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A METHOD OF ANALYTICAL DYE DENSITOMETRY UTILIZING INFRARED RADIATION

To: Senior Project Committee

by
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Rochester Institute of Technology
Rochester, New York

May 17, 1958

Senior Project Committee
Photographic Science Division
Rochester Institute of Technology
Rochester, New York

Attention: Mr. H. Todd

Gentlemen:

As a fulfillment of an assignment, due on May 23, 1958, concerning the writing of a report on my research project, I am submitting the enclosed report.

This report is intended to treat, as completely as presently possible, a densitometric technique for negative-positive color films and to outline, generally, an associated project which is now being performed by use of the aforementioned technique.

I should like to express my appreciation to Messrs. Hollis Todd, William Shoemaker and William Vogelsong for their constructive criticism rendered during the course of this work.

Yours truly,

Calvin H. Besore

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ABSTRACT

A densitometric technique is described which yields analytical dye densities from a negative-positive color print film in a time less than would normally be required to process the film. In this technique, a correlation is established between the dye density produced by the complete process and the silver density produced by the initial development, the latter being determined by an application of infrared densitometry. Equipment utilized and procedure followed are described and some theoretical aspects and limitations reviewed.

INTRODUCTION

In an experimental situation, one of the greatest limiting factors is the time per unit required for data collecting and, of course, the cost of this time.

The purpose of the present work is to illustrate a method of color densitometry which has, as one advantage, the capability of reducing the time required for data collection during some types of experimentation on color materials. The present work will consider the method's application to high contrast negative-positive color print films only.

THEORETICAL CONSIDERATIONS

Our present systems of color photography are based upon a production of dye by the oxidation products of the developer. Since the oxidation products result directly from the development of the silver image, a linear relationship would be expected between the grams of dye per unit area formed and the corresponding mass of silver per unit area. This linearity is quite well approximated in actual practice.

However, if a correlation is attempted between the densities of the corresponding dye and silver images, the relationship can not be so simply explained. Neglecting possible effects resulting from an other absorber's presence, a proportionality would seem to exist between analytical dye density and the amount of dye present.[1] This same comparison, however, can not be made concerning silver density and the mass per unit area of silver present. Since the density of the silver particle is dependent upon the surface area and the amount of oxidation products is dependent upon the mass, some deviation from linearity might be expected. For example, if one were to assume a specific geometric shape of particle at a given size, an equation would show an exponential relationship between area and mass and, hence, between silver density and dye density. An example of this would be the assumption of a spherical particle which would lead to a relationship of $A = K(\text{mass})^{2/3}$ where A equals surface area. While the assumption of a specific particle shape and size is not valid in a photographic emulsion where many shapes and sizes are present, the foregoing is sufficient to illustrate the point that the relationship between area and mass is not linear (and, therefore, neither is that between silver density and dye density).

In addition, the effect of exposure upon the relationship of silver density and surface area should be noted. As the exposure on a given emulsion sample increases, the average grain size exposed decreases,[2] resulting in a relatively larger silver density than silver mass in accordance with the consideration that the smaller the particle, the greater is its relative surface area.

Of equal importance and a serious limitation upon any method utilizing a correlation between silver and dye density is the type of silver formed during development. Generally, in "chemical" development, the silver formed is filamentary in nature. However, development solutions promote, not only "chemical" development, but solution physical development as well, at a rate dependent upon the rate of solution of silver halides.[3] This physical development plates solid silver upon the filamentary form produced by chemical development, and result~~ing~~s in an increased mass of silver with little or no increase in optical density. Under conditions where physical development is promoted (as in developer solutions containing large quantities of sodium sulfite) any attempt at correlation between silver density and mass (and, therefore, between silver and dye density) is sure to magnify experimental error.

METHOD

Basically, the method to be proposed may be broken down into five steps. These are:

1. Production of special sensitometric control strips in which each of the three layers is represented by a separate series of densities.
2. Establishment of correlation curves between the dye and silver densities.
3. Following development and fixation (hereafter referred to as interrupted processing) of the negative color material, the resultant combination silver and dye strips are read on a densitometer which has been equipped for infrared radiation readings. Since the wavelengths utilized are so selected that the dyes show no significant absorption, the resultant silver density alone is obtained here.
4. Utilizing the results of steps 2 and 3, dye densities are predicted and from these predictions, standard integral densities are plotted.
5. Evaluation of curves obtained is the final step.

