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Sensitometric Characteristics of Monobaths

Kenneth Gould

Bert Zaccaria

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SENSITOMETRIC CHARACTERISTICS OF MONOBATHS

Kenneth C. Gould and Bert Zaccaria

Prepared in partial fulfillment of the requirements for a BS in Photographic Science and Engineering

Rochester Institute of Technology
May 11, 1966
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</tr>
</tbody>
</table>
ABSTRACT

The United States Air Force presently uses SO-233 Duplicating Film for the processing of transparent prints and has achieved a long straight line curve for reproduction control purposes. Type 8430 Duplicating Film is also used for the same purpose but for different contrasts. Their problem was that and Type 8430 were not compatible and did not have a sufficiently high density or a long enough straight line. The results of this experiment have yielded a monobath formulation which when used with type 8430 film will give the desired density and straight line required.
OBJECTIVE

To test the hypothesis that an increase in the maximum density and a lengthening of the straight line portion of the characteristic curve of Kodak Type 8430 Duplicating Film will be effected by use of a monobath developer by varying the input variables of pH, time, temperature, and concentrations of solutions and by measuring the response variables of maximum density, minimum density, fog, average gradient, and speed of the uniformly exposed sensitometric strips by use of densitometric procedures.
INTRODUCTION

A monobath is a photographic processing solution that contains both developing agent and silver halide solvent, plus caustic agents, preservatives and buffering agents. The reaction kinetics are such that the development of the latent image and the solvent action of unexposed silver halide, are simultaneous. Thus, by its very nature, a monobath formulation is designed for a particular photographic emulsion or emulsion types, and for specific processing parameters, such as time, temperature, and kind of agitation.

The purpose is to show what several component parts must be varied to achieve the desired objective of longer scale and an increase in maximum density.

Monobaths are based on the premise that being an extremely active developer with a very short induction time, they must be used so that exposed silver halide grains can be developed before they are attacked by the hypo and dissolved. The difficulty involved in formulating a monobath is that all the components are interdependent. The other problem involved is that to create a monobath with sufficient activity, results in high fog, reticulation and rapid exhaustion.

It was found that the use of small percentages of hypo in a developer
crease fog, however larger amounts of hypyo act somewhat as an anti-foggant. This is beneficial since extensive use of anti-foggants such as benzotriazole and potassium bromide cause a reduction in film speed.
TEST PROCEDURE

Kodak Type 8430 film, cut to 70mm X seven inch strips were exposed to an EG&G sensitometer for 1/1000 second. Light modulation was accomplished by using a 1/100 second attenuator.

The film was refrigerated with five strips to a package to minimize any latent image change upon removal.

A study of existing monobath formulations was made to determine the proper area of study in relation to the film used and the objectives. Data obtained from the characteristic curves of this study enabled the proper selection of a monobath formula to establish grounds for final study geared toward the objectives.

A series of tests were run to determine which combination of the developing agents (metol, phenidone, hydroquinone) would give the best results with Type 8430 film. The test was accomplished by keeping the potassium alum, sulfite, sodium hydroxide, hypo, and anti-fog levels constant and varying the three developing agents. The formula used as a basis was the BU-315*, which uses 10 grams of metol and 40 grams of hydroquinone without phenidone. It was found using maximum density and average gradient as criteria, that for Type 8430 film, metol should be eliminated and a phenidone-hydroquinone formulation found most satisfactory.
A central composite design for determining optimum operating conditions was used to extract the maximum amount of information with the least number of runs in the laboratory. This design makes use of deviations from a normal value in order to determine the optimum conditions for increasing the straight line portion of the characteristic curve and produce an effective increase in maximum density.

Seven replications were run of the normal formulation which produced an estimate of experimental error and an average characteristic curve. 95% confidence limits were placed on sections in the toe, straight line, and shoulder area of the average curve.

With this estimate of error it was possible to run the central composite design and attain contour curves to determine optimum operating conditions. Axial points enabled better estimation of the contours because they are run $+\sqrt{3}$ from the normal value which extended beyond the limits set up by the design.

Upon completion of the experimental design, the data was evaluated through a regression analysis technique. The values were calculated by means of the forward Dolittle method and substituted into the mathematical model of the experiment. Partial derivatives were taken to find the maximum and minimum conditions of the developer formulations. These values being the optimum conditions for the
film-developer combination.

