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Studies on the Lith Development of a Silver Iodobromide Emulsion

Larry Zurbrick

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STUDIES ON THE LITH DEVELOPMENT OF A
SILVER IODOBROMIDE EMULSION

by

Larry S. Zurbrick

A thesis submitted in partial fulfillment of
the requirements for the degree of
Bachelor of Science in the School of
Photographic Arts and Sciences in the
College of Graphic Arts and Photography
of the Rochester Institute of Technology

October, 1979

Signature of the Author ..............................................
Larry S. Zurbrick

Certified by ........................................................
Burt H. Carroll
Thesis Adviser

Accepted by .........................................................
Ronald Francis
Department Chairman
STUDIES ON THE LITH DEVELOPMENT OF A SILVER IODOBROMIDE EMULSION

by

Larry S. Zurbrick

Submitted to the Photographic Science and Instrumentation Division in partial fulfillment of the requirements for the Bachelor of Science degree at the Rochester Institute of Technology

ABSTRACT

The lithographic development of a silver iodobromide emulsion with thiocyanate substituted for bromide in a lith developer formulation showed differences in behavior with regard to induction time and maximum rate of development at equal levels of normality.

An experiment was designed with development time, halide concentration, and exposure level as the variables with maximum rate of development, time to reach 0.20 optical density (induction time), and slope at 0.40 optical density as the response parameters.

The maximum rate of development with the developer containing bromide was found to be significantly dependent upon exposure level.
and not significantly dependent upon bromide concentration in the range of 0.020 N to 0.058 N. Significant different exists between 0.000 N and all other levels of bromide.

The maximum rate of development with developer containing thiocyanate was found not to be significantly dependent upon thiocyanate concentration nor exposure level.

Induction time with the developer containing bromide is significantly dependent upon exposure level and not statistically dependent upon bromide concentration.

Induction time with the developer containing thiocyanate is very significantly dependent upon thiocyanate concentration and exposure level.

Slope at 0.40 optical density with the developer containing bromide is independent of bromide concentration from 0.020 N to 0.058 N and development time from 1.0 to 2.5 minutes.

Slope at 0.40 density with the developer containing thiocyanate is independent of development time. Thiocyanate concentration is highly significant with the 0.000 N and 0.063 N levels as one population and the 0.021 N and 0.042 N levels as another population.
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INTRODUCTION

The use of a lith developer with a silver iodobromide emulsion fails to show the characteristics of lith development (i.e. sensitometric characteristics of a short toe and high contrast). This has been attributed by some to the strong restraining action of the iodide and by others to the latent image bleaching by quinone formed early in development.

Investigations into lith development have not yet produced a unified theory of the exact mechanism responsible for the sensitometric characteristics produced by lith development. T. Suga\textsuperscript{1-7} has published some basic investigations into this area and has reported\textsuperscript{7} that lith development was obtained with a silver iodobromide emulsion by the substitution of thiocyanate for bromide in a lith developer formulation.

The aim of this research was to reproduce Suga's results of obtaining lith development with a silver iodobromide emulsion and to further investigate to gain possible insight into a mechanism for this behavior.

The sensitometric responses of interest in this research were gamma, "toe gamma", induction time, and rate of development. The experimental parameters investigated were halide type, halide concentration, and development time.
LITERATURE RECONNAISSANCE AND IMPLICATIONS

Lith development is characterized by the sensitometric properties of high gamma, short toe, low fog, high maximum density, and a "variable" speed point independent of gamma for development times in the region of maximum gamma. Prolonged development tends to decrease gamma as latent image sites in the toe region of the characteristic curve become more "developable". The materials used to obtain the lith effect are typically an emulsion of the silver chloride or silver bromochloride type and a developer characterized by a low concentration of free sulfite, hydroquinone as the developing agent, bromide as the restrainer by itself or in combination with organic antifoggants, and a pH in the range of 10 to 12.

