5-3-1965

Use of borohydride to determine the difference in the developable density for a chemically sensitized and non-sensitized emulsion.

S. Laufer

R. Golembe

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USE OF BOROHYDRIDE TO DETERMINE THE DIFFERENCE IN THE DEVELOPABLE DENSITY FOR A CHEMICALLY SENSITIZED AND NON-SENSITIZED EMULSION.

Submitted by

S. Laufer R. Golembe

THIS PAPER IS SUBMITTED IN PARTIAL FULFILLMENT FOR THE B.S. DEGREE IN PHOTOGRAPHIC TECHNOLOGY.

May 3, 1965
ABSTRACT

An emulsion was prepared so as to minimize the effect of any chemical action on the grains was in its "primitive" state, i.e., that no chemical sensitizing had occurred during the formation of the emulsion grains in "inert" gelatin. Another emulsion was made so as to maximize the effect of any chemical action on the grains by chemical sensitizing methods. This emulsion was also prepared in "inert" gelatin. Sodium Borohydride was added at various levels of concentration to chemically fog both emulsions. The developable density was measured. Also, an attempt was made to measure the amount of reduction sensitization occurring if any.

The loss of sodium borohydride in a 1.0 N sodium hydroxide solution was minimum for the time used. An appreciable difference in the photographic effect produced by the use of sodium borohydride was measured and observed. Density is proportional to concentration of sodium borohydride added for the primitive emulsion. Some reduction sensitization was measurable on the primitive emulsion.
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INTRODUCTION

Experiments of chemical reduction by sodium arsenite dealing with fogging of single-layer emulsion grains on glass plates have been reported previously. Certain chemical reducing agents such as sodium arsenite, as the compound used by W. C. Clark, can duplicate the action of light by producing developability.

Recent innovation to the chemical industry was the introduction of alkali metal sodium borohydride, a strong reducing agent first synthesized in 1943 by H. I. Schlesinger and H. C. Brown and their co-workers at the University of Chicago. The preparative method involves reaction of methyl borate with sodium hydride at elevated temperatures.

\[ 4\text{NaH} + \text{B(OCH}_3\text{)}_3 \rightarrow \text{NaBH}_4 + 3\text{NaOCH}_3 \]
This compound has gained commercial stature and uses in the pharmaceutical industry. In 1949, S. W. Chaiken and W. G. Brown reported the reduction of aldehydes, ketones and acid chlorides with sodium borohydride.

Photographically, the reaction of major importance is in the Kodachrome II process, alkali metal sodium borohydride being used to reduce silver halide grains to metallic silver in much the same way that light forms a latent image. The equation for this reaction is:

\[ 8\text{Ag}^+ + \text{BH}_3 + 8\text{OH} \rightarrow 8\text{Ag}^0 + \text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O} \]
This reaction takes place in the magenta layer of the Kodachrome II process.
In a study by Pescok,\textsuperscript{9} he showed that sodium borohydride has a highly irreversible anodic polarographic wave yielding eight electrons per mole.

This paper treats the reaction of sodium borohydride with bromoiodide emulsions in an attempt to measure the developable density obtained at certain levels of concentration between a untreated, i.e., primitive emulsion, and a treated emulsion, i.e., chemically sensitized. Also, an attempt was made to explain the reduction of the bromoiodide emulsions and if the trapping of the electrons was due to chemical sensitization, reduction sensitization or both.

In the experiment to be described, concentrations from $10^{-3}$ to $10^{-10}$ g/l sodium borohydride in 1.0 N solution sodium hydroxide per liter of emulsion were added to 25 ml samples of emulsion (treated and primitive), and coated on 1x3-in. biological slides. At each level of concentration another set of fogged emulsions (with the same amount of sodium borohydride added), were coated and exposed in the E.G.&G. Mark VI sensitometer. Measurements were made showing a direct indication in the difference between developed density for the primitive and sensitized emulsions, and also some effect of reduction sensitization.
PROPERTIES AND HANDLING OF BOROHYDRIDE

The physical and thermodynamic properties of sodium borohydride are listed in the following two tables.