Upon attaining the desired aim points of maximum density and maximum average gradient, a series was run to determine the temperature dependence relationship. With this information the data was prepared and evaluated to suit the design of the spray processor. (See appendix for design of processor) Tests were made for agitation effects produced by the spray with rotation of the film and the spray without rotation. Developer oxidation was held to a minimum by maintaining nitrogen pressure in the processor and developer tank. A time series was made to determine the actual development time of the monobath and the minimum time required to be in solution.
TEST PROCEDURE

CUT, EXPOSE AND STORE FILM

SURVEY AND TESTING OF MONOBATH FORMULATIONS

CONTROL TEMP.-TIME-AGITATION

TEST PARAMETERS

GRADIENT & Dmax

SURVEY AND TESTING OF MONOBATH FORMULATIONS

OBJECTIVE PARAMETERS

GRADIENT AND D max

REPLICATION OF NORMAL ERROR DETERMINATION

CONTROL

TIME-TEMP.-AGITATION

VARIABLES

pH

TEMP.

HYPO CONC.

DEV. CONC.

MODEL (NORMAL) OF MONOBATH FORMULATION

EXPERIMENT

CENTRAL COMPOSITE DESIGN

EVALUATE FOR SPRAY PROCESSOR

INITIATE TO SPRAY PROCESSOR

CONTROL

TIME-TEMP.-AGITATION

OBJECTIVE PARAMETERS

GRADIENT AND D max

EVALUATE PARAMETERS

REPORT DATA
RESULTS

Varying amounts of phenidone showed a .02 change in maximum density with a .05 change in average gradient. The degree of change by varying pH was .76 delta density corresponding to a pH change of 10.20 to 13.00 and a relative speed shift of 25 to 126 which approached the normal speed of 126 (Fig. I). Increasing thiosulfate concentration produced a delta density of .26 having a maximum density of 2.64 and a relative speed shift of 160 to 318 with concentrations varying from 50 to 80 grams (Fig. III).

As expected, no single component yielded the desired aim points but rather through the interactions of pH, thiosulfate and phenidone. Using 80 grams/liter of hypo, 2.65 grams/liter of phenidone, and 42.5 grams/liter of sodium hydroxide (pH of 13.00) resulted in a gradient of .99, a maximum density of 2.28 and a relative speed of 180. Using the latter calculated optimum concentrations, resulted in a curve at 90°F (Fig. VIII) which produced an average gradient of 1.20 and a maximum density of 2.60 and a relative speed increase of 274 from the normal. This, when introduced to spray conditions produced an increase of average gradient of .09 and an increase of maximum density of .24 and a relative speed increase of 30 (Fig. IX).
DISCUSSION

By means of systematic trials of varied components of a monobath developer dictated by a central composite design a satisfactory formulation was achieved. Once the statistical analysis was tabulated, further laboratory testing was necessary to determine more accurately, its pH dependence, the optimum running temperature, and the effects of using the monobath under pressure in a spray processor.

It was found that the spray with the film platen rotating at 750 rpm gave a higher density and a longer straight line than did the spray with the platen stationary. There was little difference between the spray with the stationary platen and the tray method of agitation. An increase of the factors of pH, developing agent, agitation, and temperature and a decreasing in hypo produced, the desired maximum density and lengthened straight line portion of the characteristic curve. It was noted that changes beyond optimum concentrations resulted in excessive fog.
RECOMMENDATIONS

A. Design a recovery unit to eliminate the large amounts of chemicals used.

B. Convert the formula to a diffusion transfer system to conform to current processing methods.

C. Further test the formula to accurately determine at what conditions the desired average gradients of 1.15 and 1.45 ± .05 may be accurately achieved.

D. Consideration of Contrast Index as a more meaningful measure of the straight line and shoulder portions of the characteristic curve than the presently used average gradient method. Contrast Index is a more repeatable method when many different people are involved in making measurements. It is more meaningful in the shoulder and straight line portion where most of the reconnaissance information is recorded.

**Referenced from SPSE - see bibliography

E. Use of a computer program for statistical analysis.

F. Determination of image stability through methods such as residual silver content or degradation due to time.
ACKNOWLEDGEMENTS

The authors would like to thank the United States Air Force for their help in supplying the problem, equipment, and film for the completion of this research project. Also our thanks to H. R. B. Singer, Inc., especially to Mr. Leo Lang and Mr. Warner Elliott for helpful knowledge concerning monobath formulations, and to Mr. Charles Chidsey and Mr. Hood of the Mechanical Department at the Rochester Institute of Technology for their help in the design and construction of the spray processor.
BIBLIOGRAPHY

1-- SPSE - Vol. #2, Number 3, Oct. 1958, Combined Development and Fixation of Photographic Image With Monobaths by Marilyn Levy.
APPENDIX*

FORMULATIONS (grams/liter)

A100---

2 grams phenidone
10 grams potassium alum
50 grams sodium sulfite
40 grams hydroquinone
35 grams sodium hydroxide

VARIABLE HYPO CONCENTRATIONS

(50, 60, 70, 80 grams)

20 cc Kodak anti-fog #2 (0.5% solution)

A101---

Same as A100

VARIABLE PHENIDONE CONCENTRATIONS

(1.15 - 2.75 grams)

