A Study of Solarization in the Negative Image of Reversal Films and Sensitivity and Development Rate as a Function of First Exposure

Maximiliano Rivera

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A STUDY OF SOLARIZATION IN THE NEGATIVE IMAGE OF REVERSAL FILMS, AND SENSITIVITY
AND DEVELOPMENT RATE AS A FUNCTION OF FIRST EXPOSURE

Submitted in partial fulfillment of the requirements for the Degree of Master of
Science in the Department of Photographic Science.

by

Maximiliano Rivera, Jr.
Captain USAF

Rochester Institute of Technology
June, 1970

Approved

Burt H. Carroll

Ronald Francis

Illegible Signature
ACKNOWLEDGEMENTS

I thank Dr. B.H. Carroll, my advisor, for the original idea for this research thesis and for his diligent advice on the laboratory work and on the writing of this thesis.

I thank my wife, Patricia, for her patience and endurance throughout the school year and for her assistance in the typing of the rough draft of the thesis.

I thank Richard Norman for his assistance in the making of the plexiglas agitating brush and Harry Osborne for editing and publishing the final form of this thesis.
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ABSTRACT

This thesis has two objectives. One is to see if in reversal films solarization has begun before reaching the maximum density in the negative image. Acetone semicarbazone was added to the emulsions, so that if solarization were significant, this halogen acceptor, by elimination of the solarization, would increase the maximum density. The films tested were KODAK PLUS-X Reversal Film Type 7276, TRI-X Reversal Film Type 7278, Fine Grain Release Positive Type 5302, and PANATOMIC-X. It is concluded that solarization does not have a significant effect on the maximum density, slope near the maximum density, or density scale of the negative D Log E curve.

The second objective is a study to see what happens to the development rate and the sensitivity of the residual silver-halide emulsion after first exposure, first development, and bleaching as a function of the first exposure. The sensitivity is expected to drop quite dramatically with increasing first exposure and the results show it does. For the one film tested, PLUS-X Reversal, it was found that the development rate, corrected for change in Dmax, materially decreased with increasing first exposure. There was a decrease in development rate resulting from bleaching the first image with destruction of chemical sensitization; the effect of exposure was superimposed on this. The bleached film showed a large, unexplained increase in fog on second development.
Emulsions for reversal films generally have a thin, single-layer coating. The thin, single-layer coating is done in order to obtain clear, low-density highlights upon reversal. To get a clear highlight in reversal there must be no residual silver halide in the region of maximum exposure. If all the silver-halide grains throughout the depth of the emulsion layer are to be exposed, the exposure must be rather heavy. With the necessary exposure, though, it is possible that in spite of the thin coating of reversal films, the top silver-halide grains of the emulsion layer could solarize before all the grains at the bottom would be exposed. In addition, the larger more sensitive grains could solarize before the smaller less sensitive grains are exposed sufficiently. Thus we would see a lower than possible maximum density after the first development (see Figure 1).

The solarization effect can be eliminated by halogen acceptor. Webb and Evans experimentally proved that halogen is released by heavily exposed silver-halide grains and this free halogen can recombine with the silver of surface latent image. The halogen acceptor will absorb the halogen released during exposure and hence it does not allow the halogen to recombine with the silver latent image. This process allows the grains to remain developable. Therefore, if the solarization effect is significant, addition of halogen acceptor to the reversal-film emulsion should raise the maximum density achievable after development and before reversal.
In addition, we know that solarization effects are removed by using solvent or solution-physical developers which develop the internal latent image. For this reason I tested the hypothesis with two non-solvent or surface developers which should give a more pronounced solarization effect if present. However, I also tested for the effect with a recommended reversal-first developer (D-94) which is a solvent (high SCN⁻ content) developer. This developer contains the solvent to selectively dissolve any residual unexposed silver-halide grains, and provide clean, clear highlights upon reversal. If the solarization effect is wiped out sufficiently by the solvent, there is no need to add halogen acceptor to the emulsion.
STATEMENT OF OBJECTIVE 1

To test the hypothesis that there is a significant decrease in $D_{\text{max}}$, slope near $D_{\text{max}}$, and density scale of the negative $D \log E$ curve caused by solarization, when the emulsion is exposed sufficiently to give minimum density on reversal. These responses will be measured by comparing $D \log E$ curves of the emulsions with and without addition of halogen acceptor.

1. $D_{\text{max}}$ is defined as the maximum density reached with the highest exposure, which should give $D_{\text{min}}$ if reversed.

2. Slope near $D_{\text{max}}$ is defined as $\Delta D/\Delta \log E$ slope at a density just before the curve of the emulsion untreated with halogen acceptor begins to shoulder.

3. Density scale is defined as $D_{\text{max}} - D_{\text{min}}$ as read off the $D \log E$ curves.
EXPERIMENTAL PROCEDURE

Developer Selection

The first nonsolvent developer selected was Metol-Ascorbic acid, but the literature\(^6\) indicated it required 20 minutes development at temperature of 68°F. This seemed too time consuming, so DK-50 was selected as an adequate surface developer.

The second nonsolvent developer selected was a modified formulation of the recommended developer (D-94) for PLUS-X and TRI-X reversal films. It was used to closely approximate the activity of D-94 developer, but without the silver-halide solvent and with reduced sodium-sulfite content.

The solvent developer used was D-94. D-94 is the first developer recommended in reversal processing of PLUS-X and TRI-X reversal film.\(^4\)

Formulas for all these developers are included in Appendix I.

Reversal Film Selection

KODAK PLUS-X Reversal Film Type 7276 and KODAK TRI-X Reversal Film Type 7278 were selected because they are commonly used 16mm reversal films.

KODAK PANATOMIC-X 35mm Film was also selected even though it is a negative film and not normally used as reversal film. It is single-layer coated and can be reversed.

KODAK Fine-Grain Release Positive Type 5302 was selected as a fourth film to test because it is a cine-positive film and therefore has a single-emulsion coating of moderate thickness.
Film Preparation for Exposure

Acetone semicarbazone is a good halogen acceptor which does not usually interfere with the photographic or development characteristics of a film other than as a halogen acceptor. Bathing in a 1-percent solution is a satisfactory method for adding enough of it to the emulsion. Potassium bromide to 0.001N was included in the 1-percent solution to preclude fog formation.

Four strips of each of the reversal films were bathed in the 1-percent acetone semicarbazone solution for 5 minutes at 68F. They were then wiped gently with soft paper to remove excess solution and dried in the dark. Four other strips of the same film were left untreated.

Exposure

Preliminary tests show where to adjust the Macbeth Sensitometer for exposing to achieve maximum density - minimum density on reversal - through the 21st step of a neutral step wedge. Since the Fine Grain Release Positive has a maximum density beyond 4.00, exposure adjustment for it had to be made to give close to 4.00 density on the 21st step of the step wedge rather than D_max. (The densitometer I used does not read densities higher than 4.00). Four strips of a film prepared above (two treated with acetone semicarbazone solution and two untreated) were exposed to the predetermined exposure.

The other four strips of the same type of film (two treated and two untreated) were exposed to a predetermined lower intensity to determine the value of D_min in the negative.