PROCEDURE

Step #1

The production of the special control strips was accomplished on an

Eastman Kodak Model 101 sensitometer with a specially constructed step wedge. The wedge itself was constructed of one wedge - three inches wide and consisting of fourteen steps - divided lengthwise into three sections, one section for each layer exposure.

Filtration overlays were:

1. For red sensitive layer exposure - Wratten #70
2. For green sensitive layer exposure - Wratten #16 and #61
3. For blue sensitive layer exposure - Wratten #47B and #2B

With the Ektacolor Print Film utilized in this experiment, some difficulty was experienced in producing a magenta dye image free of cyan dye. This occurred due to the overlap of sensitivity in regions of high exposure (Fig. 2). By limiting the exposure to that producing a maximum magenta density (by green filter) of 2.70, no cyan dye could be detected visually. A subsequent evaluation of the layer density by red filter supported the assumption that any cyan dye in the upper exposure level regions was present, if at all, in amounts below the sensitivity of the densitometer utilized. Additional filtration was then added to produce approximately equal complementary filter densities for the seventh step of each layer. Control strips were then made.

Step #2

Eight runs of control strips were then accomplished. In each run, the strips were carried through the darkroom procedure according to recommended processing conditions. Prior to removal from the darkroom, each strip was split in such a manner as to yield two individual strips from each layer exposure. One-half of each layer strip was carried through the complete process. The remaining one-half was fixed in C-22 fixing bath

