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Sensitometric Characteristics of Monobaths

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SENSITOMETRIC CHARACTERISTICS OF MONOBATHS

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ABSTRACT

The United States Air Force presently uses SO-233 Duplicating Film [redacted] 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 the developer [redacted] 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 increase fog, however larger amounts of hpyo 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.[1]

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 chatacteristic 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 a 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.

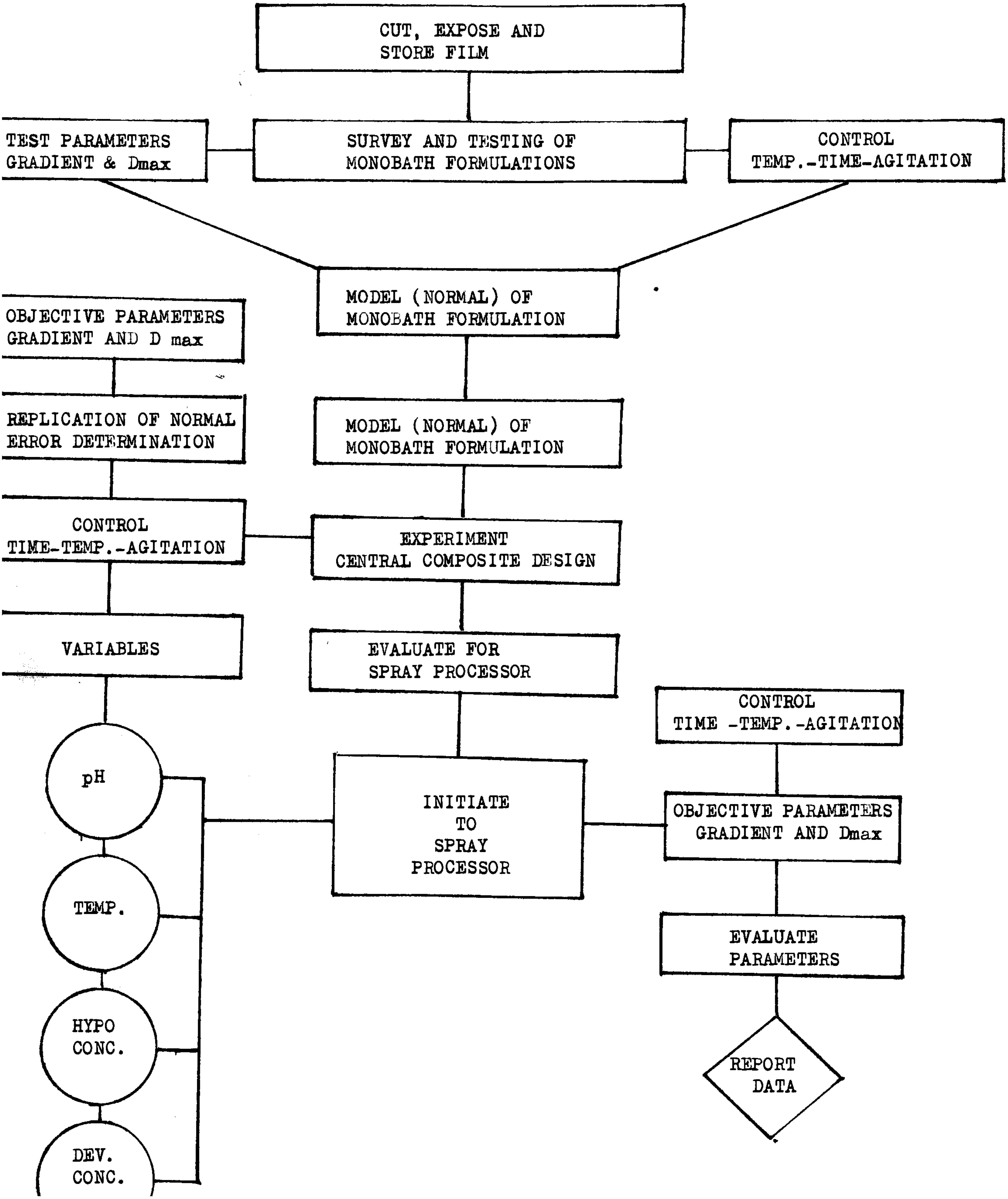
Seven replications were run of the normal formulation which produced an estimate of experimental error and an average characteristic curve. 95% confidence limits were placed on sections in the toe, straight line, and shoulder area of the average curve.

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 $\pm\sqrt{3}$ 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



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 miximum 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.

RECCOMMENDATIONS

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 $\pm$ .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., expecially 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

10 grams	metol
50 grams	sodium sulfite
40 grams	hydroquinone
20 grams	potassium alum
35 grams	sodium hydroxide
110 grams	sodium thiosulfate

Kodak anti-fog #2 (o. 5% solution)

BASIC FORMULAS TESTED

USASEL MONOBATH 24-2D

Water (100°F)	750 cc
Sodium sulfite	60 grams
hydroquinone	30 grams
sodium hydroxide	25 grams
phenidone	3 grams
potassium bromide	2 grams
benzotriazole	4. grams
sodium thiosulfate	150 grams
water to make	1000 cc
formaldehyde (38%)	10 cc

USASEL MONOBATH 24-2

water to make	1000 cc
sodium sulfite	60 grams
hydroquinone	30 grams
sodium hydroxide	25 grams
phenidone	0.9-5.0 grams
sodium thiosulfate	75-250 grams
formaldehyde (38%)	10 cc

FORMULA FOR FU JI F. G. POSITIVE

sodium sulfite	40 grams
phenidone	2 grams
hydroquinone	15 grams
sodium hydroxide	60 grams
potassium thiocyanate	120 grams
sodium thiosulfate	75 grams
2-Mercaptobenzothiazole	0.1 grams
water to make	1000 cc