All the film strips were exposed on the same sensitometer.
Processing

The eight strips were developed in D-94 for 2 minutes, stop bathed for 30 seconds, fixed for 3 minutes, rinsed, and dried. All eight strips were processed in the same tray (the specially constructed tray and agitating brush described in Appendix I). Temperature was held at 68°F for all steps.

The same procedure of treating, exposing, and processing was followed on another set of eight strips (4 treated and 4 untreated) of the same type film, except now the modified D-94 solution was used as the developer for 2 minutes.

The same procedure was repeated again on another set of eight strips (4 treated and 4 untreated) of the same type film, except now DK-50 was used for 5 minutes as the developer.

This same procedure with the three developers was repeated for each of the four films selected for testing.

Deviations from the above described experimental procedure did occur; they will be discussed in the results section of this report.

Reading and Plotting

All the film strips were read on the same Macbeth Densitometer Model TD-203. The density readings were plotted as Density versus Log E. The desired responses were measured from the curves.
Because fog and speed seemed to be affected by the acetone semi-carbazone, measurements to see if they had increased significantly were made. Speed is defined as 100/E at 0.6 density above base plus fog.

**Other Tests**

For comparison purposes, strips of the same type films were bathed in 0.001N solution of KBr (halogen acceptor solution without the halogen acceptor) and dried in the dark. They were processed along with untreated control strips, the same as previously outlined, except only D-94 was used as developer on Tri-X, Pan-X and the cine positive. Both DK-50 and D-94 were used to develop the Plus-X strips.

To determine the maximum possible density from each film, strips of each film were bathed in Sodium Borohydride solution (0.1 gm/l) for 5 minutes and developed in DK-50 for 10 minutes at 68F. Sodium borohydride causes all the silver halide grains in the emulsion to become developable.
RESULTS

Statistical Treatment of the Data

All comparisons were made between test strips processed at the same time in the processing tray and all statistical tests were performed at 90-percent confidence level.

In each case, the mean of the samples with acetone semicarbazone was tested against the mean of the samples without the semicarbazone. The replicated samples were used to calculate the standard deviation of the means and the two values obtained were pooled under the assumption that the variances were the same with or without halogen acceptor. (Sample "F" tests\(^9\) on the variances showed that this was a correct assumption.) The Student "t" test\(^9\) was applied to look for significant increases as a result of the addition of the halogen acceptor. The implication is that if the measured responses have a significant increase resulting from the halogen acceptor, then there is a significant decrease caused by solarization.

Sample calculations of the statistical tests are included in Appendix A

Tables 1, 2, 3, and 4 show the results for \(D_{\text{max}}\), density scale, slope near \(D_{\text{max}}\), fog (+base), and speed, when using DK-50 as the developer on test strips treated and untreated with the halogen acceptor. The corresponding graphs showing the average D Log E curves follow the tables and illustrate the results. The exposure is in meter-candle-second units.
### PLUS-X Developed in DK-50

#### Table 1 (Refer to graph 1)

<table>
<thead>
<tr>
<th></th>
<th>D$_{max}$</th>
<th>Den Scale</th>
<th>Slope near D$_{max}$</th>
<th>Speed</th>
<th>Fog + Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated strips</td>
<td>2.93</td>
<td>2.72</td>
<td>0.57</td>
<td>0.60</td>
<td>86.96</td>
</tr>
<tr>
<td>Average</td>
<td>2.955</td>
<td>2.695</td>
<td>0.585</td>
<td>0.611</td>
<td>85.640</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.035</td>
<td>0.035</td>
<td>0.023</td>
<td>0.019</td>
<td>1.865</td>
</tr>
<tr>
<td>Bathed strips</td>
<td>3.01</td>
<td>2.76</td>
<td>0.63</td>
<td>0.73</td>
<td>86.96</td>
</tr>
<tr>
<td>Average</td>
<td>3.015</td>
<td>2.750</td>
<td>0.63</td>
<td>0.711</td>
<td>83.770</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.007</td>
<td>0.014</td>
<td>0.00</td>
<td>0.038</td>
<td>4.511</td>
</tr>
<tr>
<td>Pooled Std Dev</td>
<td>0.025</td>
<td>0.027</td>
<td>0.017</td>
<td>0.030</td>
<td>3.452</td>
</tr>
</tbody>
</table>

Due to the addition of Semicarbazone, significant increase in both cases.

**The curves overlap, so no statistical proof is necessary to show there is no increase.**

### TRI-X Developed in DK-50

#### Table 2 (Refer to graph 2)

<table>
<thead>
<tr>
<th></th>
<th>D$_{max}$</th>
<th>Den Scale</th>
<th>Slope near D$_{max}$</th>
<th>Speed</th>
<th>Fog + Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated strips</td>
<td>2.96</td>
<td>2.66</td>
<td>0.57</td>
<td>190.11</td>
<td>0.30</td>
</tr>
<tr>
<td>Average</td>
<td>2.965</td>
<td>2.665</td>
<td>0.57</td>
<td>182.745</td>
<td>0.30</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.007</td>
<td>0.007</td>
<td></td>
<td>10.420</td>
<td>0.00</td>
</tr>
<tr>
<td>Bathed strips</td>
<td>2.96</td>
<td>2.57</td>
<td>0.63</td>
<td>231.21</td>
<td>0.39</td>
</tr>
<tr>
<td>Average</td>
<td>2.967</td>
<td>2.575</td>
<td>0.63</td>
<td>235.28</td>
<td>0.395</td>
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<tr>
<td>Std. Dev.</td>
<td>0.014</td>
<td>0.007</td>
<td></td>
<td>5.752</td>
<td>0.007</td>
</tr>
<tr>
<td>Pooled Std Dev</td>
<td>0.011</td>
<td>0.007</td>
<td></td>
<td>8.417</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Due to the addition of Semicarbazone, increase* increase** increase***

* The density scale showed a significant decrease resulting from the high fog.

** The curves overlap, so no statistical proof is necessary to show there is no increase.

*** It was found later that this increase in fog and speed resulted from infectious development. This will be discussed in the discussion of results.
PANATOMIC-X Developed in DK-50

Table 3 (Refer to graph 3)

<table>
<thead>
<tr>
<th></th>
<th>D$_{\text{max}}$</th>
<th>Den Scale</th>
<th>Slope near D$_{\text{max}}$</th>
<th>Speed</th>
<th>Fog + Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated strips</td>
<td>3.00</td>
<td>2.72</td>
<td>0.56</td>
<td>42.66</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>3.03</td>
<td>2.75</td>
<td>0.46</td>
<td>39.63</td>
<td>0.28</td>
</tr>
<tr>
<td>Average</td>
<td>3.015</td>
<td>2.735</td>
<td>0.51</td>
<td>41.145</td>
<td>0.280</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.021</td>
<td>0.021</td>
<td>0.071</td>
<td>2.145</td>
<td>0.00</td>
</tr>
<tr>
<td>Bathed strips</td>
<td>3.07</td>
<td>2.79</td>
<td>0.77</td>
<td>47.87</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>3.10</td>
<td>2.82</td>
<td>0.63</td>
<td>50.71</td>
<td>0.28</td>
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<tr>
<td>Average</td>
<td>3.085</td>
<td>2.805</td>
<td>0.700</td>
<td>49.29</td>
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<tr>
<td>Std. Dev.</td>
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<td>0.021</td>
<td>0.094</td>
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<tr>
<td>Pooled Std Dev</td>
<td>0.021</td>
<td>0.021</td>
<td>0.083</td>
<td>2.0779</td>
<td>0.00</td>
</tr>
<tr>
<td>Due to the</td>
<td>Signi-</td>
<td>Signifi-</td>
<td>Significant</td>
<td>Signifi-</td>
<td>No Signifi-</td>
</tr>
<tr>
<td>addition of</td>
<td>ficant</td>
<td>cant</td>
<td>increase</td>
<td>cant</td>
<td>cant</td>
</tr>
<tr>
<td>Semicarbazone</td>
<td>increase</td>
<td>increase</td>
<td>increase</td>
<td>increase</td>
<td></td>
</tr>
</tbody>
</table>