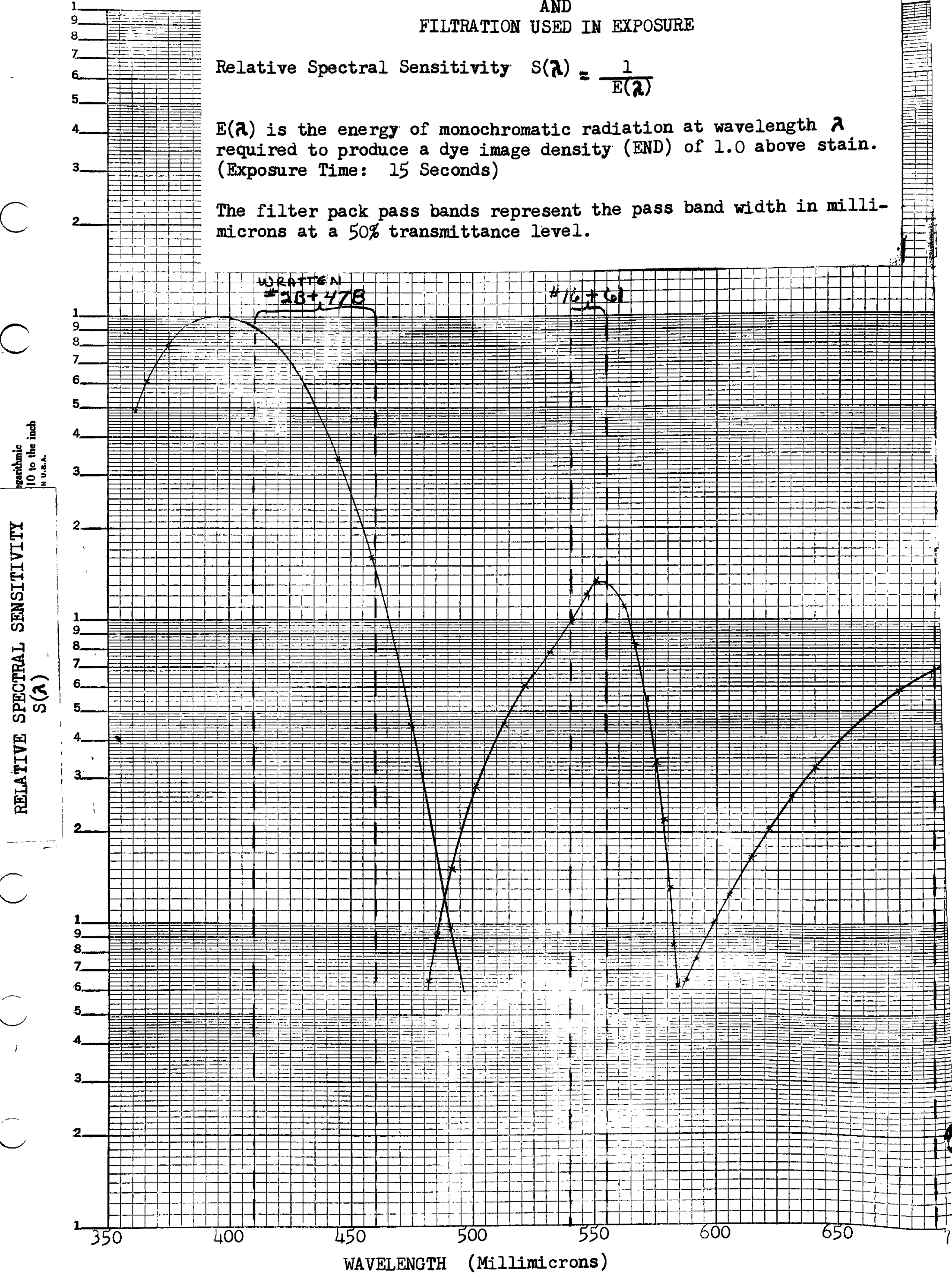
FIGURE

RELATIVE SPECTRAL SENSITIVITIES OF KODAK EKTACOLOR PRINT FILM
AND
FILTRATION USED IN EXPOSURE

Relative Spectral Sensitivity $S(\lambda) = \frac{1}{E(\lambda)}$

$E(\lambda)$ is the energy of monochromatic radiation at wavelength λ required to produce a dye image density (END) of 1.0 above stain. (Exposure Time: 15 Seconds)

The filter pack pass bands represent the pass band width in millimicrons at a 50% transmittance level.



for five minutes, washed and dried.

The dye densities of the completely processed strips were read by complementary filters on a Welch Densichron. The interrupted processing strips were read on a Welch Densichron equipped with an infrared probe and a Wratten 87C filter. The pass band of this filter in the visible region was found to be in a range of insignificant probe sensitivity and in the upper pass band (800mu and up) the dyes showed no significant absorption.

By plotting corresponding pairs of strips against one another (i.e., silver density vs. dye density), correlation curves were obtained.

RESULTS

The correlation curves for the particular emulsion type and number utilized in the development of this method and a subsequent experiment are presented in Fig. 1. The varying mark sizes represent the limits of the population of the eight replications at a 0.05 confidence level (95% probability); the crossing of the two lines represents the mean of this population. A sample calculation is shown in Table #1.

The deviations from linearity predicted by consideration of the theoretical bases were found. A fitting of the curves by matrix algebra yielded approximate fits in the form of quadratic equations as noted below:

$$D_R \text{ (cyan)} = -4.915 + 11.751\ D_{(AG)} - 4.054\ D_{(AG)}^2$$

$$D_G \text{ (magenta)} = -2.050 + 4.725\ D_{(AG)} - 1.125\ D_{(AG)}^2$$

$$D_B \text{ (yellow)} = -2.294 + 6.074\ D_{(AG)} - 2.238\ D_{(AG)}^2$$

The varying curvatures represented in the three curves present an

FIGURE 1

RELATIONSHIP OF SILVER DENSITY AND DYE DENSITY IN EKTACOLOR PRINT FILM - EMULSION #N6105-135-2

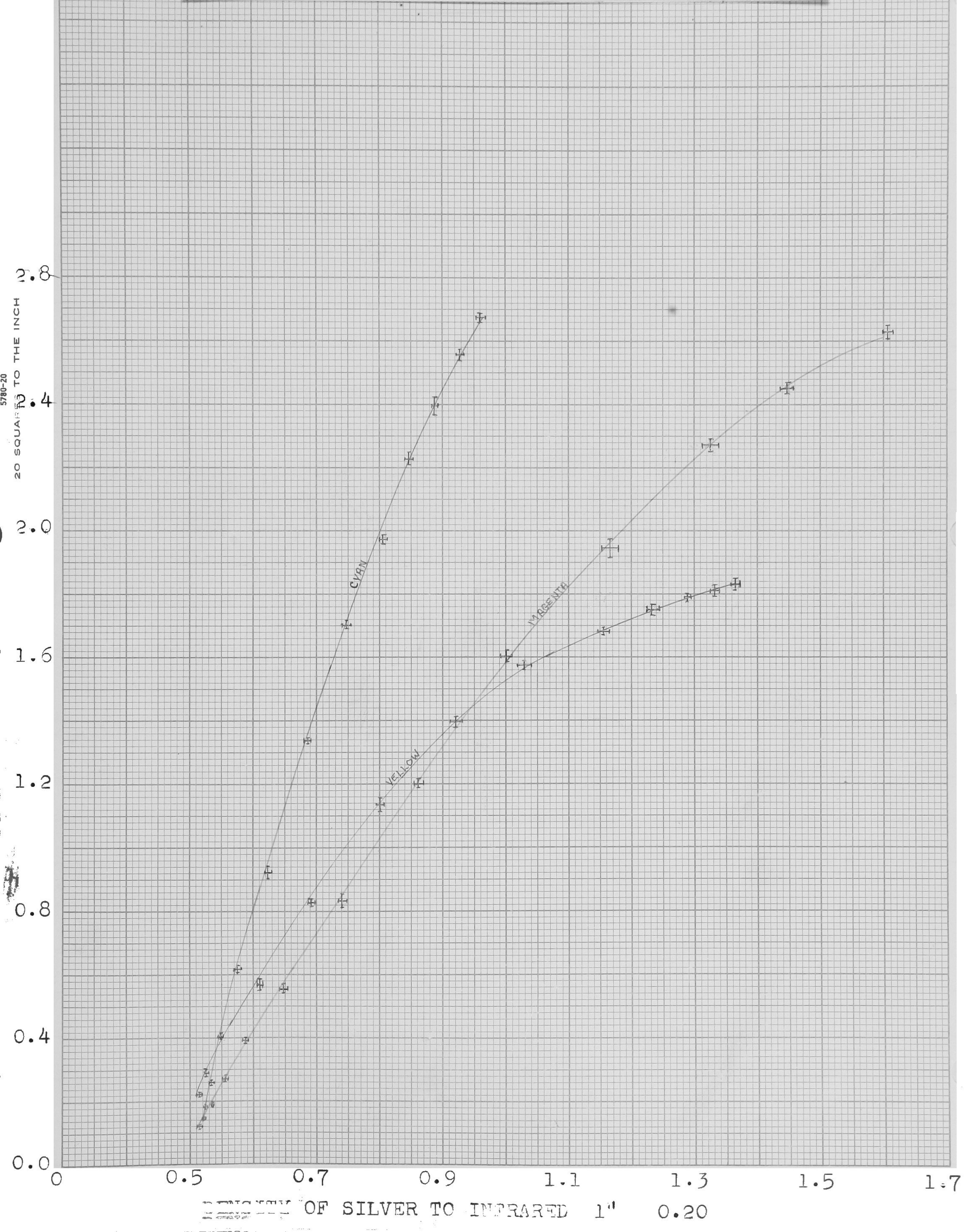


TABLE I
SAMPLE CORRELATION MEAN AND CONFIDENCE LIMIT CALCULATIONS
STEP THREE - MAGENTA DYE

DYE (ORDINATE) VALUE

Run No.	Dye Density	$\bar{X}$	σ^2	$\pm t \frac{\sigma}{\sqrt{N}}$ [1]	Ordinate Value and Ordinate Limits
1.	0.28	0.271	15.6×10^{-5}	9.0×10^{-3}	0.271 ± 0.009
2.	0.27				
3.	0.25				
4.	0.27				
5.	0.29				
6.	0.27				
7.	0.28				
8.	0.26				

CORRESPONDING SILVER (ABSCISSA) VALUE

Run No.	Silver Density	$\bar{X}$	σ^2	$\pm t \frac{\sigma}{\sqrt{N}}$ [1]	Abscissa Value and Abscissa Limits
1.	0.57	0.564	7.0×10^{-5}	6.0×10^{-3}	0.564 ± 0.006
2.	0.57				
3.	0.56				
4.	0.56				
5.	0.56				
6.	0.57				
7.	0.56				
8.	0.56				

[1] Student "t" value at 0.05 level.

interesting problem for further study. However, a possible reason for the flat shoulder of the yellow dye curve might be that a reduction of the yellow dye component (to conteract unwanted absorptions of the other dyes) had been introduced.