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

$$\text{Speed} = 1/E \times 1000$$

SAMPLE GRADIENT DETERMINATION

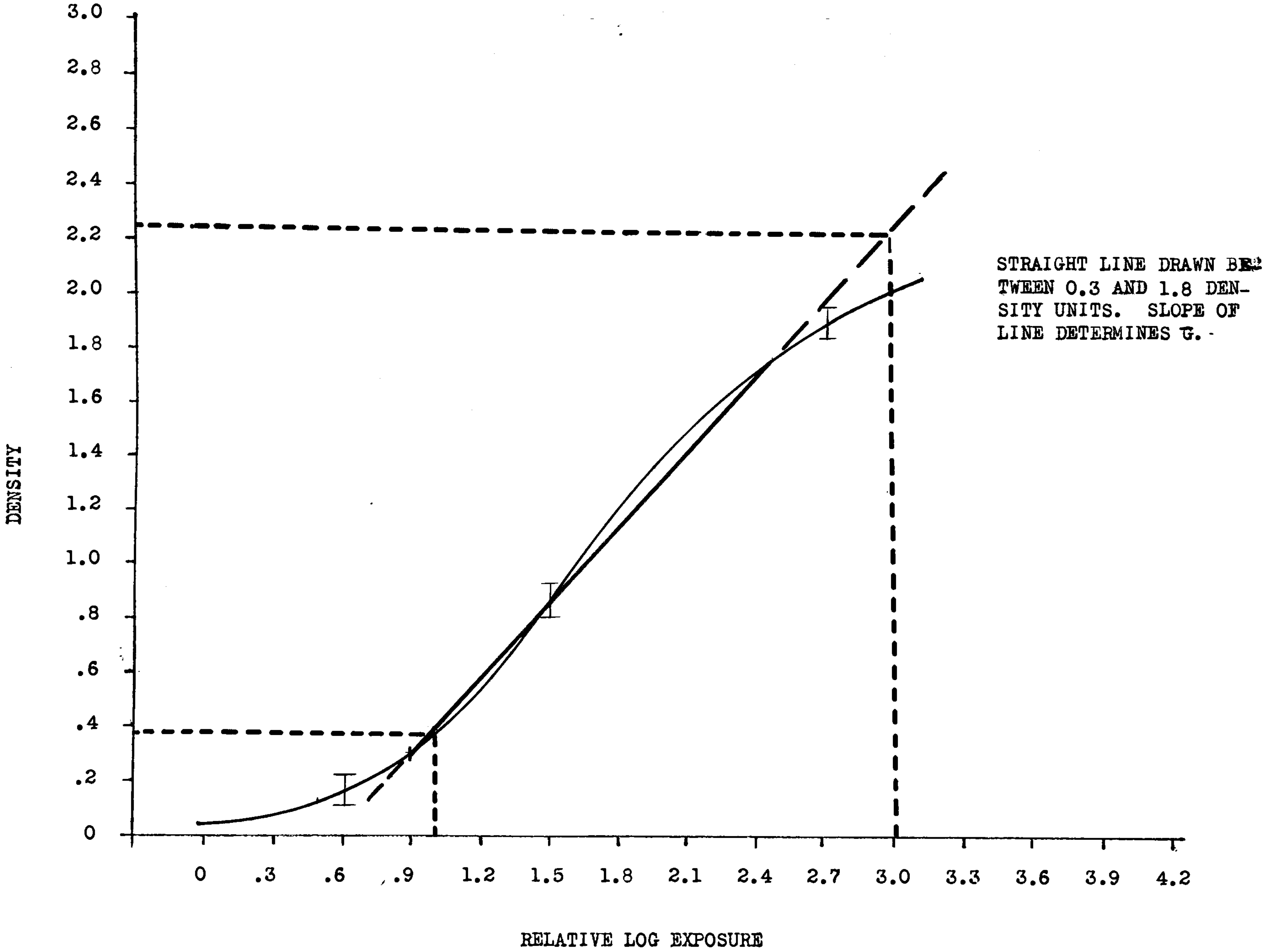
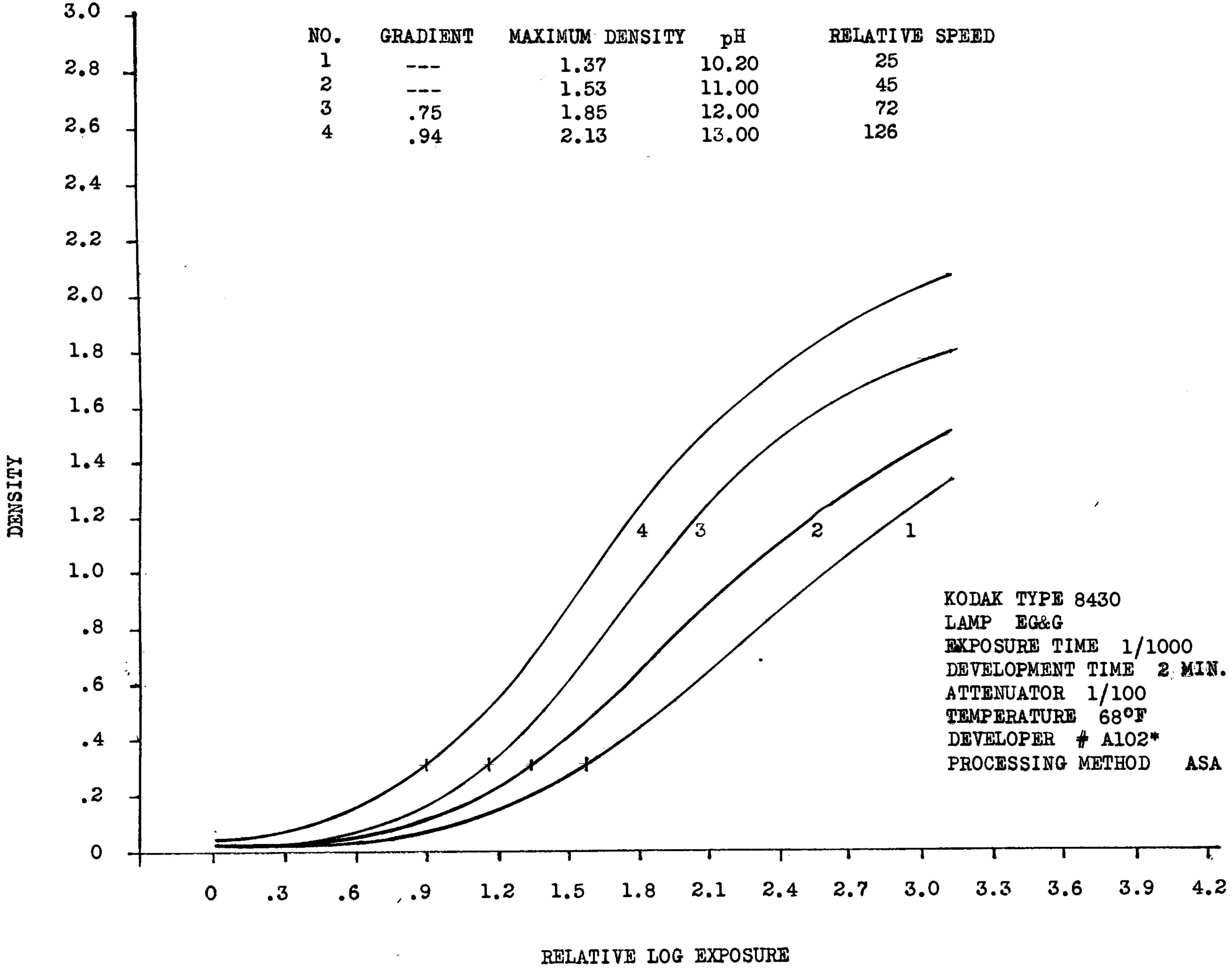