Fine Grain Release Positive Developed in DK-50

Table 4 (Refer to graph 4)

<table>
<thead>
<tr>
<th></th>
<th>D$_{\text{max}}$*</th>
<th>Den Scale</th>
<th>Slope near D$_{\text{max}}$</th>
<th>Speed</th>
<th>Fog + Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated strips</td>
<td>3.59</td>
<td>0.83</td>
<td>0.90</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>3.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>3.610</td>
<td>0.867</td>
<td>0.047</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.028</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bathed strips</td>
<td>3.70</td>
<td>0.90</td>
<td>1.13</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>3.725</td>
<td>1.017</td>
<td>0.165</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.035</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pooled Std Dev</td>
<td>0.032</td>
<td>0.121</td>
<td></td>
<td>0.00</td>
<td></td>
</tr>
<tr>
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<td>Undeter-</td>
<td>No Significant</td>
<td>No Signifi-</td>
<td>No Signi-</td>
</tr>
<tr>
<td>addition of</td>
<td>ficant</td>
<td>mineable</td>
<td>increase**</td>
<td>cant</td>
<td>cant</td>
</tr>
<tr>
<td>Semicarbazone</td>
<td>increase</td>
<td></td>
<td>rise***</td>
<td>increase</td>
<td></td>
</tr>
</tbody>
</table>

* The values are not really D$_{\text{max}}$, as is explained in the procedure.

** Not high enough up the shoulder of the curve to detect any probable increase in the slope near D$_{\text{max}}$ as defined.

***The definition for speed as used does not give a significant change in speed for this film; however, increased contrast is observed.
Graph 1. PLUS-X developed with DK-50
Graph 2. TRI-X developed with DK-50

- With Halogen Acceptor
- Without Halogen Acceptor
Graph 3. PANATOMIC-X developed with DK-50
Graph 4. Fine Grain Cine-Positive developed in DK-50
PLUS-X Developed in D-94

PLUS-X curves (graph 5) developed in D-94 show no increase in $D_{\text{max}}$ density scale, or slope near $D_{\text{max}}$, but a significant increase in contrast over most of the curve from addition of the halogen acceptor. There was no change in the fog level.

TRI-X Developed in D-94

TRI-X curves (graph 6 and 7) also developed in D-94, show that there is no increase in the maximum achievable density by addition of halogen acceptor but there is a large increase in the contrast up to $D_{\text{max}}$. The effects resembled those with PLUS-X, but were greater. The first batch of results (graph 6) obtained, show that the image was not developing evenly so the experiment was repeated (graph 7). Again, the emulsion bathed in semicarbazone showed some streaking and uneven development. Further testing in D-94 did not eliminate this seemingly infectious development. Literature search into this phenomenon lead me to find that Stauffer, Smith, and Trivelli\(^7\) observed similar infectious development with high pH developers when hydrazine derivatives were present in small amounts during development. One such derivative is semicarbazide which can result from hydrolyzing acetone semicarbazone.

PANATOMIC-X Developed in D-94

PAN-X developed in D-94 (graph 8) shows no increase in any of the desired responses. The fog is excessive in both the treated and untreated emulsions and the speed, as a result of the extremely high variability in fog, is not determinable as defined.
Fine-Grain Release Positive Developed in D-94

Fine-Grain Release Positive developed in D-94 (graph 9) also shows an increase in speed with a slight rise in fog. $D_{\text{max}}$, slope near $D_{\text{max}}$, and the density scale can not be determined as the maximum achievable density is well beyond 4.00, the maximum which could be read with the densitometer used.

Table 5 summarizes the results obtained with the D-94 developer and answers the question "Is there a significant increase resulting from addition of acetone semicarbazone?"

Table 5 (Refer to graphs 5, 6, 7, 8, 9)

<table>
<thead>
<tr>
<th></th>
<th>$D_{\text{max}}$</th>
<th>Slope near $D_{\text{max}}$</th>
<th>Den Scale</th>
<th>Fog</th>
<th>Speed</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLUS-X</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>TRI-X</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>PAN-X</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Cine Pos</td>
<td>Can not determine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
</tr>
</tbody>
</table>
Graph 7. TRI-X developed with D-94
Graph 9. Fine Grain Cine-Positive developed in D-94
Strips Developed in Modified D-94 Developer

No graphs were made of the strips (with or without addition of acetone semicarbazone) which were developed in the modified D-94 solution. The film strips bathed in acetone semicarbazone could not be developed evenly and fog was always high. The test strips showed the characteristic mottle of infectious development and it was particularly bad with TRI-X. The minimum density of the TRI-X film strips with acetone semicarbazone read about 1.14. The untreated strips gave a density of 0.35.

None of the desired responses could be measured accurately as a result of the above mentioned problems; however, even with the infectious development, there appears to be no increase in $D_{\text{max}}$ from using the acetone semicarbazone. For example, PLUS-X film with the halogen acceptor gave a maximum density of about 3.12 and without the halogen acceptor gave a maximum density of 3.10.

Strips Bathed in 0.001N KBr Solution

Strips of each type of film were bathed in 0.001N KBr solution to ensure that any resulting effects were a result of the acetone semicarbazone and nothing else. The strips were developed in D-94 and when compared to the untreated control strips no significant differences resulted. It was unnecessary to plot the data to observe this condition. The results were the same for the PLUS-X strips developed in DK-50.
Strips Bathed in Sodium Borohydride Solution

Sodium borohydride is a strong reducing agent and should make all the silver-halide grains developable. Thus after development, the maximum possible density would be obtained.

Readings of the resultant density from bathing in sodium borohydride, when compared to $D_{\text{max}}$ obtained on the control strips without acetone semicarbazone, show that there is essentially no density left to be gained by adding the halogen acceptor. See Table 6. The small gain that seems possible on PLUS-X and PANATOMIC-X developed in DK-50 is not photographically significant.