Infectious development by the hydroquinone oxidation products alone is not sufficient to explain the lith effect. In typical lith developer formulations, there is insufficient semi-quinone formation below a density level of approximately 0.2 to sustain infectious development due to the reaction with sulfite. Recent investigations attribute much importance to an induction time mechanism which is highly exposure level dependent. Several authors have proposed hypothesis as to the reason for the induction time mechanism based on charge barrier type effects relating to the size, number, and
location of the small latent image sites. Other investigators\textsuperscript{1-7} have attributed the short toe characteristics to the bleaching of small latent image sites by quinone.

The charge barrier effects address adsorption of hydroquinone, semi-quinone, and quinone to the surfaces of silver metal and various silver halides. Several workers have studied the change in redox potential on various electrodes (ie. silver, silver bromide) by various substances (ie. bromide, polyethalene oxides, hydroquinone, quinone) under different conditions of pH, temperature, and combinations of various surface active compounds. The correlation of results between large, bulk property electrodes and small silver halide grains and their latent image sites may not be valid in some cases. The results therefore may not be conclusive.

In a series of articles by T. Suga\textsuperscript{1,2,4}, he proposes that the bleaching of small surface latent image sites is in part responsible for the short toe and low fog characteristics of lith development. In this series of articles, he shows that a pre-bath treatment in a quinone, bromide, and sulfite solution at various pH's bleaches latent images. The greatest bleaching effect being at low pH. Suga states that silver chlorobromide emulsions are the most suitable for obtaining a lith effect since the toe region of the characteristic curve undergo the most oxidation. Comparing the quinone plus bromide prebath curve for the silver chlorobromide emulsion\textsuperscript{2}, we see that the least amount of latent image oxidation takes place below a density of approximately 1.0. This is in contrast with earlier work\textsuperscript{1}
where the quinone-bromide prebath the greatest effect in the toe region when compared to the bromide only and quinone only prebaths. Since Suga used a commercial lith film (Konilith) in this previous work, it may have been possible for emulsion addenda to have caused interaction. It should be noted that the least amount of "toe" oxidation with the quinone-bromide prebath takes place with the silver chloride emulsion and that the amount of bleaching appears to be proportionally related to density. In the case of silver bromide and iodobromide emulsions, large speed losses with a substantial loss in gamma occur with the quinone only and quinone-bromide prebaths. The effect of the bromide only prebath is not known since no control curves are shown.

Suga also investigated the effects of substitutions for potassium bromide in his lith developer formulation. The substitutions include no halide, ammonium bromide, cadmium bromide, sodium chloride, potassium iodide, tri-sodium phosphate, potassium thiocyanate, 5-methyl-7-hydroxy-2,3,4-triazaindalizine, and 1-phenyl-5-mercaptotetrazole. All substitutions, with the exception of no halide, were made at the 0.0168 N level, which is equivalent to the normality of potassium bromide at 2 gm/1. The films used for the experiments were a commercially available lith emulsion (Konilith) and another emulsion identified only as "Lith A". Suga claimed only to have obtained a "good" lith effect with KBr, NH$_4$Br, and CdBr$_2$ and a "small" lith effect with KSCN (KSCN concentration lowered to 0.0126 N). Due to the very different solubility products of the silver ion and substituted
halides, the pAg would be dramatically different; hence, the results are in question. A more conclusive test perhaps would maintain a constant pAg. It should be noted that bromide and thiocyanate have approximately (within an order of magnitude) the same solubility product with silver ion.

Suga draws the conclusion that the quinone-bromide bleaching mechanism is responsible for bleaching low exposure regions during the induction period. It should be noted that Suga\(^2\) carried out his prebath bleaching experiment at pH 5. In a previous paper\(^1\), he showed that very little, if any, bleaching occurred above pH 9. Bleaching in a lith developer with a typical pH greater than 10 seems improbable. However, James\(^8,9\) showed that some latent image sites could be bleached with a sulfite free quinone solution at pH values of 11.4 to 9.2.

The greatest bleaching effect according to Suga would take place in high exposure regions where the greatest amount of H\(^+\) would be produced, hence lowering the local pH closer to the required value. Taking this into account does not explain bleaching in the low exposure regions on a macro-scale such as a step wedge, but could account for the contrast enhancement of small sized images such as the dots produced the graphic arts halftone screens. The contrast enhancement may also be explained by the release of bromide by the developing grains affecting grains which haven't yet started to develop (ie. increased induction time of low exposure grains).