FIG. I

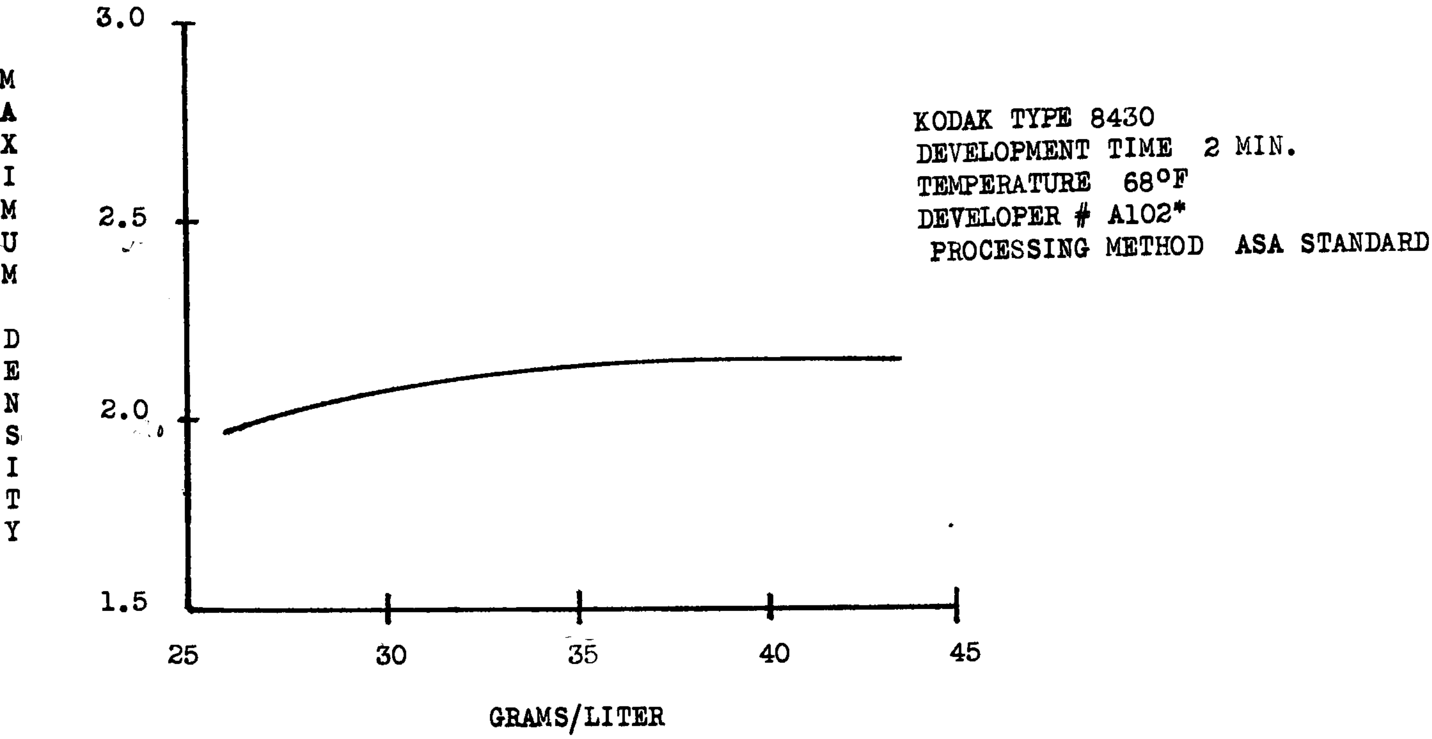
pH VARIATION

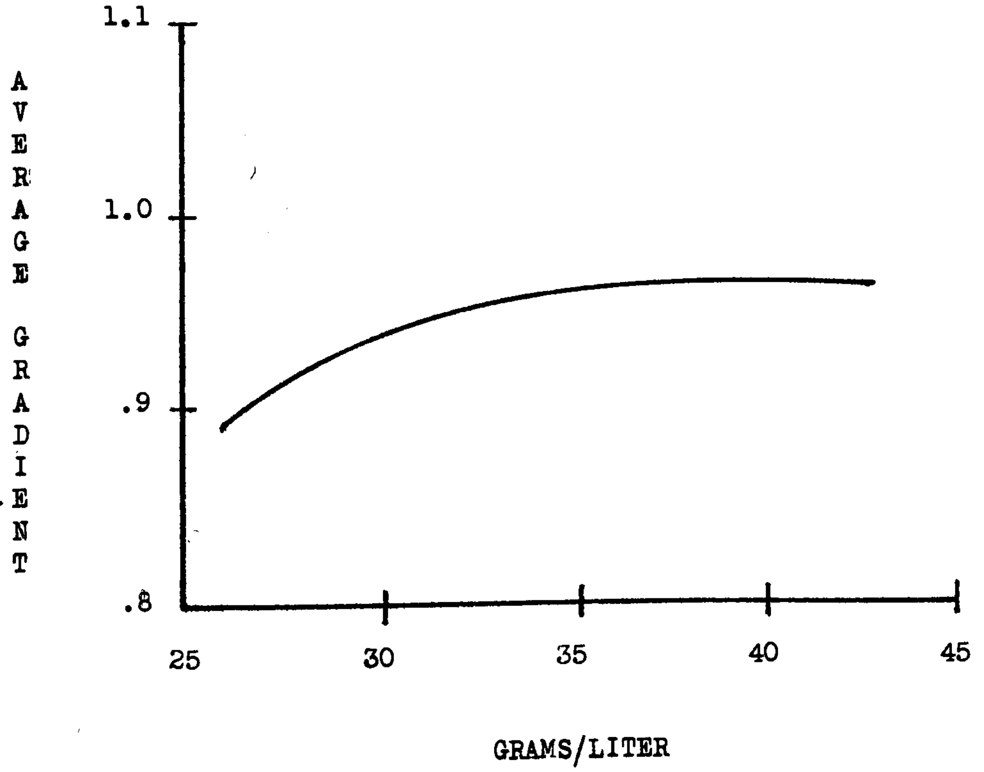
NO.	GRADIENT	MAXIMUM DENSITY	pH	RELATIVE SPEED
1	---	1.37	10.20	25
2	---	1.53	11.00	45
3	.75	1.85	12.00	72
4	.94	2.13	13.00	126



