T1=T+.273.15
480 PKSP=-12.126-5868/T1-.015953*T1
490 A=(1.1327+1.3056E-03*T+1.16836E-05*T^2)
500 I=CI
510 PBR=(1/0)*(A*SQR(I)/(1+SQR(I))+.22*I-LOG(CI))
520 VAg=EO-197+.1984*T1*(PBR-PKSP)
530 PAg= PKSP-PBR
540 PRINT;PRINT
550 PRINT;"***************************************************************************"
560 PRINT
570 PRINT;"INITIAL BROMIDE CONCENTRATION = " ; M CI; "M"
580 PRINT;PRINT
590 PRINT;"SILVER JET CONCENTRATION = " ; M CAG; "M"
600 PRINT;PRINT
610 PRINT;"BROMIDE JET CONCENTRATION = " ; M CBR; "M"
620 PRINT;PRINT

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**PREPARATION:**

- **Initial Bromide Concentration:** `|Cl|` ppm
- **Silver Jet Concentration:** `|Ag|` ppm
- **Bromide Jet Concentration:** `|Br|` ppm
- **Precipitation Time:** `|TIME|` min
- **Temperature:** `|T|` °C

**TEMPERATURE [°C]:**

1. **Calculation:**
   
   ```
   RATE = \frac{(1000/TIME) \times (CI(3) \times RAG \times TIME + RAG \times TIME \times CBR)}{(1000 \times CBR - CI(3))}
   ```

2. **Solution Calculation:**
   
   ```
   RAG = \frac{|Ag| \times TAB(40)}{VAg}
   ```

3. **Sample Calculation:**
   
   ```
   VAg = \frac{|Ag| \times TAB(40)}{RAG}
   ```

4. **Temperature Correction:**
   
   ```
   T = \frac{37 + 50563E-03 \times T + 1.16836E-05 \times T}{237.15}
   ```

**INPUT:**

1. Do you want a hard copy?
2. If yes, go to 740 ELSE GOTO 890
3. If no, go to 740

**DIMENSION:**

```plaintext
DIM [Cl(3)], [Ag(3), [Br(3)], [T(3)]
```
APPENDIX 2
EXPERIMENTAL DESIGN

Design

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
<th>Dimensions</th>
<th>Range</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>pAg</td>
<td>quantitative</td>
<td>-log(Ag⁺)</td>
<td>7 - 10</td>
<td>7, 8, 9 &amp; 10</td>
</tr>
<tr>
<td>time</td>
<td>quantitative</td>
<td>minutes</td>
<td>0 - 60</td>
<td>0, 5, 10, 30 &amp; 60</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>quantitative</td>
<td>mg/mole</td>
<td>0 - 500</td>
<td>0 &amp; 500</td>
</tr>
</tbody>
</table>

Response Variable

Photographic speed was the response variable used in this series of experiments. For each D log H curve constructed, the exposure level necessary to produce a density of 0.95 density units above base + fog was determined and used as a "speed point". This point was always on the straight portion of the D log H curve. Since the contrast of all samples used was similar at that point of the curve, its effect was considered negligible.

Statistical Method

A full three-way design was utilized.
<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>[SCN⁻]</th>
<th>Speed Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0 min</td>
<td>0 mg/mol</td>
<td>1.23±0.006</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0</td>
<td>1.20±0.01</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>0</td>
<td>1.17±0.006</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>0</td>
<td>1.14±0.01</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>0</td>
<td>1.10±0.00</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>1.12±0.006</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>0</td>
<td>1.10±0.006</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0</td>
<td>1.08±0.006</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>0</td>
<td>1.07±0.01</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>0</td>
<td>1.05±0.006</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>1.10±0.02</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>0</td>
<td>1.08±0.015</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0</td>
<td>0.98±0.006</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>0</td>
<td>0.95±0.006</td>
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<tr>
<td>9</td>
<td>60</td>
<td>0</td>
<td>1.00±0.006</td>
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<td>0</td>
<td>1.46±0.02</td>
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<td>5</td>
<td>0</td>
<td>1.45±0.006</td>
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<tr>
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<td>10</td>
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<td>500</td>
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</tr>
<tr>
<td>8</td>
<td>10</td>
<td>500</td>
<td>0.97±0.02</td>
</tr>
<tr>
<td>DAG</td>
<td>Time</td>
<td>[SCN⁻]</td>
<td>Speed Point</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>500</td>
<td>0.96±0.00</td>
</tr>
<tr>
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<td>10</td>
<td>500</td>
<td>0.95±0.006</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>500</td>
<td>0.96±0.006</td>
</tr>
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<td>8</td>
<td>60</td>
<td>500</td>
<td>1.01±0.015</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>500</td>
<td>0.83±0.006</td>
</tr>
<tr>
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<td>5</td>
<td>500</td>
<td>0.83±0.006</td>
</tr>
<tr>
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<td>10</td>
<td>500</td>
<td>0.84±0.02</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>500</td>
<td>0.84±0.006</td>
</tr>
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<td>60</td>
<td>500</td>
<td>0.87±0.01</td>
</tr>
<tr>
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<td>0</td>
<td>500</td>
<td>1.37±0.006</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>500</td>
<td>1.37±0.006</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>500</td>
<td>1.40±0.006</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>500</td>
<td>1.42±0.006</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>500</td>
<td>1.42±0.006</td>
</tr>
</tbody>
</table>