Table 6

<table>
<thead>
<tr>
<th>Strips bathed in NaBH$_4$ Developed in DK-50</th>
<th>Strips untreated Developed in D-94</th>
<th>Strips untreated Developed in DK-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLUS-X</td>
<td>3.12</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>2.98</td>
<td>2.95</td>
</tr>
<tr>
<td>TRI-X</td>
<td></td>
<td>2.97</td>
</tr>
<tr>
<td>PAN-X</td>
<td>3.18</td>
<td>3.23</td>
</tr>
<tr>
<td>Cine Pos beyond 4.0</td>
<td>beyond 4.0</td>
<td>beyond 4.0</td>
</tr>
</tbody>
</table>

24
DISCUSSION OF RESULTS

Addition of acetone semicarbazone to the films tested caused unexpected increases in speed, fog, and contrast. A literature search into this phenomenon lead me to conclude that these observed increases were likely a result of the acetone semicarbazone hydrolyzing to semicarbazide under high pH. Stauffer, Smith, and Trivelli\(^7\) found that the semicarbazide, when present in relatively small amounts, causes an infectious type development with developing agents with one or more hydroxyl groups. This infectious development effect appears as increased speed and contrast with increased graininess. When this effect is excessive, a granular type fog appears. They also found that the effect increases when the pH is increased and the sulfite concentration is decreased. We can see, then, why DK-50 with a pH of about 10 and sufficient sulfite gave mostly negligible changes. However, a high pH developer like D-94, pH of about 12.5, did cause larger, more significant increases in speed and contrast. The modified D-94 solution, still with the same high pH but with reduced sulfite content, causes an even greater effect. We now see the granular type fog appear. The extent of this infectious development effect also varies with the type of film, thus we see the greatest increase in speed and contrast with TRI-X reversal film than with the other films.

All the significant changes (in speed, fog, contrast, density scale, slope near \(D_{\text{max}}\), and \(D_{\text{max}}\)) can be explained by the above mentioned hydrolyzing of the acetone semicarbazone except for the statistically
significant increases in $D_{\text{max}}$ found for both PLUS-X and PANATOMIC-X when developed in DK-50. For these two films, it appears a heavy enough exposure and/or long enough development time was not used, hence the maximum achievable density for good comparison was not reached. I base this assumption from observing the D Log E curves (graph 1 and 4) in which it appears that at higher exposures the maximum density values will converge as did the TRI-X curves in graph 6 and 7. In addition, note that even with addition of acetone semicarbazone to the emulsion, the PLUS-X film and PAN-X film strips are still significantly lower in $D_{\text{max}}$ (3.02 and 3.08 respectively) than those bathed with sodium boro-hydride indicated $D_{\text{max}}$ should be (3.12 and 3.18 respectively).

I can also point to the $D_{\text{max}}$ read on PLUS-X without acetone semicarbazone which was developed in the nonsolvent modified D-94 solution. It read 3.10, the same as the sodium boro-hydride bathed strips read, 3.12, indicating that this more active developer did reach the maximum density possible for the film. Increased development time in DK-50 would probably have had the same effect.
CONCLUSION

The results obtained in these experiments, although statistically significant in some instances, show that nothing of any photographic significance is gained by adding halogen acceptor to the emulsions tested. There is no significant decrease in $D_{\text{max}}$, slope near $D_{\text{max}}$, or density scale caused by solarization.

Addition of acetone semicarbazone to PLUS-X reversal film and to PANATOMIC-X film when developed with DK-50 gave less than 3-percent rise in $D_{\text{max}}$ (possibly much less if heavier exposure or longer development time were used) for both films. With D-94, no desirable differences occurred. In fact PANATOMIC-X when developed in D-94 fogs badly, untreated as well as treated with acetone semicarbazone.

Addition of acetone semicarbazone to TRI-X reversal film caused only undesirable changes, rise in fog and excessive contrast; addition to the fine-grain release positive caused only very slight changes in any of the responses.
INTRODUCTION TO OBJECTIVE 2

Looking at the H and D curve of normal negative emulsions, we see, as we move up the curve, that there are increasing exposure increments required for an equal change in density, as shown in Figure 2. This implies that as the emulsion is exposed it is losing sensitivity; see Figure 3. Sensitivity here is defined as $1/E$, where $E$ is the exposure required for equal increases in density. This decrease in sensitivity occurs because there is a decrease in the number of unexposed grains left as we increase the exposure, hence, there is waste of quanta by absorption by already exposed grains. In addition to this, there is a further loss in sensitivity, because normal negative emulsion silver halide grains are not all of the same size and sensitivity. Thus, the most sensitive grains are exposed first and the least sensitive are exposed last.
The conjecture here is that, in a like manner, the sensitivity of the reversal emulsions toward re-exposure will decrease as a function of increasing first exposure. That is to say, if we expose enough to get the density D₁ on Figure 2 after development, then bleach out that density so that we now have the unexposed portion of the emulsion left for re-exposure, how will the sensitivity of that resultant emulsion compare to the original emulsion? It will be of much lower sensitivity as a result of the destruction of chemical (and probably spectral) sensitization from bleaching. But superimposed on the loss of sensitivity resulting from destruction of sensitization, are losses from the waste of exposure and loss of the most sensitive grains. Because the most sensitive grains would be exposed first, they will be selectively bleached out first.

We now expose the emulsion enough to get the density D₂. After bleaching, how will the sensitivity of that resultant emulsion compare to the previous one (resultant from bleaching out density D₁)? There should be a further loss in sensitivity. We will have selectively bleached out more of the most sensitive grains. Also, because after bleaching we will have fewer silver-halide grains left in the emulsion, there will be a loss in $D_{\text{max}}$ which affects the sensitivity determination. That is, in order to have the same density with fewer grains per unit area, we will have to make even some of the very insensitive grains developable. In addition, there may be some loss in sensitivity resulting from desensitization by oxidized developer and iodizing of the remaining silver halide.
Exposing heavier to obtain density $D_3$ after development and then bleaching, we should get a slower emulsion than the previous ones, for the same reasons. The second objective of this thesis, then, is to test the hypothesis that the residual silver-halide emulsion after the first development and bleaching will decrease in sensitivity as a function of increasing first exposure.

Although the effect of iodide on sensitivity cannot be predicted, it is expected that it will decrease the rate of development. Ballard and Dundan found that partial conversion of residual silver bromide to less readily developable silver iodide will occur during development.\textsuperscript{10} As all fast films have some iodide (up to 10 percent) in the emulsion,\textsuperscript{11} PLUS-X reversal film would be expected to undergo this conversion of silver bromide to silver iodide during first development. Thus after first development and bleaching, we should see some decrease in the rate of redevelopement as a function of first exposure.

It may be necessary to compensate for differences in the rate of redevelopement by adjusting the redevelopement time to give equal gammas. If the development time is adjusted to give equal gammas, the loss of sensitivity can be measured with more confidence. Therefore the first part of testing the aforementioned hypothesis is to ascertain this expected decrease in rate of development.

The recommended first developer (D-94) and second developer (D-95) were used for processing the PLUS-X reversal film. However the results obtained with the D-95 as redeveloper showed that it was too active and developed to maximum gamma within 30 seconds. DK-50 was selected as a
more moderate activity developer and it was used as the redeveloper in a second set of tests on the hypothesis.

The fact that during the course of these experiments, I will effectively create a new emulsion after each first exposure, development, and bleaching should be kept in mind. I am then testing the resulting new emulsion for its development rate and sensitivity by controlled re-exposure and redevelopment. So the resulting characteristic (D Log E) curves, after second exposure and redevelopment, are plotted as negative curves and not as positive or reversal curves.
STATEMENT OF OBJECTIVE 2

To test the hypothesis that the residual silver-halide emulsion after the first exposure, first development, and bleaching, decreases in sensitivity as a function of increasing first exposure. As the rate of developability is expected to decrease after exposing, developing, and bleaching, the change in development rate will be determined as a function of first exposure.