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

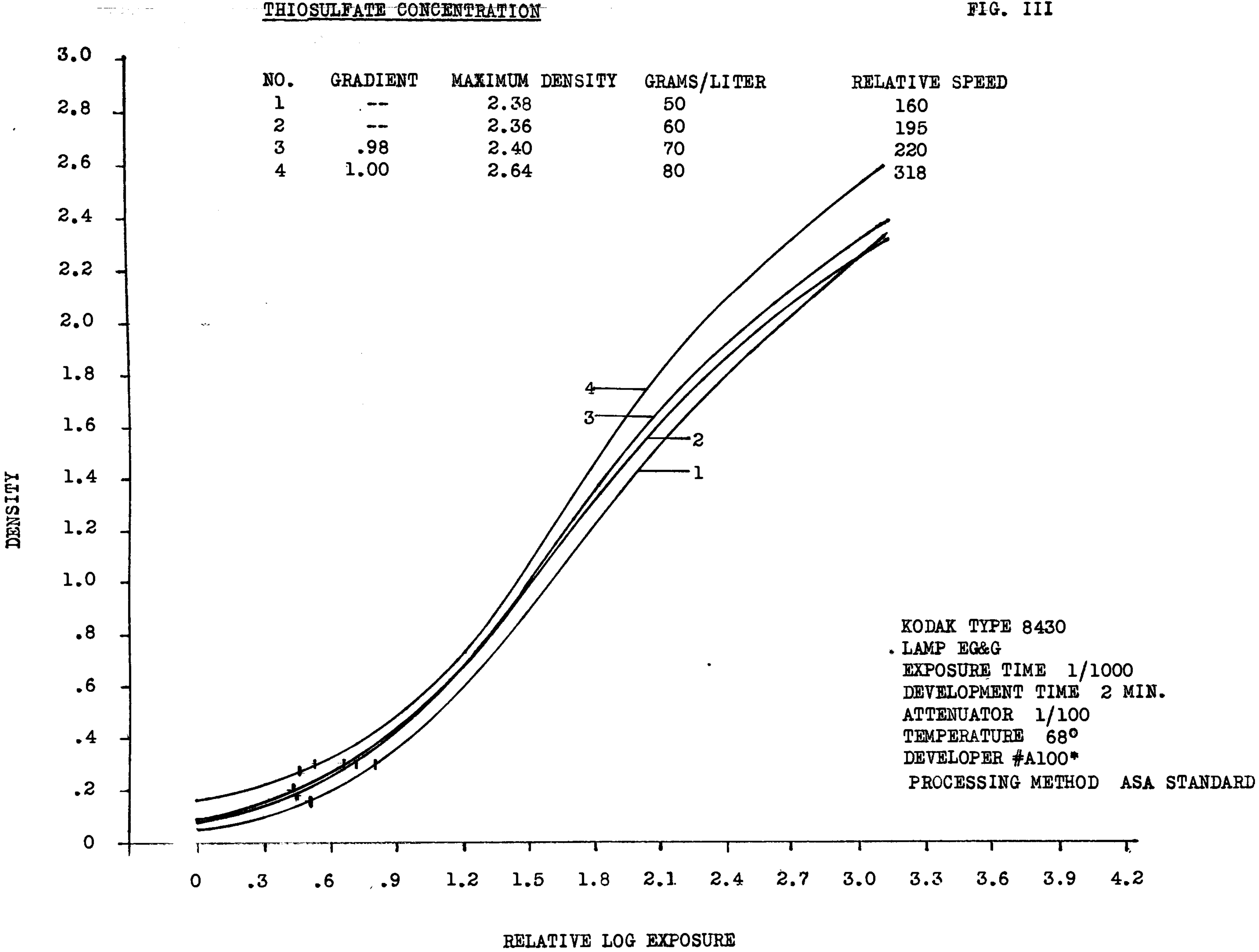
SODIUM HYDROXIDE DEPENDENCE





* See appendix for formulation

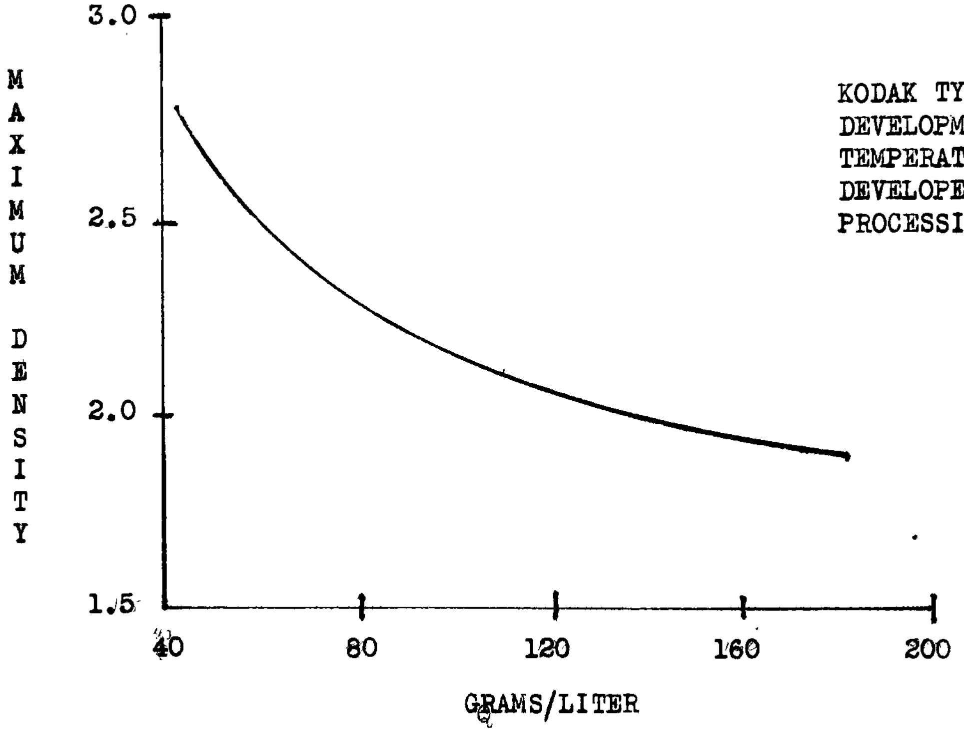
FIG. III

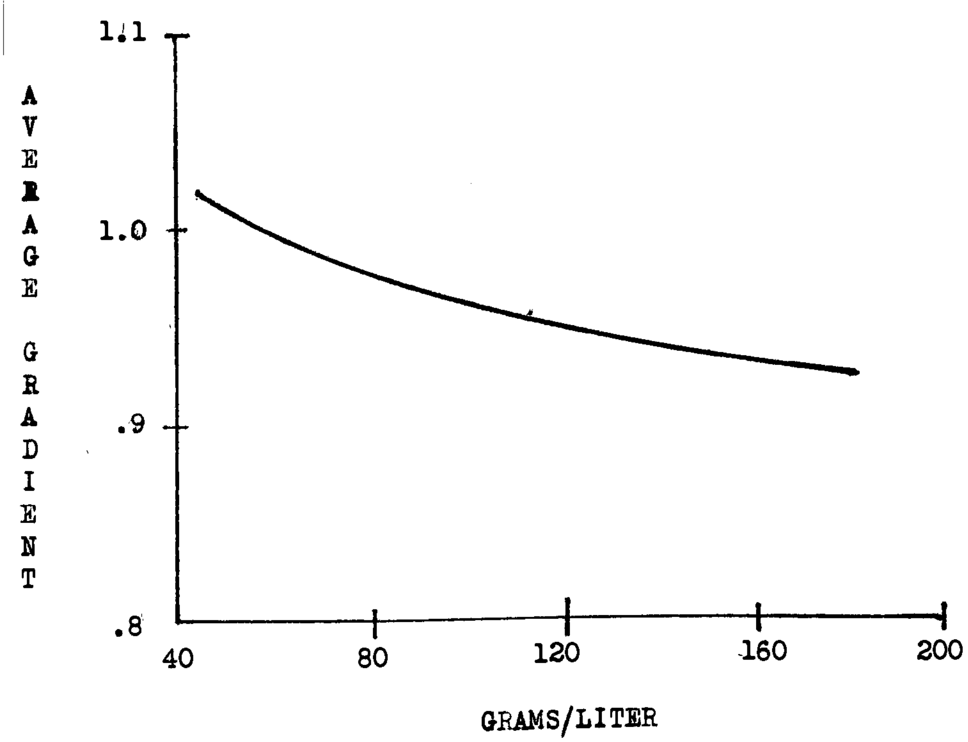

THIOSULFATE CONCENTRATION
NO. GRADIENT MAXIMUM DENSITY GRAMS/LITER RELATIVE SPEED
1 -- 2.38 50 160
2 -- 2.36 60 195
3 .98 2.40 70 220
4 1.00 2.64 80 318
DENSITY
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
4
3
2
1
KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
DEVELOPMENT TIME 2 MIN.
ATTENUATOR 1/100
TEMPERATURE 68°
DEVELOPER #A100*
PROCESSING METHOD ASA STANDARD
0 .3 .6 .9 1.2 1.5 1.8 2.1 2.4 2.7 3.0 3.3 3.6 3.9 4.2
RELATIVE LOG EXPOSURE