Table I

<table>
<thead>
<tr>
<th>Property</th>
<th>Formula</th>
<th>NaBH₄</th>
<th>Molecular Wt.</th>
<th>37.86</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity - Metal Hydrides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inc., Specifications</td>
<td>98+ %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impurities:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium methoxide</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amine nitrogen</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium metaborate</td>
<td>Remainder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decompose above 400°C in vacuum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Stability</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Will not ignite at 300°C on hot plate Ignite from free flame in air burning quietly.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.074 g/cc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apparent Bulk Density</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 lbs./gal.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table II

| Thermodynamic Properties     |         |       |       |       |
| Heat of Formation             | -45.53  |       |       |       |
| Heat Capacity                 | 20.67   |       |       |       |
| Ionization                    | NaBH₄ = Na⁺ + BH₄⁻ | -5660  |       |       |
| Hydrolysis                    | BH₄⁻ + H⁺ + 3H₂O = H₃BO₃ + 4H₂ | -88    |       |       |
| Reduction                     | BH₄⁻ + 8OH⁻ = B(OH⁻)₄⁻ + 4H₂O + 8e⁻ | -228.9 |       |       |
Sodium borohydride may be handled in air according to safe practice for inflammable hygroscopic powders. The uncon- fined does not ignite on contact with moisture. It is stable in dry air in a tightly closed container. It is stable to shock, but decomposes slowly in moist air evolving trace amount of hy- drogen.¹² Both dry and aqueous solutions of sodium borohydride are relatively safe to handle.
EXPERIMENTAL METHOD

I. Preparation of Sodium Borohydride solutions.

The required amount of sodium borohydride was weighed to the nearest tenth of a milligram and diluted in a 1.0 N solution of sodium hydroxide. All dilutions were made with boiled distilled water. To obtain lower concentrations, the primary solution was further diluted in 1.0 N solution of sodium hydroxide by volumetric and quantitative transfer methods. Different glassware was used for each dilution and the number of dilutions was kept to a minimum whenever practical.

II. Stability Data.

To obtain data on the stability in solution and the purity of sodium borohydride, a volumetric iodate method of quantitative analysis was used.13

The sample to be analyzed was pipetted into an Erlenmeyer flask. A standard iodate solution was pipetted into the flask and potassium iodide was then added. The solution was stirred with a magnetic mixer and then stoppered and allowed to stand in the dark for two and ahalf minutes. Finally, the partially reduced iodine was back titrated with a standard sodium thiosulfate solution.

III. Emulsion Making.

The first requirement for emulsion makeup was to obtain
an inert gelatin to show any difference of developed density with the addition of sodium borohydride, between the treated and untreated emulsions.

Such a material does not occur naturally and the gelatin used was Eastman Kodak Purified, Calfskin. (see appendix p.)

The preparation of the bromoiodide emulsion was simply made by precipitating the following:

Into a beaker: Gelatin (Atlantic Gel) 10.0 g
KBr 21.1 g
KI 0.3 g
Distilled water 240 ml

Let swell at least ten minutes at room temperature.

Into 600 ml glass beaker:

AgNO₃ 25.5 g
Dissolve in distilled water. 360 ml

For the precipitation stage, a different gelatin (Atlantic Gel) was used. The reason for this being that problems of coagulation of the Kodak Gelatin were encountered. So to save time, precipitation was carried out with the Atlantic gelatin. This meant of course, that the emulsion was not as free from impurities as one would like. The beaker containing gelatin and salts was placed into a controlled water bath set at 65.0°C ± 0.5°C.