Experiments have shown that low exposure latent image sites are not irreversibly bleached and also from the practical experience of prolonged development causing contrast to decrease due to the toe
region of the characteristic curve developing. This tends to increase the validity of an induction time mechanism hypothesis. However, an alternate hypothesis is that internal latent image sites become developable.

Based on predictions of the silver electrode potential verses various halides and previous work on quinone bleaching with various halides, Suga\textsuperscript{1} predicted that lith development should be possible with a silver bromide or iodobromide emulsion with thiocyanate substituted for bromide in the lith developer due to the smaller electrochemical potential between the silver bromide and the thiocyanate ions. Suga\textsuperscript{7} stated that he obtained a lith\textsuperscript{6} effect (sharp gradation in the toe region of the sensitometric curve and perceptable image spreading) with a silver iodobromide emulsion by the substitution of potassium thiocyanate for potassium bromide in a lith developer formulation.

It was the purpose of this thesis to duplicate Suga's work with a silver iodobromide emulsion and the thiocyanate substituted lith developer.
EXPERIMENTAL METHODOLOGY

Preliminary Experiments

Due to time restrictions, a commercially made and coated emulsion was chosen over the preparation of an emulsion. Factors which affected the choice of the emulsion were type of dye sensitization, addenda, mole percent ratio of iodide to bromide, sensitization, and grain size distribution. The film found best suited to these restrictions was Eastman Kodak Film Type 5302, Fine Grain Release Positive. This emulsion has no dye sensitization, no polyethylene oxides in the addenda, one percent mole ratio of iodide to bromide, reduction sensitization with formaldehyde, and a moderately narrow grain size distribution.

Initial work was done with Suga's\(^1\) lith developer formulation in an attempt to repeat Suga's results. The initial developer formulation used was:

- Sodium formaldehyde bisulfite \(60 \text{ gm}\)
- Hydroquinone \(18 \text{ gm}\)
- Sodium carbonate \(42 \text{ gm}\)
- Potassium thiocyanate \(1.22 \text{ gm}\)
- Water to \(1.000 \text{ liter}\)

This initial experiment used modified RIT tray rock agitation. The modified RIT tray rock procedure used six cycles per minute for the first minute of development and one cycle every fifteen
seconds for any remaining time in the time development series. The resulting sensitometric strips showed poor density uniformity and a high fog level. The sensitometric strips showed little, if any, "lith effect". The free sulfite concentration was not known and did not lend itself to easy measurement. The results of this experiment were disregarded in relation to sensitometric parameters and a different experimental procedure formulated.

Experimental Procedure

The developer formulation was modified by replacing the 60 gm/l of sodium formaldehyde bisulfite with 2 gm/l of sodium sulfite. Special precautions had to be observed in the mixing of the developer solution. The mixing procedure consisted of the following steps:

1. Degas distilled water of O2 by bubbling N2 through a fritted glass aerator while stirring on a Corning magnetic stirrer/hotplate.
2. Continue to burst N2 through the solution as developer constituents were added.
3. Purge volumetric flask with N2 before transferring developer solution.
4. Bring volumetric flask to volume with distilled water.
5. Purge neck of volumetric flask with N2 before stoppering and inverting to mix.

The pH of the developing solution was measured using a Corning Model 12 pH meter. The pH meter was standardized before use with pH 10.00 buffer solution. pH values of 10.25 ± 0.10 @ 20°C were measured on all developer solutions. No correlation between level of
halide and pH level was noted.

The sodium thiocyanate was precisely weighed out and mixed to a given volume (250.0 ml) with distilled water in a volumetric flask. The required volume of solution needed for the normality required was computed and pipeted to the developer solution as an aliquiot during the mixing procedure. The aliquiot was added as the final constituent immediately before the developer solution was transferred to the volumetric flask.

A control developer containing bromide at equal normality to the thiocyanate in the experimental developer was used to compare the relative sensitometric parameters.

The original experimental design was to be two 3X3 factorial experiments, twice replicated. One experiment was to be run with thiocyanate and the other with bromide. The experimental design was changed to a 4X4 design when preliminary data indicated that too narrow a range of halide concentrations and development times had been chosen.