Use of this method in an experimental investigation of agitation effects on a color material yielded statistically significant results at a high level of probability and at the same time reduced processing laboratory time by sixty percent. In addition, the simplicity of reading all three layers by use of one infrared filtration further reduced the time required in densitometric work.

Of equal importance was the ability to disregard, in the design of the subsequent experiment, the variations attributable to temperature change, changes in chemical composition and agitation effects introduced by the usually included steps of the color process past those at which interrupted processing had been accomplished.

Extension of this method to other types of color materials will be dependent upon the user's ability to produce sensitometric control strips with a good approximation of individual layer exposures.

ACKNOWLEDGMENTS

The author desires to express his appreciation to Messrs. Hollis Todd, William Shoemaker and William Vogelsong for their constructive criticism rendered during the course of this work.

REFERENCES

1. Mees, C. E. K., *Theory of the Photographic Process*, *rev*. *ed*., Chap. 25. The Macmillan Co., New York (1954).

2. Sheppard, S. E., and Trivelli, A. P. H., *J*. *Franklin Inst*., Vol. 203, p. 829 (1927).

3. James, T. H., *Photographic Science and Engineering*, Vol. 1, p. 143 (1958)

The investigation from which the foregoing paper evolved was designed to yield, in addition to the densitometric method, information concerning the influence of variations in nitrogen burst agitation upon the degree of development of the individual color film layers. The following section shall present a limited outline of this project; a more detailed paper to be initiated when the experimental errors noted in this section have been corrected.

METHOD

As previously noted, the investigation was designed to yield information concerning the degree of development variations for individual color film layers resulting from variations in nitrogen burst agitation. In order to accomplish this, a three factor, three level replicated experimental design (Table Ib) was instituted which considered variables of burst duration, burst pressure, and time of development. The inclusion of development time served two purposes:

1. It was hoped that a set of development conditions could be determined for the burst apparatus which would allow production of results at the level specified by the manufacturer.
2. The time of development provided a known effect and, in this manner, served as a reference to the reliability of the data collected and the methods used.

By introducing the use of an electronic temperature control unit (Fig.Ib) with tolerances ranging in the 0.1° Centigrade level, the variable of temperature was considered to be insignificant.