1. No attempt will be made to determine the absolute development rate (change in density with respect to change in development time). I do intend to show through resultant curves whether the development rate is decreasing with increasing first exposure.

2. Compensation for development rate differences will be made by adjusting the development time so that the same gamma, $\Delta D/\Delta \log E$ slope of straight line portion, is achieved at each first exposure level.

3. Sensitivity is defined as speed = $1/E$ at 0.3 density above base density.
EXPERIMENTAL PROCEDURE

First Exposure Levels

The KODAK 101 sensitometer with a 2.3 ND filter (1.704 mcs) was used to exposure a strip of the PLUS-X reversal film through a 21 step neutral density wedge. The resulting density readings were used to determine the following first exposure levels as adequate for this experiment:

0.136 m cd sec
0.068 m cd sec
0.034 m cd sec
0.017 m cd sec
0.000 m cd sec

The test strips with 0.000 mcs first exposure were developed and bleached, so any fog silver inherent in the emulsion was removed and chemical sensitization was attacked. The 0.017 mcs level, after developing and bleaching, gives a slightly lower $D_{\text{max}}$ than the 0.000 mcs level. The first exposure was exposed evenly across the width and length of the film strips.

D-95 REDEVELOPMENT TIME SERIES

The first processing routine used with D-95 as the redeveloper did not seem to be adequately in control. It was decided to repeat the whole experiment changing the processing routine to the following:

First Exposure

Eight strips were exposed at each of the five first-exposure levels, for a total of 5 sets of 8 strips each. (One set at a time was exposed then processed before another was exposed.)
First Development

The eight strips of one exposure level were processed (all in one tray) as follows: Temperature was held at 68F for all steps.

1. First development
   D-94
   2 minutes

2. Rinse
   water
   30 seconds

3. Bleach
   R-9
   50 seconds

4. Rinse
   water
   30 seconds

5. Clearing bath
   modified CB-2
   30 seconds

6. Rinse
   running water
   1 minute

7. Dried in the dark
   30 to 60 minutes

The eight strips were now ready for the second exposure.

Second Exposure

The eight strips were re-exposed to a level previously determined by trial and error as correct for that specific first-exposure level. The re-exposure was through a 21 step ND wedge.

<table>
<thead>
<tr>
<th>First-Exposure Level</th>
<th>Second Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.136 mcs</td>
<td>1700 mcs</td>
</tr>
<tr>
<td>0.068 mcs</td>
<td>1020 mcs</td>
</tr>
<tr>
<td>0.034 mcs</td>
<td>680 mcs</td>
</tr>
<tr>
<td>0.017 mcs</td>
<td>170 mcs</td>
</tr>
<tr>
<td>0.000 mcs</td>
<td>85 mcs</td>
</tr>
</tbody>
</table>

Second Development

The eight strips were divided into two sets of 4 each. Four strips were then redeveloped (with D-95) in one tray but the strips were pulled out of the redeveloper successively at 30 seconds, 1, 2, and 4 minutes and were placed in stop bath. The four strips were then all fixed for 2 minutes, rinsed for 5 minutes, and dried as required. This same procedure for second development was repeated on the remaining four strips, the replicates.
The entire procedure was repeated for each set of eight strips at each first exposure level.

Reading and Plotting

The density was read with a Macbeth densitometer model TD-203. The density readings were plotted as $D$ versus $\log E$. The results were slightly better than the previous results using the first processing routine. In both cases it appeared that the D-95 was too active and was difficult to control beyond 30 seconds development. Also, maximum gamma was reached with 30 seconds development. DK-50 was selected as a moderately active developer which should give better results.

DK-50 REDEVELOPMENT TIME SERIES

The exact same procedure and exposure values as the "repeat" in D-95 redeveloper was followed with DK-50, with two exceptions. The 0.034 mcs first exposure level had its second exposure changed from 680 to 340 mcs, and no 4-minute redevelopment was done.

I accidently made the DK-50 solution with half the recommended potassium bromide, so I continued to make the developer with half the recommended KBr for the entire experiment. It shall hereafter be denoted as DK-50 ($\frac{1}{2}$KBr).
Other Tests

For comparison purposes, four strips plus replicates were exposed with the KODAK 101 sensitometer through 2.3 ND (1.70 mcs) and 21 step ND wedge then developed in D-95 for 30 seconds, 1, 2, and 4 minutes and fixed - No reversal. (Note: the much lower exposure required for the unbleached emulsion compared to the second exposures required for the bleached emulsions.)

For comparison purposes, strips were exposed and processed the same as described above, except that DK-50 (½KBr) was used as the developer - No reversal - for 20 seconds, 30 seconds, 1, and 2 minutes.

$D_{\text{max}}$ for each emulsion resulting from each first exposure and bleaching, was determined by exposing heavily during the second exposure and doing the redevelopment in DK-50 (½KBr) for 2 minutes at 68°F. Results are as follows:

<table>
<thead>
<tr>
<th>First Exposure</th>
<th>$D_{\text{max}}$ (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.136 m cd sec</td>
<td>0.96</td>
</tr>
<tr>
<td>0.068 m cd sec</td>
<td>1.45</td>
</tr>
<tr>
<td>0.034 m cd sec</td>
<td>2.01</td>
</tr>
<tr>
<td>0.017 m cd sec</td>
<td>2.54</td>
</tr>
<tr>
<td>0.000 (No.1st Exp.)</td>
<td>2.89</td>
</tr>
</tbody>
</table>

$D_{\text{max}}$ for the film without reversing was determined in the testing of objective 1, and was found to be about 3.12.
RESULTS

D-95 Development Time Series

Graphs 10 and 11 show the characteristic curves, density versus absolute Log E, resulting from each first-exposure level with variations in the second development time of 30 seconds, 1, 2, and 4 minutes. The average D Log E curves from each of the two processing routines used with D-95 redeveloper, agreed quite well at 30-second and 1-and2-minutes redevelopment times. But the variability among the samples was relatively high except for the 30-second development time. The agreement among the 30-second runs was excellent. For example, a density of about 1.0 gave the following variability (5 samples each):

<table>
<thead>
<tr>
<th>First-Exposure level</th>
<th>Second Exposure</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 mcs</td>
<td>3.56</td>
<td>0.032</td>
</tr>
<tr>
<td>0.017 mcs</td>
<td>7.10</td>
<td>0.040</td>
</tr>
<tr>
<td>0.034 mcs</td>
<td>28.4</td>
<td>0.036</td>
</tr>
<tr>
<td>0.068 mcs</td>
<td>165</td>
<td>0.098</td>
</tr>
<tr>
<td>0.136 mcs</td>
<td>538</td>
<td>0.042</td>
</tr>
</tbody>
</table>

(The 0.136 mcs level shows the standard deviation for a density level of about 0.75 since $D_{\text{max}}$ was below 1.0.)