A problem with high fog level in the first few runs of the new experimental procedure was experienced. The potassium thiocyanate (Baker Analysed) was changed to sodium thiocyanate (Eastman Kodak) and the fog level greatly decreased. This was thought due to a stability problem with the thiocyanate or a possible contamination problem. Early experiments were repeated.
The equipment used in these experiments was:

Sensitometer- EG&G Model VI xenon flash sensitometer,
  exposure time = $10^{-2}$ second, color temperature
  $6000^\circ$K, exposure = 1000 MCS, intensity modula-
  tion by a 21 step, 0.15 density per step, step
  wedge

Development agitation- Nitrogen burst apparatus with water
  jacket, 0.6 second burst duration at 10
  second intervals, nitrogen pressure = 5 lb. in$^{-2}$

Densitometry- MacBeth Model TD-504 transmission densito-
  meter (2 mm aperature) interfaced with a
  Hewlett-Packard Model 9830A Desk Top Calcu-
  lator and Model 9862A Plotter (courtesy of
  E.I. DuPont de Nemours & Co., Rochester
  Photo Products)

The development of the exposed sensitometric strips took place in
the nitrogen burst apparatus. At the end of the development time, the
rack holding the sensi strips was transferred to a stop bath consisting
of 28% acetic acid diluted 1:20 by volume with water for 15 seconds.
The sensi strips were then transferred to a tank of Kodak F-6 Fixer
for 1 minute. Strips were then washed in running water for 10 minutes,
squeegeed, and air dried.

Plotting of the D-log H curves via a Hewlett Packard Model 9830A
calculator and model 9862A Plotter. A parabolic curve fitting routine$^{13}$
was used to smooth the curves. This routine parabolically interpolated
two points between the actual data points. The routine was found to work
satisfactorily with most data. However, some plots show "kinks" in the
toe region of the characteristic curves. Better routines\textsuperscript{14-20} were sought to mathematically model the D-log H curves. Due to the time restrictions, slope at 0.40 optical density was chosen to represent the response variable describing toe "behavior".
DISCUSSION

The three response parameters investigated were the slope at 0.40 optical density, maximum rate of development, and induction time. Slope at 0.40 optical density was chosen as the response parameter that would give an indication of the toe contrast characteristics. The choice of 0.40 density was empirically based on the inspection of resulting characteristic curves since this density appeared to be close to the point where the largest change in slope occurred. Maximum rate of development was determined by plotting kinetic densities after Turbide and Williams\textsuperscript{11} and then graphically determining the steepest slope on the curves. Induction time was defined as the time required to reach 0.20 optical density.

Analysis of Variance (ANOVA) tests were run on the reduced data. In all cases, except where noted, the assumed alpha risk was equal to 0.05. A summary of the results of the statistical tests follows.

Summary of Results

Slope at 0.40 density

With bromide, development time is not significant and does not become significant even when the alpha risk is set to 0.10. Concentration of bromide is significant. The analysis shows that the 0.000 N is an individual population and the higher levels of bromide (0.020 N to 0.058 N) behave as one population. With thiocyanate, development time is not significant and does
not become significant even when the alpha risk is set at 0.10. Concentration of thiocyanate is highly significant and remains significant when the alpha risk is set equal to 0.01. The analysis shows that the 0.000 N and 0.063 N levels behave as one population and the 0.021 N and 0.042 N levels behave as a different population. This is taken to signify that as the thiocyanate concentration increases, slope at 0.40 density increases, reaches a maximum, then decreases. The interaction term is also significant in the thiocyanate ANOVA. This is understood to mean that a change in development time changes the direction in which a change is induced by concentration.

Maximum Rate of Development
With bromide, the concentration does show significance only at an alpha risk of 0.10. The 0.020 N level appears as an individual population and the other levels appear as one separate population. Exposure is significant and the three levels of exposure tested appear as three separate populations. With thiocyanate, neither the concentration nor the exposure level have significant affects upon the maximum development rate. Increasing the alpha risk to 0.10 does not make either factor significant.