A102---

Same as A100

VARIABLE SODIUM HYDROXIDE CONCENTRATIONS

(Dependent upon pH - 10.00, 11.00, 12.00, 13.00)

A104---

2.5 grams phenidone
10.0 grams potassium alum
50.0 grams sodium sulfite
40.0 grams hydroquinone
42.5 grams sodium hydroxide
80.0 grams sodium thiosulfate

20 cc Kodak anti-fog #2 (0.5% solution)

A105---

2 grams phenidone
10 grams potassium alum
50 grams sodium sulfite
40 grams hydroquinone
35 grams sodium hydroxide
110 grams sodium thiosulfate

20 cc Kodak anti-fog #2 (0.5% solution)
APPENDIX

ORIGINAL BU-315

<table>
<thead>
<tr>
<th>Grams</th>
<th>Ingredient</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>metol</td>
</tr>
<tr>
<td>50</td>
<td>sodium sulfite</td>
</tr>
<tr>
<td>40</td>
<td>hydroquinone</td>
</tr>
<tr>
<td>20</td>
<td>potassium alum</td>
</tr>
<tr>
<td>35</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>110</td>
<td>sodium thiosulfate</td>
</tr>
<tr>
<td></td>
<td>Kodak anti-fog #2 (0.5% solution)</td>
</tr>
</tbody>
</table>

BASIC FORMULAS TESTED

USASEL MONOBATH 24-2D

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Grams</th>
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<tbody>
<tr>
<td>Water (100°F)</td>
<td>750 cc</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>60 grams</td>
</tr>
<tr>
<td>hydroquinone</td>
<td>30 grams</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>25 grams</td>
</tr>
<tr>
<td>phenidone</td>
<td>3 grams</td>
</tr>
<tr>
<td>potassium bromide</td>
<td>2 grams</td>
</tr>
<tr>
<td>benzotriazole</td>
<td>4 grams</td>
</tr>
<tr>
<td>sodium thiosulfate</td>
<td>150 grams</td>
</tr>
<tr>
<td>water to make</td>
<td>1000 cc</td>
</tr>
<tr>
<td>formaldehyde (38%)</td>
<td>10 cc</td>
</tr>
</tbody>
</table>

USASEL MONOBATH 24-2

<table>
<thead>
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<th>Ingredient</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>water to make</td>
<td>1000 cc</td>
</tr>
<tr>
<td>sodium sulfite</td>
<td>60 grams</td>
</tr>
<tr>
<td>hydroquinone</td>
<td>30 grams</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>25 grams</td>
</tr>
<tr>
<td>phenidone</td>
<td>0.9-5.0 grams</td>
</tr>
<tr>
<td>sodium thiosulfate</td>
<td>75-250 grams</td>
</tr>
<tr>
<td>formaldehyde (38%)</td>
<td>10 cc</td>
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</table>

FORMULA FOR FUJI F. G. POSITIVE

<table>
<thead>
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<th>Ingredient</th>
<th>Grams</th>
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<tr>
<td>sodium sulfite</td>
<td>40 grams</td>
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<td>phenidone</td>
<td>2 grams</td>
</tr>
<tr>
<td>hydroquinone</td>
<td>15 grams</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>60 grams</td>
</tr>
<tr>
<td>potassium thiocyanate</td>
<td>120 grams</td>
</tr>
<tr>
<td>sodium thiosulfate</td>
<td>75 grams</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td>0.1 grams</td>
</tr>
<tr>
<td>water to make</td>
<td>1000 cc</td>
</tr>
</tbody>
</table>
Missing Page
APPENDIX

SPECIFICATIONS OF SPRAY PROCESSOR

For constructural design see enclosed drawings

Nitrogen pressure -------- 40 lbs/sq. in.

Spray nozzels used----
  Type 1/8 K #1. 5
    .37 gal/min. @ 15 lbs pressure
    .60 gal/min. @ 40 lbs pressure
  Type 1/8 K # 3
    .18 gal/min. @ 15 lbs pressure
    .30 gal/min. @ 40 lbs pressure

10 gallon developer tank fed processor supplied from demand system.

Materials used --- plexi-glass and stainless steel.

Speed criterion

\[
\text{Speed} = \frac{1}{E} \times 1000
\]
SAMPLE GRADIENT DETERMINATION

STRAIGHT LINE DRAWN BETWEEN 0.3 AND 1.8 DENSITY UNITS. SLOPE OF LINE DETERMINES \( g \).
**pH Variation**

<table>
<thead>
<tr>
<th>NO.</th>
<th>GRADIENT</th>
<th>MAXIMUM DENSITY</th>
<th>pH</th>
<th>RELATIVE SPEED</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>---</td>
<td>1.37</td>
<td>10.20</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>---</td>
<td>1.53</td>
<td>11.00</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>.75</td>
<td>1.85</td>
<td>12.00</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>.94</td>
<td>2.13</td>
<td>13.00</td>
<td>126</td>
</tr>
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</table>