Sensitometric strips of the kind mentioned in Section A were given

DESIGN OF EXPERIMENT

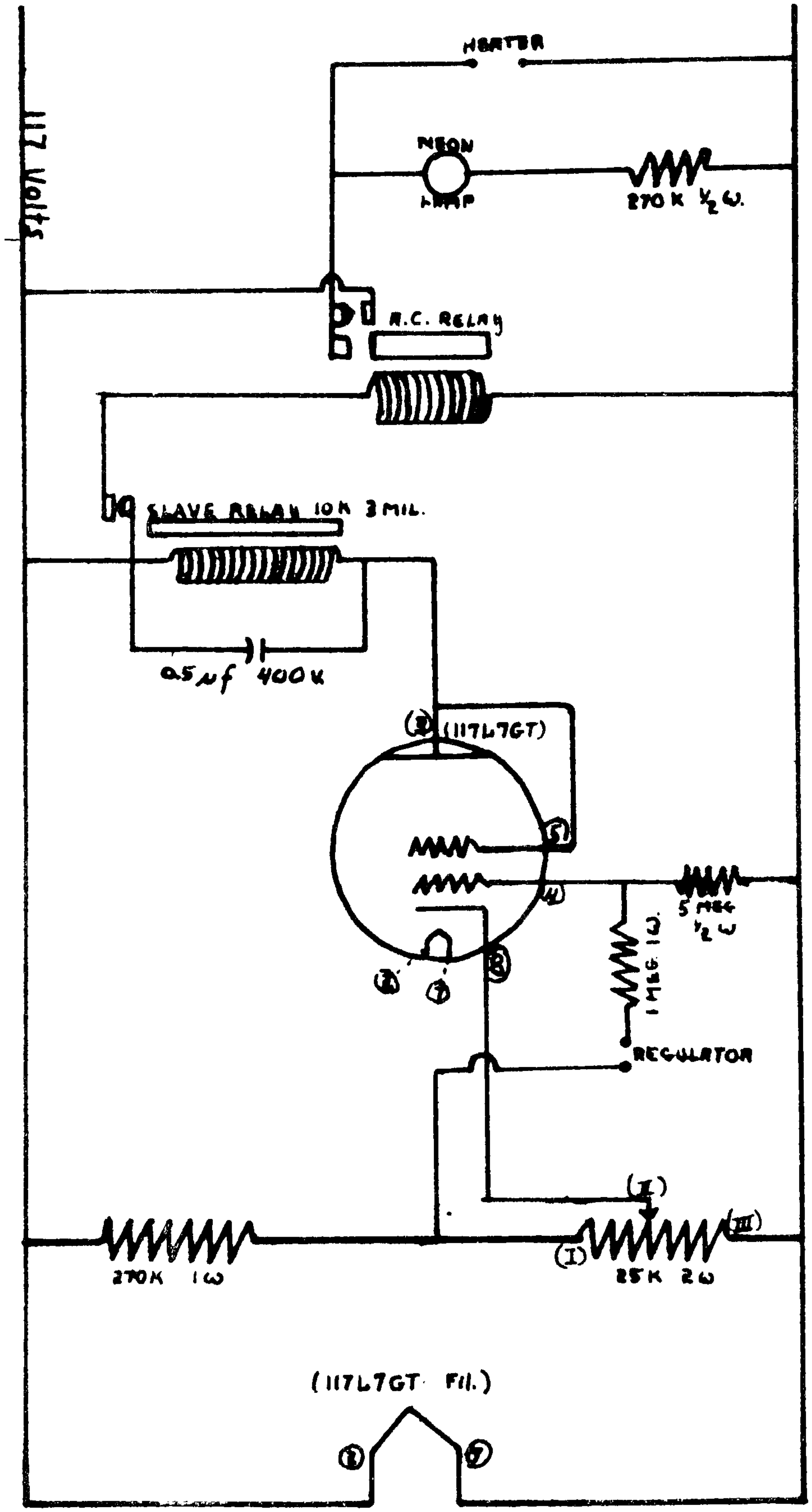
TIME I									TIME II									TIME III								
PRESSURE I			PRESSURE II			PRESSURE III			PRESSURE I			PRESSURE II			PRESSURE III			PRESSURE I			PRESSURE II			PRESSURE III		
B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3
X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3	X_1 X_2 X_3

Where: B is the burst duration

X is a sample run

FIGURE Ib

TEMPERATURE CONTROL UNIT



interrupted processing in accordance with the levels in the experimental design and a series of eighty-one dye curves predicted by the use of these strips. (Fig. IIb)

The degree of development designation was chosen as the slope of a straight line connecting the intercepts of a D Log E curve at the density levels of 0.6 and 1.4. Gradient determination was then made for each of the curves. This particular method of determining a gradient was chosen rather than a fixed Log E range in order to:

1. Minimize the effect of any speed change upon the gradient.
2. Utilize the maximum length of approximately linear curve portions while maintaining a consistent method for determining the gradient of the three different curves.

Analyses of variance were then completed for the three layers.