Induction Time
With bromide, concentration does not affect induction time. Concentration remains insignificant even when the alpha risk is increased to 0.10. However, a trend in the data can be observed showing an increase in induction time with an increase
in bromide concentration. Exposure affects the induction time, but the test shows just barely so. Only two levels of exposure could be tested since the high exposure (Step 20) level data was out of range of this test. An increase in exposure caused a decrease in induction time.

With thiocyanate, both concentration and exposure are highly significant and remain significant even when the alpha risk is lowered to 0.01. An increase in thiocyanate concentration increased induction time. An increase in exposure decreased induction time.

James\textsuperscript{10} showed that a low sulfite (less than 5 gm/l), pH 12.7, hydroquinone developer produced a sensitometric curve with high contrast and a short toe in the partial development of a high contrast motion picture positive material. The partial development curves show approximately twice the gamma as the curve obtained at gamma-infinity. James attributes this behavior to the autoacceleration of development by hydroquinone oxidation products. "Normal" sensitometric curves were obtained when the sulfite level was increased to 5 gm/l. The halide level and type in the experimental developer used by James was not mentioned.

The shape of the sensitometric curves and conditions for which they were obtained in this set of experiments are similar to James' experiment\textsuperscript{10}. The autoacceleration of development by hydroquinone oxidation products could explain the abnormal shapes of the curves obtained in this set of experiments. The grain size distribution may also be in part responsible for the shape of the sensitometric
curves.

A problem encountered with the higher levels of thiocyanate (greater than 0.042 N) was that silver sludging tended to occur. Sludging would first manifest itself by causing the developer solution to first discolor gray, and then become turbid. The silver would deposit on the sensitometric strips being developed; however, it was easily removed with a wet paper towel during the wash step following fixation. The problem was much more severe at the high sulfite levels (30 gm/l, see Auxiliary Experimentation). It is felt that a two part mechanism of silver ion exchange between the thiocyanate and sulfite is responsible for this effect.

**Hypothesis**

The mechanism that is hypothesized as being responsible for the behavior of the thiocyanate containing developer results is that the thiocyanate is a stronger development restrainer than bromide, but it is capable of accelerating development by "additional" development through solution-physical development once development has been initiated. The basis of this conclusion is based upon the observations that induction time is longer than with the bromide containing developer when comparing equal normalities, the maximum density for a given exposure is greater with thiocyanate than bromide, the maximum rate of development is greater with thiocyanate than bromide at low exposure levels (Step 7), and that thiocyanate is a stronger silver halide solvent than bromide. An alternate hypothesis to the development acceleration by a solution-physical mechanism may be that the
thiocyanate makes the subsurface latent image sites available for development by removing the silver iodobromide that covers them.

Suga's hypothesis of a bleaching mechanism by quinone has not been disproven by this set of experiments and may in fact account for the results found in this research. The bleaching by quinone is felt to be improbable since it would not account for the macro-scale sensitometric results nor the differences in development rate between thiocyanate and bromide as found in this thesis.
CONCLUSIONS

The maximum rate of development with bromide is not statistically
dependent upon bromide concentration, but dependent upon exposure
level. The no halide run was significantly different from all of the
runs made with any level of bromide.

The maximum rate of development with thiocyanate was found not
to be dependent upon exposure level nor thiocyanate concentration.

The induction time with bromide is dependent upon exposure level,
decreasing with increasing exposure. Bromide concentration does not
statistically affect induction time. This may be in part due to
experimental error.

Induction time with thiocyanate is very significantly dependent
upon thiocyanate concentration and exposure. An increase in concentration
increases induction time. An increase in exposure decreases induction
time.

Slope at 0.40 density with bromide is independent of both
bromide concentration and development time.