**FIG. 1**

KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
DEVELOPMENT TIME 2 MIN.
ATTENUATOR 1/100
TEMPERATURE 68°F
DEVELOPER # A102*
PROCESSING METHOD ASA STANDARD
SODIUM HYDROXIDE DEPENDENCE

KODAK TYPE 8430
DEVELOPMENT TIME 2 MIN.
TEMPERATURE 68°F
DEVELOPER # A102*
PROCESSING METHOD ASA STANDARD

* See appendix for formulation
THIOSULFATE CONCENTRATION

<table>
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<th>NO.</th>
<th>GRADIENT</th>
<th>MAXIMUM DENSITY</th>
<th>GRAMS/LITER</th>
<th>RELATIVE SPEED</th>
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<tbody>
<tr>
<td>1</td>
<td>.--</td>
<td>2.38</td>
<td>50</td>
<td>160</td>
</tr>
<tr>
<td>2</td>
<td>.--</td>
<td>2.36</td>
<td>60</td>
<td>195</td>
</tr>
<tr>
<td>3</td>
<td>.98</td>
<td>2.40</td>
<td>70</td>
<td>220</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>2.64</td>
<td>80</td>
<td>318</td>
</tr>
</tbody>
</table>

KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
DEVELOPMENT TIME 2 MIN.
ATTENUATOR 1/100
TEMPERATURE 68°
DEVELOPER #A100
PROCESSING METHOD ASA STANDARD

RELATIVE LOG EXPOSURE

DENSITY

FIG. III
THIOSULFATE DEPENDENCE

FIG. IV

KODAK TYPE 8430
DEVELOPMENT TIME 2 MIN.
TEMPERATURE 68°F
DEVELOPER # A100*
PROCESSING METHOD ASA STANDARD

* See appendix for formulation
<table>
<thead>
<tr>
<th>NO.</th>
<th>GRADIENT</th>
<th>MAXIMUM DENSITY</th>
<th>TEMPERATURE (°F)</th>
<th>RELATIVE SPEED</th>
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<tbody>
<tr>
<td>1</td>
<td>.93</td>
<td>2.28</td>
<td>68</td>
<td>180</td>
</tr>
<tr>
<td>2</td>
<td>.96</td>
<td>2.33</td>
<td>75</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>1.20</td>
<td>2.60</td>
<td>90</td>
<td>400</td>
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<tr>
<td>4</td>
<td>1.53</td>
<td>2.65</td>
<td>105</td>
<td>590</td>
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KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
ATTENUATOR 1/100
DEVELOPMENT TIME 2 MIN.
DEVELOPER #A104*
PROCESSING METHOD ASA STANDARD
TEMPERATURE VS. GRADIENT AND SPEED

FIG. VI

KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
ATTENUATOR 1/100
DEVELOPMENT TIME 2 MIN.
DEVELOPER #A104
PROCESSING METHOD ASA

TEMPERATURE (°F)

RELATIVE SPEED

TEMPERATURE (°F)
PHENIDONE DEPENDENCE

KODAK TYPE 8430
DEVELOPMENT TIME 2 MIN.
TEMPERATURE 68°F
DEVELOPER # A101*
PROCESSING METHOD ASA

* See appendix for formulation
COMPARISON OF NORMAL AND MODIFIED MONOBATH FORMULATIONS

<table>
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<th>NO.</th>
<th>GRADIENT</th>
<th>MAXIMUM DENSITY</th>
<th>DEVELOPER</th>
<th>TEMPERATURE (°F)</th>
<th>RELATIVE SPEED</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.94</td>
<td>2.13</td>
<td>A105</td>
<td>68</td>
<td>125</td>
</tr>
<tr>
<td>2</td>
<td>.99</td>
<td>2.28</td>
<td>A104</td>
<td>68</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>1.20</td>
<td>2.60</td>
<td>A104</td>
<td>90</td>
<td>400</td>
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DEVELOPER
1  # A105
2  # A104
3  # A104

KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
ATTENUATOR 1/100
DEVELOPMENT TIME 2 MIN.
PROCESSING METHOD ASA STANDARD

RELATIVE LOG EXPOSURE
AGITATION

FIG. IX

<table>
<thead>
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<th>NO.</th>
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<th>MAXIMUM DENSITY</th>
<th>CONDITIONS</th>
<th>RELATIVE SPEED</th>
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<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>2.53</td>
<td>spray with no rotation</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>1.05</td>
<td>2.57</td>
<td>spray with rotation</td>
<td>280</td>
</tr>
</tbody>
</table>

KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
ATTENUATOR 1/100
DEVELOPMENT TIME 2 MIN.
TEMPERATURE 90°F
DEVELOPER # A104
PROCESSING METHOD ASA