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Dye Sensitization of a Photothermographic Emulsion

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DYE SENSITIZATION
OF A
PHOTOTHERMOGRAPHIC EMULSION

A THESIS

SUBMITTED TO THE PHOTOGRAPHIC FACULTY

OF

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BY

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Abstract

The objective of this paper is to sensitometrically evaluate the effect of five sensitizing dyes (Acridine Orange, Pyronin B, Thionin, Erythrosin B, and Pinacyanol) on a photothermographic emulsion containing a 43-7-50 mole % ratio of mercurous oxalate, mercurous iodide, and silver iodide. The choice of dyes was based on their ability to sensitize into the longer wavelength region of the visible spectrum. Three concentrations of dye were used - 50, 100, & 200 micromoles per liter of emulsion.

The sensitometric evaluation was based on the exposure of a neutral step wedge to tungsten light. . The parameters investigated are those of relative speed, slope, maximum and minimum density, plus the effect of coating thickness on these factors.

Background

Photothermography is a non-silver halide imaging system with a heat and light-unstable emulsion which is developed upon heating. An interesting aspect of photothermography is its apparent lack of recorded development.[1] Most of the available information is derived from patent literature and several articles in professional journals. Present day textbooks and references volumes on photography make little or no mention of the process or its background.

The earliest reference to photothermography is a French Patent[2] issued to Kodak Pathe' in 1932. Sheppard and Vanselow were issued patents in 1934, 35, and 37[1,3,4] describing several different photothermographic emulsions.

The work done by Paul A. Van der Meulen and his associates at Rutgers University is the basis for the work described in this paper and is typical of the research done in photothermography. Van der Meulen and R. C. Countryman prepared several of the emulsions suggested by Sheppard and Vanselow[4] and coated them on glass microscope slides. These slides were then exposed by a Lab Arc, one meter distant and then heated in an oven to develop the image. Comparable densities were obtained from the slides and the exposure times required to produce them were used as a measure of the relative sensitivity.

They found that mercury and silver salts gave better images than those of any other cation examined. The oxalates were superior to other anions and the formates were very unstable. Mercurous oxalate seemed to be the most sensitive compound and was examined in greater detail.

Mercurous oxalate may be prepared by adding mercurous nitrate solution containing a small amount of nitric acid to a solution of potassium oxalate, and the resulting insoluble precipitate formed is mercurous oxalate. Caution is necessary however, for rapid heating of the substance would cause an explosion.

Studies were made on the decomposition of mercurous oxalate upon heating. X-Ray powderphotographs show no change in patternas this reaction proceeds. This indicates that the only decomposition products are carbon dioxide and metallic mercury.[1]

Mercurous oxalate emulsions may be coated on film base, glass, or paper to produce a negative image. Mercurous oxalate is considerably less sensitive than conventional silver halide emulsions and Robert H. Brill[5] notes this to be the result of two main factors:

1) The photothermographic process appears to be less efficient by its nature than the silver halide process.
2) The inherent sensitivity of mercurous oxalate lies in the ultraviolet region and there is little, if any, natural sensitivity to the visible region, which is of course the most interesting for the photographic process.

In recent years, the basic photothermographic emulsion has been modified in an attempt to increase the sensitivity. Two substances, mercurous and silver iodide, were chosen because of their photosensitivity and because mercurous iodide absorbs visible light. This represents work done in the field of sensitization by Van der Meulen, Gilman, and Vaughan at Rutgers University.[6,7] Although silver iodide does not sensitize the photothermal decomposition of mercurous oxalate it does increase the sensitizing action of mercurous iodide.

An interesting sidelight was found in testing these emulsions by Gilman, Vaughan, and Van der Meulen.[6] Their results show that mercurous emulsions sensitized with mercurous iodide or mercurous and silver iodide were very sensitive print-out systems.

Van der Meulen and R. Countryman examined the spectral sensitivities of a mercurous oxalate emulsion sensitized with mercurous iodide, silver iodide, and an emulsion sensitized with mercurous iodide only. They found that the spectral sensitivities were almost identical and were very similar to the reflectance spectrum of mercurous iodide. Therefore the sensitization is probably due to absorption of light by mercurous iodide and the increased efficiency of the photolysis of this compound by the silver iodide.[6]

Experimental Procedure

Studies made by Dr. Paul Gilman indicate that the three-component emulsion would be suitable for further testing.[6] This emulsion is a very recent development in the area of photothermography and no attempt has previously been made to sensitize it by using dyes. The ratio of the components used were: 43-7-50 mole % of mercurous oxalate, mercurous iodide, and silver iodide. The findings of Dr. Gilman indicate that this is the emulsion containing the greatest inherent sensitivity.