Slope at 0.40 density with thiocyanate is independent of
development time. Thiocyanate concentration is highly significant
with the no halide and 0.063 N levels behaving as one population and
the 0.021 N and 0.042 N levels behaving as another population. The
interaction term is significant indicating that a change in development
time changes the direction of the change induced by thiocyanate
concentration.
An experiment was run at one of the halide levels (0.040 N) by increasing the Na₂SO₃ level to 30 gm/l to determine the extent of the acceleration of development by the hydroquinone oxidation by-products. The 0.039 N Br⁻ + 30 gm/l Na₂SO₃ curves and the 0.039 N Br⁻ curves show strong similarity below a density of 0.2 to 0.3. The increased level of sulfite appeared to have no great effect on induction time. It appears in the case of low sulfite, that the autoacceleration of development by the oxidation products would be sufficient to explain the abnormal curve shapes. However, the autoacceleration effect is not sufficient to explain the shortened toes of the curves. This is evidenced by comparison to the curves at the 0.000 N level. Induction time with the high level of sulfite is approximately equal to the low sulfite level case. The maximum rate of development is also approximately equal between high and low sulfite levels.

In the case of thiocyanate with the high sulfite level, the induction time appears to be shorter at the higher sulfite level. The high sulfite level appears to take longer to reach maximum development rate than the low sulfite levels, but the maximum development rates appear to be approximately equal.

A brief experiment was carried out using a polyethylene oxide addition to the 0.042 N thiocyanate containing developer. 1.5 gm/l of Carbowax 1540 was added to the developer and a time development
series performed. The characteristic curves show that a speed loss resulted and that the toe has become "softer". The density verses development time graph (Appendix C) shows an increase in induction time. The increase in induction time appears to be greater a lower exposure levels than higher exposure levels. This agrees with the published literature concerning the effects of PEO's.

Another brief, unreplicated experiment was performed using a positive print emulsion prepared and coated by the junior class of 1976. The emulsion was prepared by the double-jet method and ripened with thiosulfate. The ratio of iodide to bromide is not known. The emulsion was processed in the 0.020 N thiocyanate and bromide containing developers. The thiocyanate shows an approximately 9 times higher development rate at the two levels of exposure investigated (Steps 13 and 17). The thiocyanate curves appear to have a speed increase when compared to the bromide curves. The gammas are approximately equal. The mechanism for this behavior may be related to the development acceleration effect where the thiocyanate promotes additional solution-physical development. The alternate hypothesis is that the thiocyanate makes the subsurface latent image sites available for development.
RECOMMENDATIONS

Further research into the lith development of the silver iodobromide emulsion could encompass the following areas:

1- Partial development of the emulsion in the lith developer formulation, followed by development in a low solvent action M-Q or P-Q developer to investigate whether surface latent image sites are bleached. Some work has been reported in this area, but for specific cases.

2- A more comprehensive experiment investigating the effects of the level of concentration of other developer components such as sulfite, hydroquinone, and pH.

3- Use of an emulsion with a higher level of iodide. Suga's original works used unripened and ripened (with sulfur via thiosulfate) silver iodobromide emulsions with one mole percent iodide. Due to the uncertainty of the addenda and dye sensitization, the emulsion would have to be prepared and coated by or under the supervision of the experimenter.

4- Use of a silver halide solvent with bromide in order to attempt to produce solution-physical development. The choice of silver halide solvent should take into account that it should not be a development restrainer like thiocyanate and should ideally have a rate of solution equal to thiocyanate.

5- An experiment to investigate the micro-image characteristics
to observe whether or not the contrast of small images is enhanced.
APPENDIX A

Analysis of Variance Summaries
APPENDIX A
ANOVA of Maximum Rate of Development

Bromide

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ANOVA Table

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APPENDIX A
ANOVA of Slope at 0.40 Density

Bromide

<table>
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<tr>
<th>dev. time</th>
<th>concentration 0</th>
<th>0.02</th>
<th>0.04</th>
<th>0.06</th>
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ANOVA Table

<table>
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<tr>
<th>source</th>
<th>SS</th>
<th>v</th>
<th>MS</th>
<th>F_{calc}</th>
<th>F_{table}</th>
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Since interaction was not significant, the error and interaction term were pooled.
### Thiocyanate

<table>
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<tr>
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<th>0.02</th>
<th>0.04</th>
<th>0.06</th>
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#### ANOVA Table