The silver nitrate solution was transferred to a separatory funnel with a fine tip so that the time of precipitation would be approximately 22 minutes. The funnel was clamped in a position so that the solution would fall in a well-stirred area. The precipitation was carried out under 1A safelight conditions.
After precipitation was complete, the beaker was removed from the water bath and cooled to approximately 38°C. A solution of 0.05 N \( \text{H}_2\text{SO}_4 \) (10 ml), was added to bring \( \text{pH} \) to the isoelectric point. For coagulation, 100 ml of saturated \( \text{Na}_2\text{SO}_4 \) solution was added, stirred, and if no coagulation occurred, solid \( \text{Na}_2\text{SO}_4 \) was added slowly with mixing until the coagulation point was reached.

When the coagulation was settled, the supernatant liquid was carefully drained off proceeding with the addition of 1 liter of cold distilled water. The beaker was placed in the refrigerator overnight for the washing stage.

After washing, two beakers of the Kodak gelatin were prepared, one for chemical treatment and the other unmodified for the primitive state emulsion. In each beaker, 18 g of the gelatin was added, swelled in 200 ml of \( 5 \times 10^{-4} \) N KBr and 42 ml of 0.054 N NaOH.

For the treated emulsion, the hydrogen ion concentration was adjusted to a \( \text{pH} \) 6.2 for maximum chemical sensitization. Also added was 3.75 mg of \( \text{Na}_2\text{S}_2\text{O}_3 \) to induce sulfur sensitization on the surface of the crystal. The overall chemical reaction during sensitization with \( \text{Na}_2\text{S}_2\text{O}_3 \) is shown in the following equations:

\[
\text{S}_2\text{O}_3^- + 2\text{AgBr} \rightleftharpoons \text{Ag}_2\text{S}_2\text{O}_3 + 2\text{Br}^-
\]
\[
\text{Ag}_2\text{S}_2\text{O}_3 + 6\text{H}^- \rightleftharpoons \text{Ag}_2\text{S} + 3\text{HSO}_4^-\]

After the adjustments, both beakers were brought up to temperature (55°C ± 0.5°C.), in the water bath. The beaker containing the
coagulum was removed from the refrigerator and the water drained off. By a weight method, the coagulum was split in two equal parts. The gelatin solution was redispersed into the respective beaker, mixed and the treated emulsion placed into the water bath for a 40 minute digestion period. The primitive emulsion was cooled and placed in a water bath at 90°F. for use latter. After digestion, the emulsion was cooled and the pH adjusted with 1.0 N Citric Acid so that with the addition of 1.0 ml of NaOH containing sodium borohydride, the final pH of both emulsions would be 6.2.

With two coating plates set up; one hot and the other cold, 1 X 3-in. biological slides were pre-weighed and placed on the hot plate for pre-heating. The method of coating was by pipetting 20 drops of emulsion onto the slide. For example, when the first level of borohydride concentration was received, a 25 ml sample of primitive emulsion was measured and put into a small beaker. Several drops of saponin solution were added for ease of spreading. A 1.0 ml sample of sodium borohydride was pipetted into the beaker and stirred vigorously for one minute. Following, a 2.0 ml pipet was used to deliver the twenty drops of emulsion containing sodium borohydride. The pipet end was then used for evening out the emulsion over the entire glass area. The emulsion set for about one minute and was then transferred to the cold plate for gelling. The same procedure was carried out for the sensitized emulsion using different pipettes for each emulsion and BH₄ concentration.
Immediately after the emulsion set on the cold plate, the slide was re-weighed to determine the amount of emulsion coated on each slide. Drying followed for the next several hours.

IV. Sensitometry.

Many slides were exposed in the E.G.&G. Mark VI Zenon Flash Sensitometer for indication of process control and reduction sensitization data. All slides were processed in D19, diluted 1:1 for 5.0 minutes at 68°F ± 1°F. The usual following procedures of stop, fix, wash and dry were executed.