DISCUSSION OF RESULTS

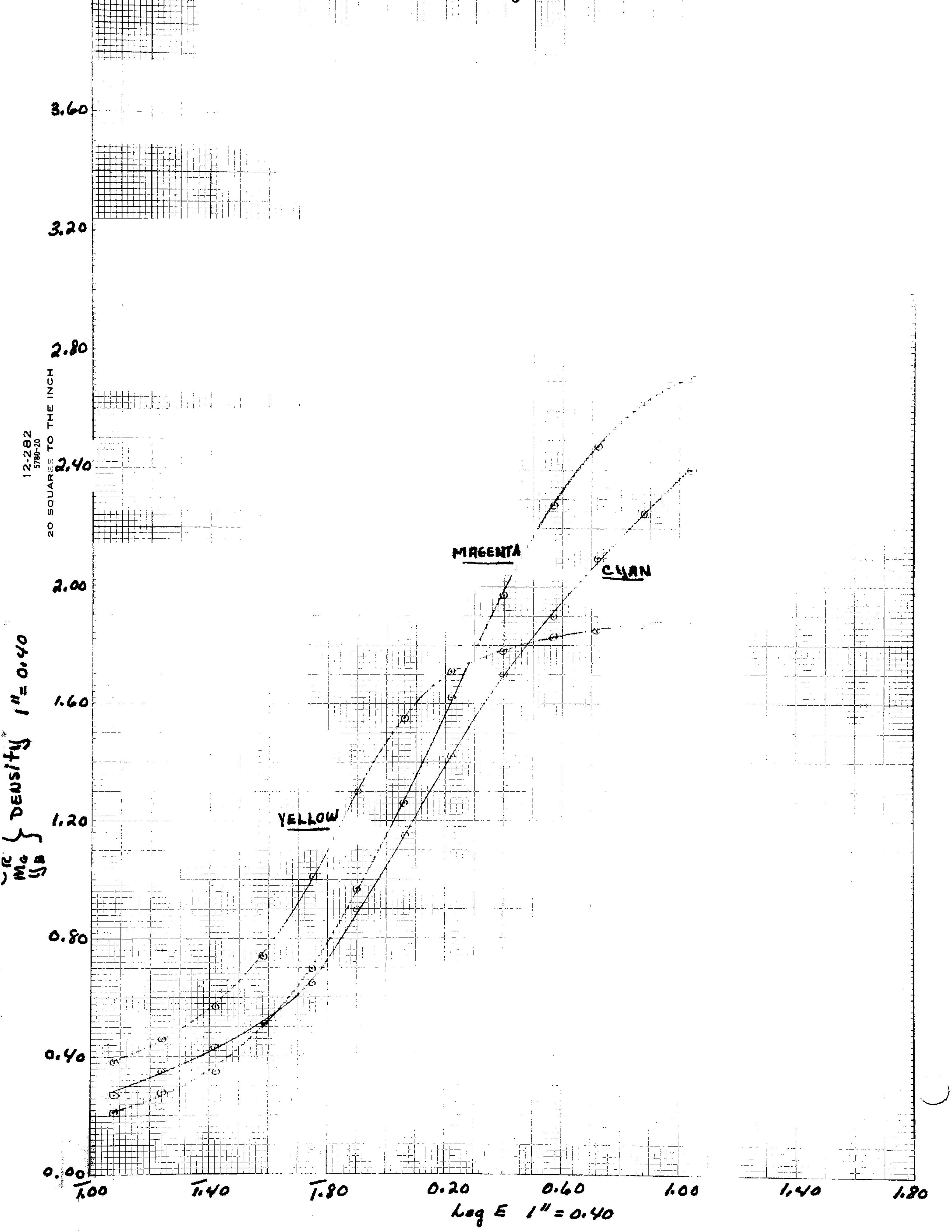
Significant levels of variation were found to be present in all three layers for the pressure and time variations. However, upon plotting the trends, a maximum point was noted in a development time versus gradient plot for the magenta layer at a mean development time and a similar plot for the yellow layer indicated a constantly decreasing gradient with increasing time of development.

A visual comparison of the curves indicated that this effect was the result of the type of gradient measure (at a fixed density level) being influenced by a changing fog level on the film and, hence, the gradient, at times, decreased. Other factors may also be affecting this single value measurement.

For this reason, it will be necessary to re-evaluate the data collected

FIGURE II b.

SAMPLE PREDICTED DYE CURVE



in terms of one or more different statistical values in order to adequately treat the data obtained.

AN ADDITIONAL PROBLEM

Despite the use of the aforementioned temperature control unit in a water bath, a temperature change was noted in the development solution over a fourteen minute development period. In some cases, this change exceeded the tolerances published by the film manufacturer. Preliminary investigations suggest that this temperature change is the result of heat absorption by expanding nitrogen at a rate greater than the rate of heat transfer across the hard rubber tank from the controlled water bath. The investigation of this effect is being continued.

ADDITIONAL PROJECT DATA

Total hours required	218½
Total expenses	$195.32