THIOSULFATE DEPENDENCE

FIG. IV

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



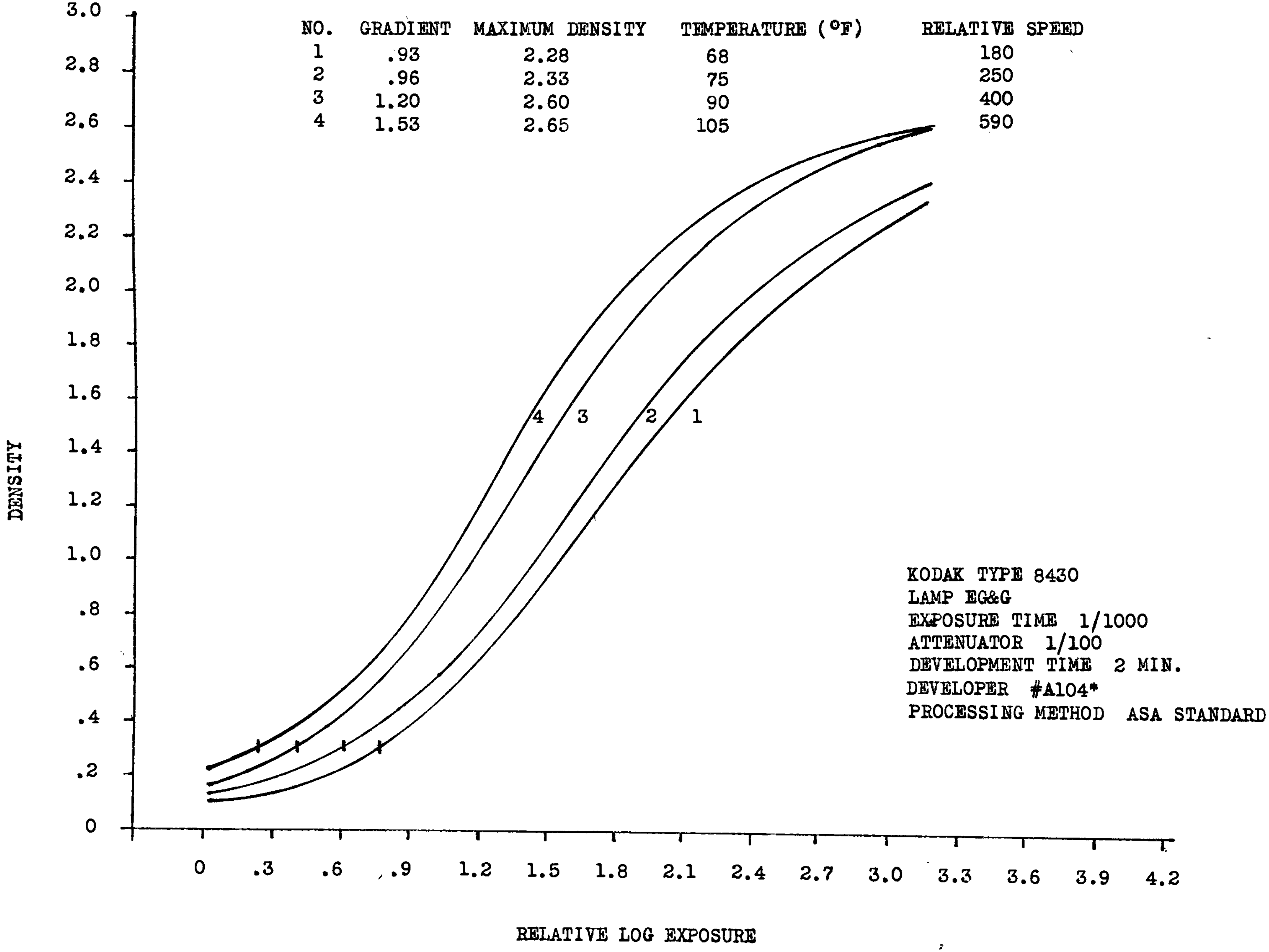


* See appendix for formulation

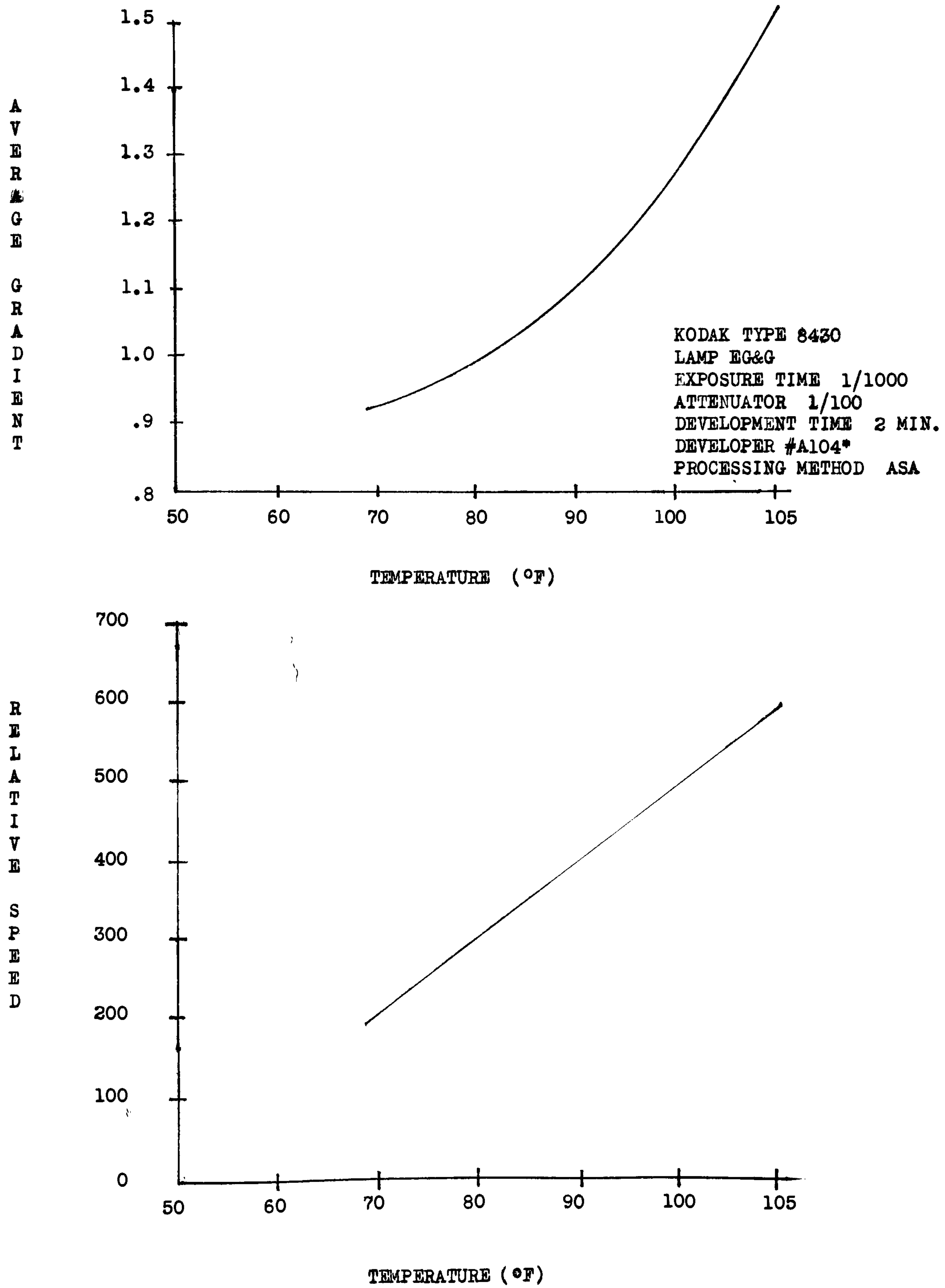
TEMPERATURE

FIG. V

NO.	GRADIENT	MAXIMUM DENSITY	TEMPERATURE (°F)	RELATIVE SPEED
1	.93	2.28	68	180
2	.96	2.33	75	250
3	1.20	2.60	90	400
4	1.53	2.65	105	590