Density measurements were recorded with the use of the Mac Beth Quanta Log, OP 110.
RESULTS

The first data obtained was the stability of sodium borohydride in a 1.0 N solution of sodium hydroxide. Although fresh solutions were made for each emulsion run, an approximate time of 6 hours from the beginning of volumetric dilutions intervened, therefore, requiring an indication of stability. The stability of 0.1 g/l NaBH₄ in 1.0 N NaOH solution at room temperature is shown in Fig. 1. The curve illustrates that there is about a 1% loss of sodium borohydride in approximately the first 19 hours and the concentration becomes relatively constant for the next 53 hours. In the time interval of 6 hours that the BH₄ was used, there was no appreciable loss to cause sufficient error for a 0.10 g/l solution of NaBH₄.

Levels of concentration below 0.01 g/l were not measurable by the method used and therefore the amount in solution is uncertain.

For maximum chemical sensitization; maximum density with minimum fog, a digestion series was run. (See Fig. 2) A digestion time of 40 minutes was choosen because it fulfilled the above requirements and also showed little increase in chemical sensitization with time of use.

The developed density produced by varying concentration of sodium borohydride for the primitive emulsion is shown in Fig. 3. *Average of threen.*

For the sensitized emulsion, quantitative measurements
of the developed density were not measurable because all levels of concentration produced a maximum density. While extraneous base + fog was present at lower concentrations, an appreciable difference in fog density between the primitive and sensitized emulsions was observed.

As a control, the primitive and sensitized emulsions were coated at the beginning and end of the laboratory session to determine any change in the emulsion characteristics. Little change for the primitive emulsion was taking place as illustrated by Fig. 4. Also, this curve is significantly different from that in Fig. 2, but because of the repeatability to produce these curves, they are representative of what our results are based on.

The sensitized emulsion shows a significant increased chemical sensitization during the coating session. (See Fig. 5) It was assumed that the earlier coatings were closely representative of the reaction with sodium borohydride. Therefore, differences in density between the primitive and sensitized emulsions were observed.

The reduction sensitization data were based on the primitive emulsion since this emulsion was the only one measurable. Some reduction sensitization was evident. An example of this effect is shown in Fig. 6. No reduction sensitization was measured for the sensitized emulsion.

In some instances, desensitization occurred for the emulsions treated with sodium borohydride. Fig. 7.
Stability of Sodium Borohydride for 0.1g/l in a 1.0 Normal Solution of Sodium Hydride
**Fig. 2**

Title: **DIGESTION SERIES OF COATED SLIDES (PRIMITIVE & SENSITIZED)**

Exposure Data: Date: **February 19, 1965**

Sensitometer: **E & G**

N. D.: **1.60**

Time: **10^{-4} sec**

Processing: Date: **February 19, 1965**

Developer: **D-19 1:1**

Time: **5:00 minutes**

Temperature: **70°F**

Agitation: **A.S.A. Specification**

Densitometer: **Mac Beth Quanta Log**

Date Read: **February 23, 1965**

---

<table>
<thead>
<tr>
<th>Digestion</th>
<th>B+F</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th</td>
<td>0.10</td>
<td>0.37</td>
</tr>
<tr>
<td>2nd</td>
<td>0.08</td>
<td>0.72</td>
</tr>
<tr>
<td>20th</td>
<td>0.09</td>
<td>1.02</td>
</tr>
<tr>
<td>40th</td>
<td>0.10</td>
<td>1.34</td>
</tr>
<tr>
<td>60th</td>
<td>0.14</td>
<td>0.96</td>
</tr>
</tbody>
</table>

The 20th, 40th, and 60th digestion series contain Na$_2$S$_2$O$_3$ as a chemical sensitizer.
Fig. 4 Title: PRIMITIVE EMULSION AT THE BEGINNING AND END OF THE LABORATORY SESSION.

Exposure Data: Date __________________ Sensitometer __________ N. D. __________
Processing: Date __________________ Developer __________ Time __________
Temperature __________ Agitation __________

Density: __________________ Date Read __________

Log Exposure: 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Fig. 5 Title: INCREASE IN SENSITIZATION DURING THE LABORATORY SESSION. (SENSITIZED EMULSION)

Exposure Data:
- Date
- Sensitometer
- N. D.