Densities along the straight line portions of the 2-and 4-minute curves gave variability such that these curves overlapped in three of the first exposure levels (0.000, 0.136, and 0.068 mcs). Thus the 4-minute redevelopment-time curves can not be used in the development rate and
sensitivity analysis. Note also that at the higher development times, fog becomes excessive. Maximum gamma is reached within 30 seconds and begins to drop after 1 minute. This happens because of the high rise in fog with increasing development time.

Graphs 10 and 11 show the average D Log E curves resulting from the second processing routine with D-95. Graph 12 shows the curves for the reversal film developed in the same developer but not reversed. Density versus development time curves using the D-95 as redeveloper will be discussed later.

**DK-50(½KBr) Redevelopment Time Series**

Graphs 13 and 14 show the mean characteristic curves resulting from each first-exposure level but using DK-50(½KBr) as the redeveloper at redevelopment times of 30 seconds and 1 and 2 minutes. Only two sample strips were processed for each level of first exposure, as explained in the experimental procedure; but none the less, the error seems to be quite low. For example, a density of about 0.80 reached after 1-minute development gives a standard deviation of 0.007 at the 0.000 mcs level and 0.021 at the 0.136 mcs level.

Note that approximately the same gamma is reached at 30 seconds development at all the first-exposure levels. Gamma continues to rise through 1- and 2-minute development; except at the two highest first exposure levels (0.136 and 0.068 mcs) the maximum gamma is reached at less than 2-minutes development time. This is further illustrated by Figure 4.
For comparison to the above results, graph 15 shows D Log E curves for PLUS-X reversal film when developed in the same developer but not reversed. Note that the gamma of 0.40 is reached after 20 seconds development rather than 30 seconds as in the bleached emulsions.

Although I cannot explain it, it is interesting to note that the bleached emulsions show considerable rise in fog with increased development time, whereas the unbleached emulsion shows only a slight rise in fog. This same effect is observed when using D-95 as the redeveloper.

**Gamma vs Development Time with DK-50(½KBr)**

Figure 4 shows what happens to gamma with changes in development time at each first-exposure level and on the original unbleached emulsion. The curves in themselves do not present sufficient evidence to say anything definite about the development rate. But we can try and correlate what they appear to show about the relative rates of development with results from density versus time of development curves.

![Figure 4](image-url)
PLUS-X REVERSAL FILM
First Developer D-94 For 2 min
Second Developer DK-50 (1/2 KBr)
For Times Indicated

FIRST EXPOSURE LEVELS

- 0.000 mcs
- 0.034 mcs
- 0.156 mcs

Density

Log E

Graph. 13
PLJHS-X REVERSAL FILM
First Developer D-94 For 2 min
Second Developer DK-50 (1/2 KBr)
For Times Indicated

FIRST EXPOSURE LEVELS
0.017 mcs ———— 0.068 mcs

Density

\[ \begin{align*}
\log E & \quad \text{Graph. 14}
\end{align*} \]
PLUS-X REVERSAL FILM
Original Emulsion (No Bleaching)
Developed with DK-50 (1/2 KBr) for Times Indicated

Density
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2

Log E
0.192
0.592
2.691

Graph. 15

30 sec $\gamma = 0.47$
20 sec $\gamma = 0.40$
(Both)

1 min
2 min
Note that the original emulsion without reversal reaches higher gammas at the same development times except the maximum $\gamma$ reached is no higher. This seems to indicate that the original emulsion without reversal has the highest rate of development and is further confirmed by the $D/D_{\text{max}}$ versus development time plots, Figure 7.

Curves 2 and 3 overlap and appear to show the same development rate, and curves 4, 5, and 6 seem to show successively decreasing rates of development. However, this may not be true, we need to investigate the change in density with development time to gain better insight into what is actually happening to the development rate.

$D/D_{\text{max}}$ vs Development Time with DK-50(½KBr)

On Figure 5 are curves relating density to time of development at a constant second exposure at each of the various first-exposure levels. However, these density values do not take into account the fact that the emulsion has become thinner, less silver halide per square unit, with increasing first exposure. Each density should be divided by its corresponding $D_{\text{max}}$. Dividing by $D_{\text{max}}$ will place curve 5 above curve 4, but this can be corrected by subtracting out the differences in fog levels. The reason for subtracting fog is that as $D_{\text{max}}$, which diminishes with increasing first exposure, approaches the value of fog, $D/D_{\text{max}}$ approaches the value of 1.
Figure 5

Figure 6 is the result of subtracting out the fog and dividing by $D_{\text{max}}$. On Figure 6, we see that the rate of increase of density with time of development is decreasing as a function of increasing first exposure, but it seems to reach a limit at 0.068 mcs, curve 4. (The statistical calculations done on this curves are illustrated in Appendix III.) Sets of curves were done for constant second exposures other than 77.9 mcs, and the results were the same.

Note that because there is no difference in the rate of development between the 0.068 and 0.136 mcs first exposures, the implication is that the large differences in gamma at 1- and 2-minutes development time (curves 5 and 6 of Figure 4) are primarily a result of the difference in $D_{\text{max}}$ of the two emulsions.
Figure 7 shows that the rate of development for the original PLUS-X emulsion with no bleaching is higher than the rate for the bleached emulsion with no first exposure (0.000 mcs). This corresponds to the normal difference that we would expect from a fully sensitized emulsion and a bleached emulsion with chemical and spectral sensitization destroyed. The difference is perhaps magnified by the difference in the regions of the D Log E curves from which the data were obtained.
Rate of Development with D-95

Gamma versus development time plots were not made for the D-95 developer, because maximum gamma was reached after about 30 seconds of development. The results from density, adjusted for differences in \(D_{\text{max}}\) and fog, plotted against time of development, Figure 8, are not sufficiently accurate because development was too rapid and fog was too high; however, they do not seem to contradict the results obtained with the more moderately active developer, DK-50(\(1/2\)KBr).

Figure 9 compares the original emulsion processed with D-95 but not bleached to the 0.000 mcs first-exposure level. The slope is significantly higher for the original emulsion and so it appears the development rate is higher for the unbleached emulsion. However, an accurate comparison can not be made. No constant second exposure is available where the unbleached emulsion is not too near \(D_{\text{max}}\), and the bleached emulsion not too close to fog.

<table>
<thead>
<tr>
<th>D-95 Redeveloper Curve</th>
<th>First Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000 mcs</td>
</tr>
<tr>
<td>2</td>
<td>0.017</td>
</tr>
<tr>
<td>3</td>
<td>0.034</td>
</tr>
<tr>
<td>4</td>
<td>0.068</td>
</tr>
<tr>
<td>5</td>
<td>0.136</td>
</tr>
</tbody>
</table>

![Figure 8](image1)

![Figure 9](image2)
DISCUSSION OF RESULTS

Development Rate vs First Exposure

The question now is: "why did the changes in development rate occur as they did?"