**Control**

An unsensitized sample was taken at each of the runs.

**Replication**

From past experience with the facilities and processes, it was known that most variability in this project would come from the coating step. Three coatings were made for each run. Each coating was further cut into three to twelve 10 cm stripes.
Randomization

Randomization was practiced wherever possible and practical. Sensitization and coatings were partially randomized. Exposure and processing were done in blocks.

A typical run consisted on two sensitizations (for example pAg 7 Ir and pAg 9 Ir + SCN−) which were coated at the same time. They were then exposed and processed a week later, in a randomized fashion. The procedure was then repeated with two more sensitization. All eight sensitization took about 10 weeks to complete.

Analysis

Due to the relative complexity of the design, multiple regression was used to determine the significance of the data. The following computer programs were used on the Apple Macintosh 512K:

Engineering Tool Kit 3.0, Sof-Ware Tools

CLR ANOVA, Clear Lake Research

Attached to the appendix are the regression statistics.
REGRESSION STATISTICS

REGRESSION SUM OF SQUARES = .5897
REGRESSION SUM OF SQUARES = .9701
TOTAL SUM OF SQUARES = 1.5678
COEF OF DETERMINATION (R SQ) = .3761
COEF OF MULTIPLE CORRELATION = .6133
STANDARD ERROR OF ESTIMATE = .1648
F-RATIO (REGRESSION) = 7.2348
DEG OF FREEDOM = 3 & 36
PROBABILITY OF CHANCE = .00576E-04
NUMBER OF CASES (SUBJECTS) = 10
" OF INDEPENDENT VARIABLES = 3

REGRESSION COEFFICIENTS

<table>
<thead>
<tr>
<th>VAR. NAME</th>
<th>MEAN</th>
<th>STD. DEV.</th>
<th>COEFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td></td>
<td></td>
<td>.4031</td>
</tr>
<tr>
<td>IV # 1</td>
<td></td>
<td></td>
<td>.0319</td>
</tr>
<tr>
<td>IV # 2</td>
<td></td>
<td></td>
<td>-.0003</td>
</tr>
<tr>
<td>IV # 3</td>
<td></td>
<td></td>
<td>.1255</td>
</tr>
<tr>
<td>DV</td>
<td></td>
<td></td>
<td>.2005</td>
</tr>
</tbody>
</table>

REGRESSION EQUATION:

\[ DV = {.4031} + (.0319 \times IV_1) + (.0003 \times IV_2) + (.1255 \times IV_3) \]

AVERAGE ERROR (COMPEARED TO REGRESSION LINE) = .1343
### Total Developer

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methyl-p-aminophenol sulfate</td>
<td>2.0g</td>
</tr>
<tr>
<td>Sodium sulfite, anh.</td>
<td>90.0g</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>8.0g</td>
</tr>
<tr>
<td>Sodium carbonate monohydrate</td>
<td>52.0g</td>
</tr>
<tr>
<td>Potassium bromide</td>
<td>5.0g</td>
</tr>
<tr>
<td>Potassium iodide</td>
<td>0.5g</td>
</tr>
<tr>
<td>Dist. Water to make</td>
<td>1.0 l</td>
</tr>
</tbody>
</table>

### Eastman Kodak D-72 Developer

<table>
<thead>
<tr>
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<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methyl-p-aminophenol sulfate</td>
<td>3.0g</td>
</tr>
<tr>
<td>Sodium sulfite, anh.</td>
<td>45.0g</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>12.0g</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>80.0g</td>
</tr>
<tr>
<td>Potassium bromide</td>
<td>2.0g</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
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</tbody>
</table>

### Eastman Kodak D-76 Developer

<table>
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<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methyl-p-aminophenol sulfate</td>
<td>2.0g</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>100.0g</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>5.0g</td>
</tr>
<tr>
<td>Borax</td>
<td>2.0g</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
</tr>
</tbody>
</table>
REFERENCES


27. Konishiroku, Jap. Pat. 7-4,033,781.

28. C. G. Dostes, D. C. Dubromel and J. F. M. LeGuen, Fr. Pat. 2,296,204