Processing:
- Date
- Developer
- Time
- Temperature
- Agitation

Densitometer:
- Date Read

Log Exposure

Density

END

BEGINNING
**Fig. 6  Title: REDUCTION SENSITIZATION**

<table>
<thead>
<tr>
<th>Exposure Data: Date</th>
<th>Sensitometer</th>
<th>N. D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing: Date</td>
<td>Developer</td>
<td>Time</td>
</tr>
<tr>
<td>Temperature</td>
<td>Agitation</td>
<td></td>
</tr>
<tr>
<td>Densitometer:</td>
<td>Date Read</td>
<td></td>
</tr>
</tbody>
</table>

**LINE A:** Fog level produced by $10^{-4}$ g/l NaBH₄.

**CURVE B:** Characteristic curve for primitive emulsion.

**CURVE A+B:** Fog density plus primitive emulsion curve.

**CURVE C:** Pre-fogged emulsion + sensitometric exposure.

Since curve 'C' is greater than curve 'A+B', reduction sensitization has occurred.
Primitives emulsion with $10^{-4}$ g/l NaBH$_4$ exposed in EG&G sensitometer.
The addition of sodium thiosulfate into the emulsion formed \( \text{Ag}_2\text{S} \), one of the first known chemical sensitizers which apparently act as a trap for holes by holes. The primitive emulsion, as the name indicates was given no treatment, thereby forming very shallow traps in which electrons can readily escape; hence no efficient trap site to increase its photographic sensitivity and the probability to trap electrons provided by the sodium borohydride.

Sodium borohydride, a strong reducing agent, hydrolyses in an alkalin solution e.g. \( \text{NaOH} \), yielding 8 e\(^{-}\) per mole. The electron transfer, reduction of the \( \text{AgBr} \) grain is:

\[
\text{AgBr} + 1\text{e}^{-} \rightarrow \text{Ag}^{0} + \text{Br}^{-}
\]

It is theorized that all the borohydride reacted in both emulsions producing the same amount of silver. It is believed that the same number of electrons were required to form a stable latent image center in both emulsions. The difference in developable density can be attributed to more highly concentrated silver atoms near the sensitivity specks in the chemically sensitized emulsion.

It was thought that sodium borohydride in very small quantities sensitize the silver bromide emulsion in the presence of sulfur sensitizing. The effect obtained with such a sensitizer is called reduction sensitization. In reduction sensitization, the silver halide grain is partially reduced to silver metal which allows latent image centers to be more readily formed. It differs from sulfur sensitization in that the effect acts on
the surface and interior of the grain with about equal efficiency, while sulfur sensitizers are almost entirely a surface-sensitizing mechanism. Reduction sensitizing and sulfur sensitizing are additive.\textsuperscript{21}

\textbf{CONCLUSION.}

The loss of sodium borohydride in a 1.0 N NaOH solution was minimum for the time used. An appreciable difference in the photographic effect produced by the use of sodium borohydride was measured and observed. Density is proportional to concentration of sodium borohydride added for the primitive emulsion. Some reduction sensitization was measurable on the primitive emulsion.

\textbf{ACKNOWLEDGMENT.}

The authors wish to acknowledge the help and guidance of the senior research faculty and special assistance of Instructor Richard Norman and especially to Dr. B.H. Carroll for his suggestions concerning the mechanism and experimental method.
REFERENCES

2. Ibid., p. 462.
4. Ibid., p.1.
5. Ibid., p.1.
11. Ibid.
12. Ibid.
13. Ibid.
21. Op. cit., p. 120.
Statement of Objectives

1. To standardize the processing procedures for determining the amount of Borohydride to achieve a maximum density.

2. To test the hypothesis that density is proportional to the concentration of Borohydride added.

3. To determine the difference in the developable density in a chemically sensitized and non-sensitized emulsion by the use of Borohydride.
FLOW CHART OF EXPERIMENTAL PROCEDURE

Determine the R.H., pH and Temperature range for BH₄ use.