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<th>MS</th>
<th>F&lt;sub&gt;calc&lt;/sub&gt;</th>
<th>F&lt;sub&gt;table&lt;/sub&gt;</th>
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</table>
APPENDIX A
ANOVA of Induction Time

| Exp. | Concentration | | | | |
|------|---------------|---|---|---|
|      | 0.02          | 0.04 | 0.06 | |
| 7    | 1.275         | 1.825 | 2.200 | |
| 11   | 0.0950        | 1.125 | 1.425 | |

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>V</th>
<th>MS</th>
<th>F_{calc}</th>
<th>F_{table}</th>
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| Exp. | Concentration | | | | |
|------|---------------|---|---|---|
|      | 0.02          | 0.04 | 0.60 | |
| 7    | 1.525         | 2.150 | 2.625 | |
| 11   | 1.050         | 1.575 | 1.950 | |

<table>
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<tr>
<th>Source</th>
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APPENDIX B

Kinetic Density Graphs
Graph 1
Bromide - Relative exposure = Step 7

Development Time (Minutes)
Graph 2
Bromide- Relative exposure = Step 11

Development time (Minutes)
Graph 3
Bromide - Relative exposure = Step 20
Graph 4
Thiocyanate - Relative exposure = Step 7
Thiocyanate - Relative exposure = Step 11

Graph i

Development time (Minutes)
Graph b
Thiocyanate - Relative exposure = Step 20

Development time (Minutes)
APPENDIX C

Graphs from Auxiliary Experimentation
Graph:

0.042 N Thiocyanate, Relative exposure = Step 7
Graph

0.042 N Thiocyanate, Relative exposure = Step 11

Development time (Minutes)
Graph y

0.042 N Thiocyanate, Relative exposure = Step 20

Development time (Minutes)
APPENDIX D

Curve Fitting Program
40 DIM A$(17), B(21)
20 DISP "N"
30 INPUT N
40 MAT B=ZER
60 FOR K=N TO 21
70 ENTER (3*K+C), B(K)
90 BEEP
100 WAIT 200
110 B(K)=ABS(B(K))/100
120 NEXT K
130 DISP "ND FILTER"
140 INPUT N1
150 R=N1/0.15
160 SCALE 0.24,0.5
170 FOR K=1 TO 19
180 IF B(K)=0 THEN 250
190 M1=B(K+1)
200 M2=(B(K)-2*B(K+1))/2
210 M3=(B(K+2)-B(K))/2
220 M4=M2*(4/9)-M3*(2/3)+M1
230 M5=M2*(1/9)-M3/3*M1
240 PLOT K-R,B(K)
250 NEXT K
260 PLOT 20-R,B(20)
270 PLOT 21-R,B(21)
280 PEN
290 DISP "A$"
300 INPUT A$
310 PLOT 21.3-R,B(21),1
320 COPLE 0,-0.3
330 LABEL (+,1,1.7,0,11/8.5),A$(1,1),A$(2,2)
340 STOP
350 PLOT 1,4,1
360 LABEL (+)A$(3,3),A$(4,5),A$(6,8)
370 PLOT 24,5,1
380 PRINT A$(1,1),A$(2,2),MIN ("A$(3,3),A$(4,5),A$(6,8),A$(9,17)
390 FOR K=1 TO 11
400 WRITE (15,490)B(K)
410 NEXT K
420 PRINT
430 FOR K=12 TO 21
440 WRITE (15,490)B(K)
450 NEXT K
460 PRINT
470 PRINT
480 END
490 FORMAT F5.2,2

BIBLIOGRAPHY

13- Bergren, C.A., "Do Parabolic Interpolation With Less Memory", Control Engineering, p 44-5, May 1975
16- Dietrich, O. and Rathman, O., "Generalized Linear Least-Squares Fitting", Keyboard (A Hewlett-Packard publication), December 1975
GENERAL REFERENCES


3.40 SCN
WITH 1.06M/L CARBOWAX 1540
4.00 BR
WITH 30GM/L SODIUM SULFITE
3.40 SCN with 30 gm/l Sodium Sulfite
2.0 Br, Replicate #2

Millimeters to the Centimeter
REPLICATE #2

5.10 SCN

0.40

1.0

1.5

2.0

2.5

3.0

3.5