The reason we suspected there would be a change in development rate is that we expected some conversion of the silver bromide into silver iodide grains which are not as easily reduced by the developing agent. This conversion can take place during the first development. First development is done in D-94 developer which contains no iodide, however iodide is present in the emulsion as silver iodobromide grains. As the development proceeds, silver iodide would be reduced to silver and the released iodide can then displace bromide. Increasing the first exposure would increase the amount of this conversion taking place. And after bleaching, the proportion of silver iodide to silver bromide in the emulsion would be greater at the higher first exposure levels because the higher the first exposure, the fewer the number of silver halide grains remaining after bleaching. The results seem to confirm this theory; refer to Figure 10. Figure 10 shows how the rate of development (relative) compares for each emulsion when using DK-50(½KBr). The rate of development is computed as the relative slope of the D/D_max curves (Figure 6) between 30 and 60 seconds time of development. Any differences beyond 0.068 mcs first exposure are lost in the error.
Figure 10
RESULTS

Sensitivity as a Function of First Exposure (D-95 Developer)

Because adjustment for differences in the development rate could not be made by adjusting the development time, the 30-second development-time curves (refer to graphs 10 and 11) were used to determine the speed of the resultant emulsion from each first-exposure level. Because the gamma of these curves was not the same, the speed definition was changed to $1/E$ where the gradient is $0.3\gamma$. Figure 11 shows the resulting plot of sensitivity, defined as speed, versus first exposure level. As was expected, there is a significant drop in speed with increasing first exposure.

The speed for the original emulsion without reversal was calculated and was found to be about 10 times the speed of the most sensitive (0.000 first exposure) bleached emulsion. The original emulsion speed calculated to 14.3, with standard error of 0.4, and the bleached emulsion speed calculated to 1.35, with standard error of 0.09.
Sensitivity as a Function of First Exposure (DK-50(\%KBr))

Adjustment for the differences in development rate can be done by adjusting the developing time when using DK-50(\%KBr), such that approximately the same gamma is achieved at all the first exposure levels. But because the speed definition was redefined for determining sensitivity with D-95, it was decided to use the same speed definition for this developer too. The speed definition, \(1/E\) at gradient of 0.3\(\gamma\), should compensate for different gammas and the development time can be held constant instead. One minute development was selected because it gave reasonably high gammas for best precision; refer to graphs 13, 14 and 15.

The resulting plot, Figure 12, of sensitivity versus first exposure shows the decrease in sensitivity as the first exposure is increased. This was seen to occur also with the D-95 developer. The drop in speed is significant at all levels except between the last two, 0.068 and 0.136 mcs, where differences are lost in the error.

The original film without bleaching was found to be about 19 times faster than the most sensitive bleached emulsion. The original emulsion speed came to 28.0 and the 0.000 mcs first-exposure speed came to 1.48.

I checked the validity of the speed definition used here by using the originally planned speed definition of \(1/E\) at 0.3 density above base density on a set of curves with equal gammas. I found that if I multiply the speeds shown in Figure 12 by a constant factor, I will get the same speeds as using the originally planned speed definition.
DISCUSSION OF RESULTS

Sensitivity vs First Exposure

As was mentioned in the introduction we expected loss in sensitivity (defined as speed) with increased first exposure. The results confirm this. First, we observe the greatest loss in speed between the original emulsion and bleached emulsion with no first exposure. This large loss in speed is due primarily to bleaching out chemical sensitization. The next first exposure level dropped in sensitivity by about half and the next level by half again. This we noted would be similar to an ordinary negative if we find its speed along its characteristic curve; speed defined as 1/E, where E is the exposure required for equal increases in density. Refer to Figures 2 and 3.

An accurate comparison between the drop in speed due to exposure effects along the D Log E curve and this drop in speed from first exposure and bleaching can be done if you do the following:

1. Find the density reached with developer "X" at 0.017, 0.034, 0.068, and 0.136 mcs exposures, or some other predetermined first exposures. (Just develop then fix.)

2. Follow the same procedure done in this thesis except use developer "X" as the first developer and the second developer.

3. Now select curves with the same gamma at each first exposure level and determine the 1/E speed at a constant density above fog and plot the speed against first exposure.
4. Select a curve of the original unbleached emulsion with the same gamma and locate the densities found in step 1 above. Measure the speed at these densities using the speed definition described with Figure 2 and 3. Plot the resulting speeds on the speed versus first exposure plot from step 3.

5. Compare the curve shapes.

Unfortunately, I did not follow such a procedure, therefore I cannot make such a comparison of curve shapes.
CONCLUSIONS

The development rate does drop significantly as a function of increasing amount of first exposure after the reversal emulsion undergoes development and bleaching, reaching a practical minimum after an exposure corresponding to 0.068 mcs. It is believed that this drop in development rate is primarily caused by conversion of silver bromide to silver iodide, which reduces more slowly.

We can conclude that the sensitivity defined as speed decreases significantly as a function of increasing first exposure. Since the drop in speed is somewhat exponential, at the highest first exposures the differences can get lost in the error. This decrease in speed is attributed to a combination of several things.

1. Bleached out chemical and spectral sensitization.
2. Most sensitive grains exposed and bleached out first.
3. Drop in maximum density (probably compensated for by the 0.3 gamma gradient speed definition).
4. Some conversion of silver bromide to silver iodide (evidenced by the drop in rate of development).
5. Desensitization by oxidized developer (no evidence here but a possibility).

An unexplained large rise in fog with increased development was found at several first exposure levels. Such a rise in fog does not occur on the original unbleached film when developed for the same amounts of time.
APPENDIX I
SOLUTION FORMULAS

First Developer^4 D-94

Water about 70F 750 ml
Elon developing agent 0.6 gm
Sodium sulfite dissicated 50.0 gm
Hydroquinone 20.0 gm
Potassium Bromide 8.0 gm
Sodium Thiocyanate 6.0 gm
Sodium Hydroxide 20.0 gm
Water to make 1.0 liter

Dissolve in the order shown

Second Developer^4 D-95

Water about 70F 750 ml
Elon developing agent 1.0 gm
Sodium Sulfite dissicated 50.0 gm
Hydroquinone 20.0 gm
Potassium Bromide 5.0 gm
Potassium Iodide 0.25 gm
Sodium Hydroxide 15.0 gm
Water to make 1.0 liter

Dissolve in the order shown

Developer^12 DK-50

Water about 125F 500 ml
Elon developing agent 2.5 gm
Sodium Sulfite dissicated 30.0 gm
Hydroquinone 2.5 gm
KODAK Balanced Alkali 10.0 gm
Potassium Bromide 0.5 gm
Water to make 1.0 liter

Dissolve in the order shown
Modification to Above Formulas

Modified D-94 solution was the same as D-94 above except only 20.0 grams of Sodium Sulfite and no Sodium Thiocyanate were used. Modified DK-50 solution called DK-50(\(\frac{1}{2}\)KBr) was the same as DK-50 above except only half the required Potassium Bromide was used.

Bleaching Bath\(^4\) R-9

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.0 liter</td>
</tr>
<tr>
<td>Potassium Dichromate</td>
<td>9.5 gm</td>
</tr>
<tr>
<td>(This was not available so Sodium Dichromate was used.)</td>
<td></td>
</tr>
<tr>
<td>Sulfuric Acid concentrated</td>
<td>12.0 ml</td>
</tr>
</tbody>
</table>

Dissolve in the order shown

Clearing Bath\(^4\) CB-2

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>750.0 ml</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>25.0 gm*</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 liter</td>
</tr>
</tbody>
</table>

Fixing Bath

Fixer was KODAK F-5 prepared from packaged chemicals.