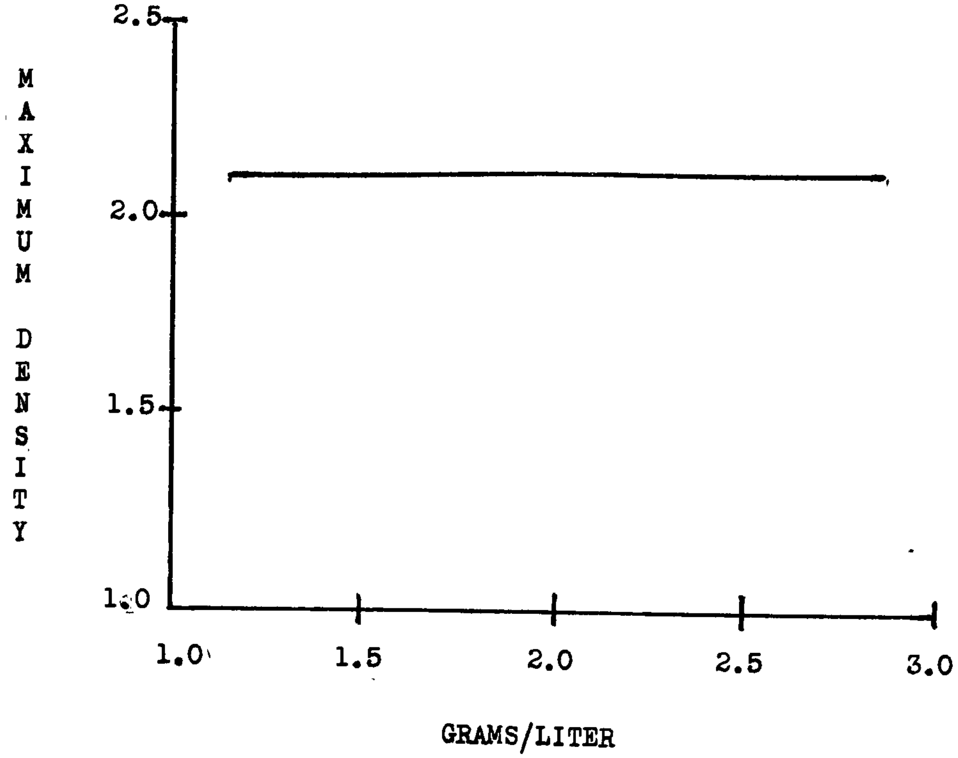


TEMPERATURE vs. GRADIENT AND SPEED FIG. VI

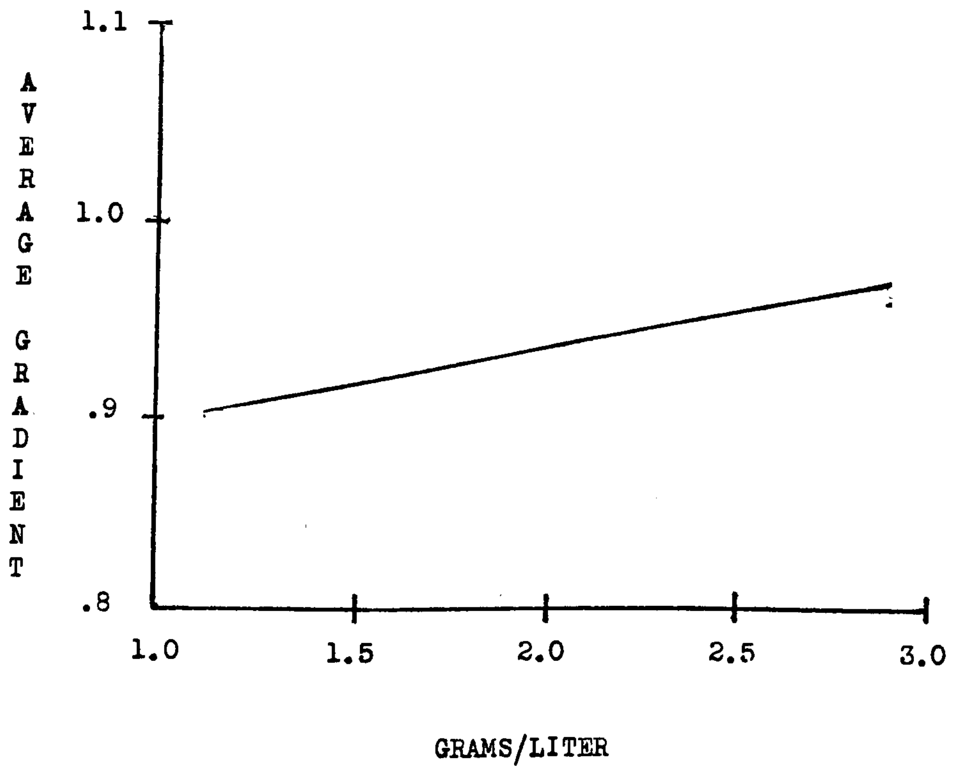


PHENIDONE DEPENDENCE

FIG. VII



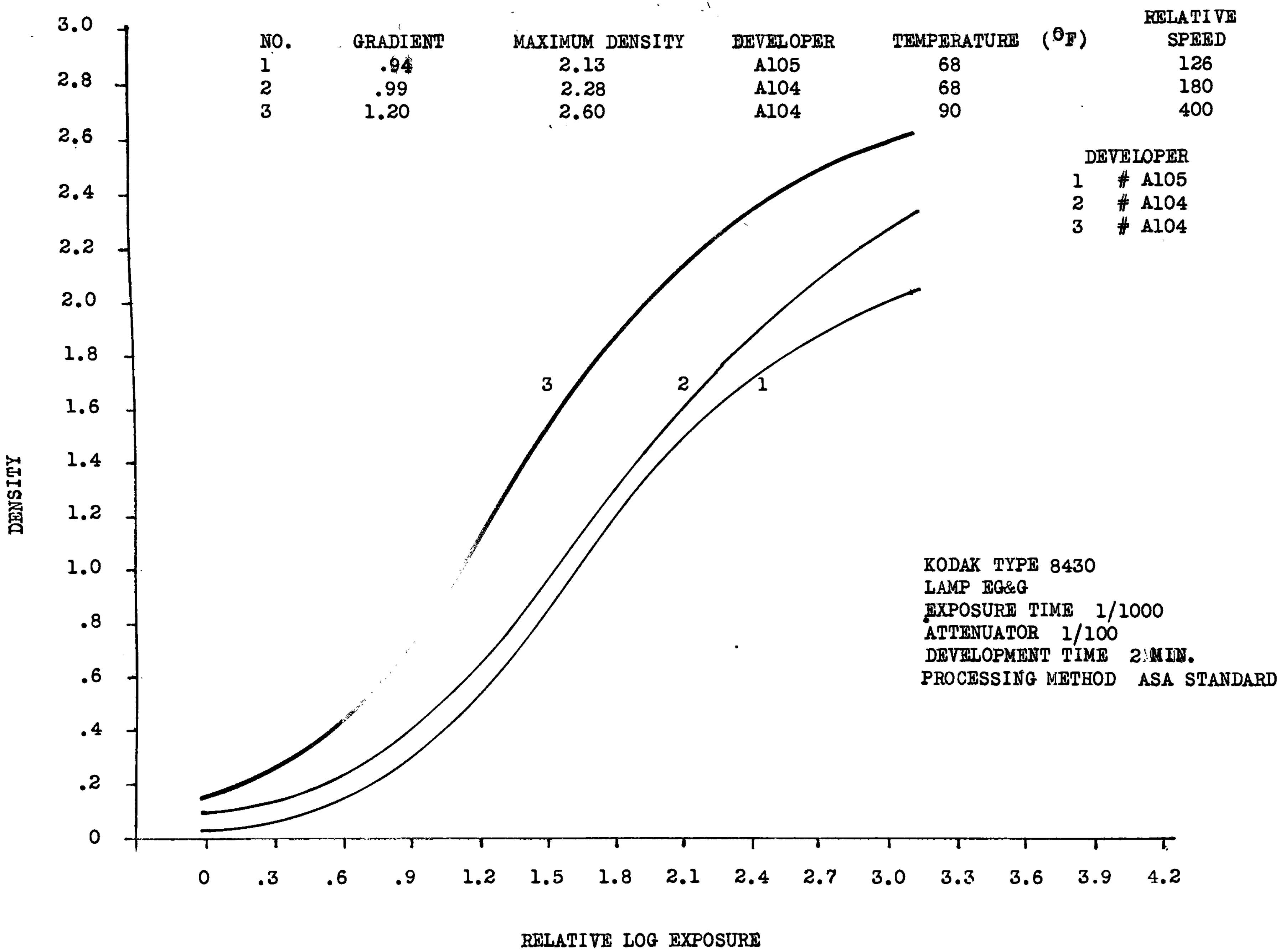
KODAK TYPE 8430
DEVELOPMENT TIME 2 MIN.
TEMPERATURE 68°F
DEVELOPER # A101*
PROCESSING METHOD ASA



* See appendix for formulation

FIG. VIII

COMPARISON OF NORMAL AND MODIFIED MONOBATH FORMULATIONS



AGITATION

FIG. IX

NO.	GRADIENT	MAXIMUM DENSITY	CONDITIONS	RELATIVE SPEED
1	1.00	2.53	spray with no rotation	220
2	1.05	2.57	spray with rotation	280