Standardize reagents

Use Metal Hydrides analytical procedure for 1g/l of NaBH₄

Make fast emulsion

Add sensitizer
Na₂S₂O₃

Add NaBH₄

Coat on glass slides

Develop in M.Q. developer

Determine the difference in Density for sensitized and non-sensitized emulsions.

Non-Sensitized
Summary of Calculations

A. Formula for Analysis of Borohydride

\[
\text{NaBH}_4 \text{ grams/liter} = \frac{(IN_1 - MN_2)(4.732)}{S}
\]

Where: 
- \(I\) = ml. of potassium iodate
- \(N_1\) = normality of potassium iodate (0.100N)
- \(M\) = ml. of sodium thiosulfate
- \(N_2\) = normality of sodium thiosulfate (0.097N)
- \(S\) = sample size in ml.

B. Calculation of the amount of Na\(_2\)S\(_2\)O\(_3\) for Chemical Sensitization, for 50mg. Na\(_2\)S\(_2\)O\(_3\)/mole Ag.

\[
\frac{\text{AgNO}_3}{\text{equiv.}} \cdot \frac{25.5 \text{ g.}}{170 \text{ g. wt.}} = 0.15 \text{ equiv. Ag/600ml emulsion.}
\]

\[
(\# \text{ equiv. Ag})(\text{AgBr g/equiv.}) = \text{g. AgBr/600ml.}
\]

\[
(0.15)(188) = 28.3 \text{ g AgBr/600ml.}
\]

\[
(\text{g. AgBr})/\text{Molecular Weight} = (\text{moles AgBr})(50\text{mg. Na}_2\text{S}_2\text{O}_3)/\text{mole of Ag.}
\]

\[
= \text{mg. of Na}_2\text{S}_2\text{O}_3/600\text{ml. emulsion.}
\]

\[
(28.3)/188 = (0.15)(50\times10^{-3} \text{ g.}) = 7.5\times10^{-3} \text{ g. Na}_2\text{S}_2\text{O}_3/600\text{ml. emulsion.}
\]

or \(0.0375\text{ g. Na}_2\text{S}_2\text{O}_3/200\text{ml. emulsion.}

C. Calculation of the amount of Na BH\(_4\) required to start fogging levels at \(10^{-6}\) moles Ag/moles BH\(_4\)

\[
\frac{\text{g. BH}_4}{\text{g. emul.}} = (\text{moles Ag})(4.732\text{equiv/gram.})(10^{-6} \text{ moles Ag})/\text{mole BH}_4
\]
Statistical Tests Used (Computer Program)

Test of Means:

Hypothesis: Two populations have the same mean when $\sigma^2$ is not known.

1. $H: \mu_1 = \mu_2$
2. Choose Alpha Risk:
3. Statistic:
   \[ t = \frac{\bar{x}_1 - \bar{x}_2}{s_p \sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} \]
   Where $s_p = \sqrt{\frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2}}$
4. Rejection Region:
   \[ t < t_{\alpha/2} (N_1 + N_2 - 2) \]
   \[ t > t_{1-\alpha/2} (N_1 + N_2 - 2) \]
5. Mean Difference: $\bar{x}_1 - \bar{x}_2$
6. Interval:
   \[ \mu = t_{1-\alpha/2} s_p \sqrt{\frac{N_1 + N_2}{N_1 N_2}} \]
   \[ \bar{x}_1 - \bar{x}_2 \pm \mu \]
7. Test of Homogeneity: $F_1 / F_2 = \frac{s_1^2}{s_2^2}$
   (Sample F Test)
Formula for Standard Deviation:

\[ s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \]