* 250 g is recommended for use in rapid processing, but this concentration was not needed.
APPENDIX II

Effect of Adding NaSCN to DK-50

Refer to the following graph. Curve 1 is the characteristic curve that resulted from developing KODAK TRI-X reversal film with DK-50 formulated as indicated in Appendix I. Curve 2 is the result of developing the same film with DK-50 which has had 6 grams of sodium thiocyanate added to the formula. The DK-50 with the solvent, NaSCN, now is definitely a solvent or physical developer. Other than the NaSCN, there were no other differences in formula or processing procedure. The development was done for 5 minutes at a temperature of 68F, stop bathed for 30 seconds, then fixed for 3 minutes.

Curve 2 is significantly lower than curve 1, for densities higher than 0.95. Below 0.95 curve 2 is higher than curve 1 probably as a result of the increased activity of DK-50 caused by addition of NaSCN. Because the NaSCN has apparently not retarded development, the lower density of curve 2 is probably the result of the lower covering power which is characteristic of silver deposited by solution-physical development.13, 14 Thus, curve 1 is probably higher because of the higher covering power of a silver image developed with mostly surface development.
APPENDIX III
SAMPLE STATISTICAL CALCULATIONS

"F" Test on Variances

I assumed that the variances achieved from sensitometric strips untreated and treated with halogen acceptor were the same. But the "F" test will tell us if my assumption is correct (within the 90-percent confidence limits used throughout this thesis).

\[ F = \frac{S_1^2}{S_2^2} \]

where \( S_1^2 \) and \( S_2^2 \) are the two sample variances of process 1 and 2 respectively, and the larger of the two variances is the numerator.

Example from Table 1: \( S_1 = 0.035 \), \( S_2 = 0.007 \), \( n_1 = n_2 = 2 \) samples.

\[ F = \frac{(0.035)^2}{(0.007)^2} = 25 \]

Critical F from F table \( ^9 \) = 161.45. Twenty-five does not exceed the critical F, therefore these variances are equal.

Pooled Variances

Because the variances of the two samples are the same, we can pool them using the following equation \( ^9 \): \( S_p^2 = \frac{v_1 S_1^2 + v_2 S_2^2}{v_1 + v_2} \)

where \( v_1 \) and \( v_2 \) are the degrees of freedom of sample test 1 and 2. Using the above example, \( S_p = 0.025 \).

Test for Difference Between Two Means

The Student "t" test can provide us with an answer to the hypothesis that the mean of sample test 1 is the same, different, greater than, or less than the mean of sample test 2, if the samples have a normal
distribution and equal variances. Equal variances was determined by the F test and it is safe to assume that density on film has a normal distribution around any mean density.

$$t = \frac{\bar{X}_1 - \bar{X}_2}{S_p \sqrt{1/n_1 + 1/n_2}}$$

where: $X_1$ and $X_2$ are the means of sample test 1 and 2. Using the average $D_{max}$ values from Table 1 as examples:

$$t = \frac{3.015 - 2.955}{0.025 \sqrt{1/2 + 1/2}} = 2.4.$$ 

The critical $t$ for 90-percent confidence from the student $t$ Table is 1.886. Because the critical $t$ was exceeded, we can conclude that 3.015 is significantly larger than 2.955.

The same tests were applied to look for increases in the density scale, slope near $D_{max}$, speed, and fog.

Analysis of Variance

To determine whether there was a significant effect on the rate of development resulting from the first exposure, the analysis of variance technique was used. An example using a constant second exposure of 77.9 mcs is illustrated below:

The response variable is $\Delta [(D - \text{Fog})/(D_{max} - \text{Fog})]$ between 30 and 60 seconds development.
<table>
<thead>
<tr>
<th>First Exposure level</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>( T_i )</th>
<th>Average X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 mcs</td>
<td>0.235</td>
<td>0.248</td>
<td>0.483</td>
<td>0.2415</td>
</tr>
<tr>
<td>0.017</td>
<td>0.226</td>
<td>0.188</td>
<td>0.414</td>
<td>0.2070</td>
</tr>
<tr>
<td>0.034</td>
<td>0.154</td>
<td>0.142</td>
<td>0.296</td>
<td>0.1480</td>
</tr>
<tr>
<td>0.068</td>
<td>0.050</td>
<td>0.052</td>
<td>0.102</td>
<td>0.0510</td>
</tr>
<tr>
<td>0.156</td>
<td>0.0278</td>
<td>0.1006</td>
<td>0.1284</td>
<td>0.0642</td>
</tr>
</tbody>
</table>

\[ T.. = 1.4234 \]

Sum of Squares Total = SST = \( \Sigma X_{ij}^2 - (T..)^2/n \) = 0.0605392

Sum of Squares due to the response = SSR = \( \Sigma (T_i)^2/j - (T..)^2/n \) = 0.0570110

Sum of Squares as a result of error = SST - SSR

ANOVA Table

<table>
<thead>
<tr>
<th>Source</th>
<th>Sums of Squares</th>
<th>( \nu )</th>
<th>Mean Square</th>
<th>F</th>
<th>Critical F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure levels</td>
<td>0.0570110</td>
<td>4</td>
<td>0.0142528</td>
<td>20.198</td>
<td>3.5202</td>
</tr>
<tr>
<td>Error</td>
<td>0.0035282</td>
<td>5</td>
<td>0.0007056</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.0605392</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ F = \text{mean square for level/mean square for error} \]

Critical F is from F table with \( \alpha \) risk of 0.10. The critical F was exceeded, thus the response varies with first exposure level.

To see if there was a significant decrease between the levels the least significant difference test\(^9\) was applied.

\[ \text{LSD} = t_{\nu e, \alpha} \sqrt{2(S_e^2)/n} \]

\[ \text{LSD} = (1.476) \sqrt{2(0.0007056)/10} \cdot \]

\[ \text{LSD} = 0.01753 \]
The average responses decreasing by more than this LSD are significant decreases. Thus the response did decrease significantly with increasing first exposure except beyond 0.068 mcs.
APPENDIX IV

Processing Tray and Brush

A processing tray and brush were constructed to give uniform agitation across the entire tray. An 8-by 10- by 1/8-inch piece of flat glass was cemented to the bottom of an 8-by 10-by 2-inch plastic tray (metal tray is preferrable) using silicon rubber. Two 1/8-by 1/4-inch plastic (plexi-glass) ridges were glued onto the long edges of the glass to act as guides for the brush see illustration. The brush was constructed of plexi-glass as illustrated.
The separation between the plexi-glass inserts and the top of the glass was uniformly 1/8 inch. The film strips were taped lengthwise on the glass for processing. The separation from the film emulsion to the brush (plexi-glass inserts) was sufficiently uniform down the center of the film. The sides of the 16mm film apparently curled up slightly during processing, so that the sides did not develop uniformly enough. But reading density down the center of the film gave very small variability as long as the film was placed approximately lengthwise. The film strips were always read down the center of the film.

Care was taken also to ensure approximately the same rate of movement of the brush up and down the tray. This was done by counting about 45 up and 45 down strokes per minute. Referring to tables 1, 2, 3, and 4, we can see that the highest standard deviation reached at the maximum density of the films was 0.035.
REFERENCES