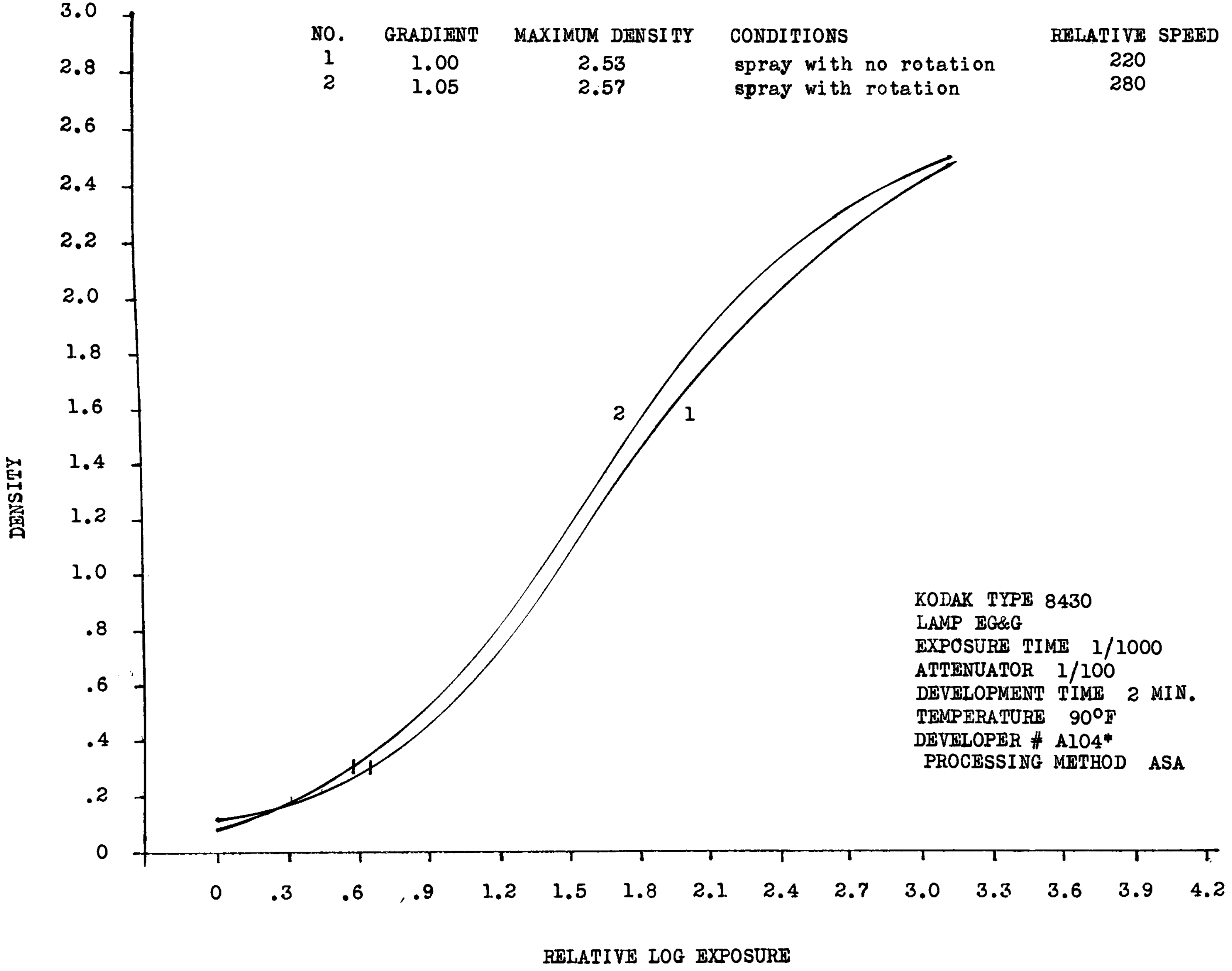
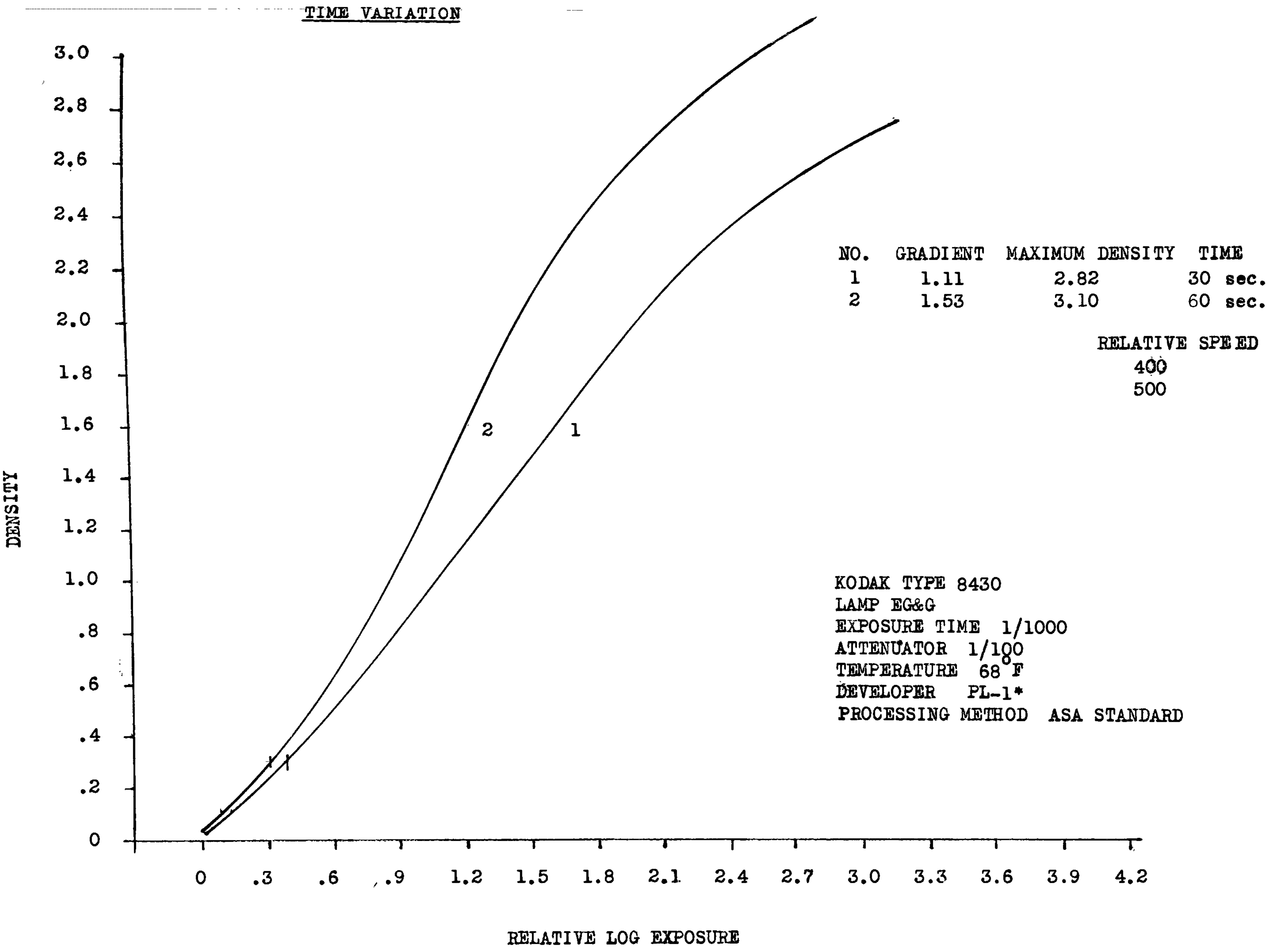
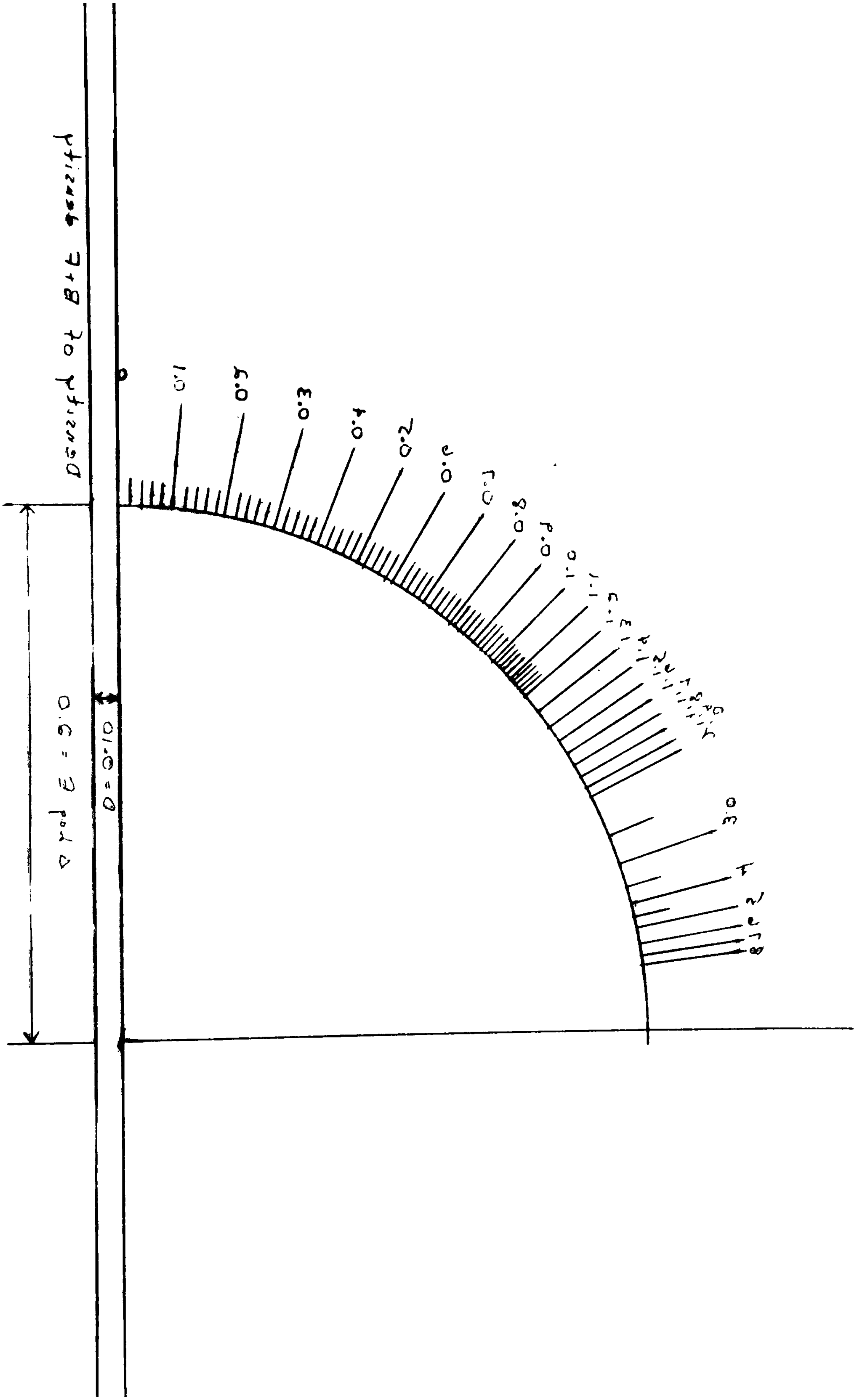


FIG. X


TIME VARIATION
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
DENSITY
0
.3
.6
.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3
3.6
3.9
4.2
RELATIVE LOG EXPOSURE
2
1
NO. GRADIENT MAXIMUM DENSITY TIME
1 1.11 2.82 30 sec.
2 1.53 3.10 60 sec.
RELATIVE SPEED
400
500
KODAK TYPE 8430
LAMP EG&G
EXPOSURE TIME 1/1000
ATTENUATOR 1/100
TEMPERATURE 68°F
DEVELOPER PL-1*
PROCESSING METHOD ASA STANDARD



Density of B+E density
Δ rod E = 9.0
D = 0.10