Sample output of the IBM 1620:

```
C TO COMPUTE THE MEAN, MEDIAN, ST. DEV. OF N NUMBERS
C EMULSION BATCH V COATED ON 4/2/65 N=41 WITH 8 LEVELS OF BH4
Ø3380 CORES USED
19999 NEXT COMMON (B DATA)
END OF COMPILATION
EXECUTION

41 59 3.7800000E+00 .7700000E+00 .85877827E-01
MEAN MEDIAN STD. DEV.

END OF JOB
```

```
**FORX
C TEST OF TWO MEANS AND VARIANCE TEST OF HOMOGENITY
C AT ANY SIGNIFICANCE LEVEL DESIRED (TWO TAILED) (94%)
Ø2386 CORES USED
19999 NEXT COMMON
END OF COMPILATION
EXECUTION

MEANS ARE DIFFERENT (\( \bar{\mu} \neq \bar{\nu} \))

<table>
<thead>
<tr>
<th>POOLED VAR. STATISTIC</th>
<th>MEAN DIFF.</th>
<th>UPPER LIM.</th>
<th>LOWER LIM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>.10290357E+00 .57130767E-01 .9277000E-01 .14990076E+00 .35639233E-01</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TESTING.. HOMOGENITY OF TWO VARIANCES
VARIANCES ARE HOMOGENIOUS
COMPUTED F VALUE = .18148381E+01
END OF JOB
```
PROGRAM WRITTEN BY R. GOLEMBE, S. LAUER FOR SENIOR RESEARCH

TEST OF TWO MEANS AND VARIANCE TEST OF HOMOGENITY
AT ANY SIGNIFICANCE LEVEL DESIRED (TWO TAILED)

AN=47,
XA=0.68723
SAD=0.11569
BN=41,
XB=0.78
SBD=0.085877
TV=2.598
FV=2.2622
FVL=2.2128
FVL2=1.0/FVL
SA=(SAD)*(SAD)
SB=(SBD)*(SBD)
SP=((AN-1.0)*SA+(BN-1.0)*SB)/(AN+BN-2.0)**.5
O=TV*SP
P=((AN+BN)/(AN*BN))**.5
U=0*P
R=ABS(XA-XB)
R1=R+U
R2=R-U
IF (R-U)1,1,2
1 PRINT 14
14 FORMAT (15HMEANS ARE EQUAL/)
GO TO 99
2 PRINT 15
15 FORMAT (19HMEANS ARE DIFFERENT/)
99 PRINT 20
20 FORMAT (2X,11HPOOLED VAR.5X,9HSTATISTIC5X,10HMEAN DIFF.4X
11HUPPER LIM.4X,10HLOWER LIM./)
PRINT 13,SP,U,R,R1,R2
13 FORMAT (5E14.8/)
PRINT 40
40 FORMAT (38HTESTING.. HOMOGENITY OF TWO VARIANCES/)
F1=SA/SB
IF (F1-FV)4,4,70
4 IF (FVL2-F1)60,60,70
60 PRINT 100
100 FORMAT (25HVARIANCES ARE HOMOGENIOUS/)
GO TO 400
70 PRINT 200
200 FORMAT (29HVARIANCES ARE NON HOMOGENIOUS/)
400 PRINT 405,F1
405 FORMAT (18HCOMPUTED F VALUE =E14.8)
CALL EXIT
END

ALL VALUES ARE SUPPLIED INCLUDING CRITICAL REGIONS OF REJECTION
DEPENDING UPON THE ALPHA CHOOSE.

Properties of Kodak Purified Calfskin Gelatin

Characteristic:
Moisture—4.6%
Ash———0.02%
pH———4.20
Viscosity-144.5
Albumen—.03%
Jelly Strength—321
Iso-Electric Point-pH 4.70
Sources of Variability

During the laboratory experiment some major sources of variability can be accounted for. Developed Density was chosen as a response variable, but the following attribute to this produced density:

1. Coating Thickness
2. Drying Evenness
3. Contamination
4. Glassware Variability
5. Safelight Conditions
6. Light Leaks
7. Humidity
8. Temperature

An indirect method for statistical analysis of coating thickness was the weight of the emulsion coated on a specified area.