The choice of dyes was based on work done by Robert H. Brill,[5] Van der Meulen,[1] and Countryman[1] with sensitizing dyes on the basic mercurous oxalate emulsion. Only those dyes were tested which were rated as "strong" sensitizers and whose sensitization extended into the longer wavelength region of the visible spectrum.[1,6]

A sensitometric evaluation of the sensitized emulsion shows the relative effects of each of these dyes in terms of maximum and minimum density, relative speed, and slope.

One-hundred milliliter samples were taken from a 2000 gram batch of emulsion to which the dyes were added. The following amounts were used in preparing the emulsion: 1) 21 grams of recrystallized mercurous nitrate dissolved in 250 milliliters of water plus 12 milliliters of 6N nitric acid; 2) 104 grams potassium oxalate dissolved in 32 milliliters of water; 3) 6.4 grams of silver nitrate dissolved in 300 milliliters of water; 4) 8 grams of potassium iodide was dissolved in 300 milliliters of water; and 5) 75 grams of gelatin.

The dyes were added to the samples in 50, 100, and 200 micromoles/liter of emulsion concentrations.

The preparation of the emulsion was based on the procedure as outlined by Dr. P. D. Gilman.[6]

In preliminary tests, using the unsensitized emulsion, it was found that the coating thickness had to be distributed very evenly. A coating machine was employed to obtain this required uniformity. The coatings were made on clear acetate film base at the concentration 0.06 milliliters/ square inch (the maximum for the machine). These were thoroughly dried by storing in a refrigerator for several days.

To show the difference due to coating thickness, samples were coated on glass plates (total area - 12 square inches) with 6 milliliters of emulsion. This was done by pouring the emulsion at 35 Degrees Centigrade onto the plate - "swirling" it evenly over the plate and cooling it on an inverted tray (levelled) filled with ice cubes. These were also allowed to dry thoroughly in a refrigerator.

The exposure was obtained by a high intensity tungsten bulb, a 375 Watt reflector-flood lamp (Sylvania Reflector SuperFlood - R32) an aluminum reflector which was suspended 6.5 inches above the plane of the sample. The heat formed by the lamp was dissipated by directing a small fan onto the sample throughout the exposure. The sample to be exposed was positioned emulsion up and a Kodak Step Tablet #2 was placed in contact with it. This was covered by a thin plate of glass.

Development was obtained by an ordinary household iron mounted in an inverted position on a ring stand. The current was controlled by a variable rheostat. Temperature control was maintained by a mercury thermometer placed in contact with surface of the iron near its center. At a reference temperature of 100 Degrees Centigrade, the variation during development was maintained at plus and minus 2 Centigrade Degrees. The time of development was 4 minutes in all cases at the reference temperature.

To develop the emulsion, the film base samples were placed between two thin glass plates, hinged together to hold the sample flat and in contact with the iron. The glass plate samples were laid on the surface of the iron for the required time without any modification.

The densities recorded from the samples were made with a Welch Densichron Densitometer with transmitted light and the #94 blue filter in place. Density, as a function of relative log exposure, was plotted to show the contrast, relative speed, and the maximum and minimum density of the materials. In the cases where there were no visible steps, only the maximum and minimum density areas were recorded (Table I).

Contrast (slope) was calculated by:

$$\text{Slope} = \frac{\Delta D}{\Delta \text{Relative Log E}}$$

The speed is the log exposure change for a fixed reference density (step 15), where:

$$\text{Speed} = \text{Antilog}\,\Delta\,\text{Log E}$$

Results

The data obtained from these tests is presented in figures 1 thru 6 and is summarized in Table I.

Because of the extremely low range of densities as shown in Figure 6, no graphs were drawn on several of the samples.

To check on the effect of combination of dyes, the 100 micromole concentrations of Acridine Orange and Erythrosin B, both of which show no step-wise gradation and have low density ranges, were chosen. Table I shows that the resulting density range of the sample, 0.20, approaches the sum of the two individual ranges and the relative speed reached 27.5. This indicates superadditivity.

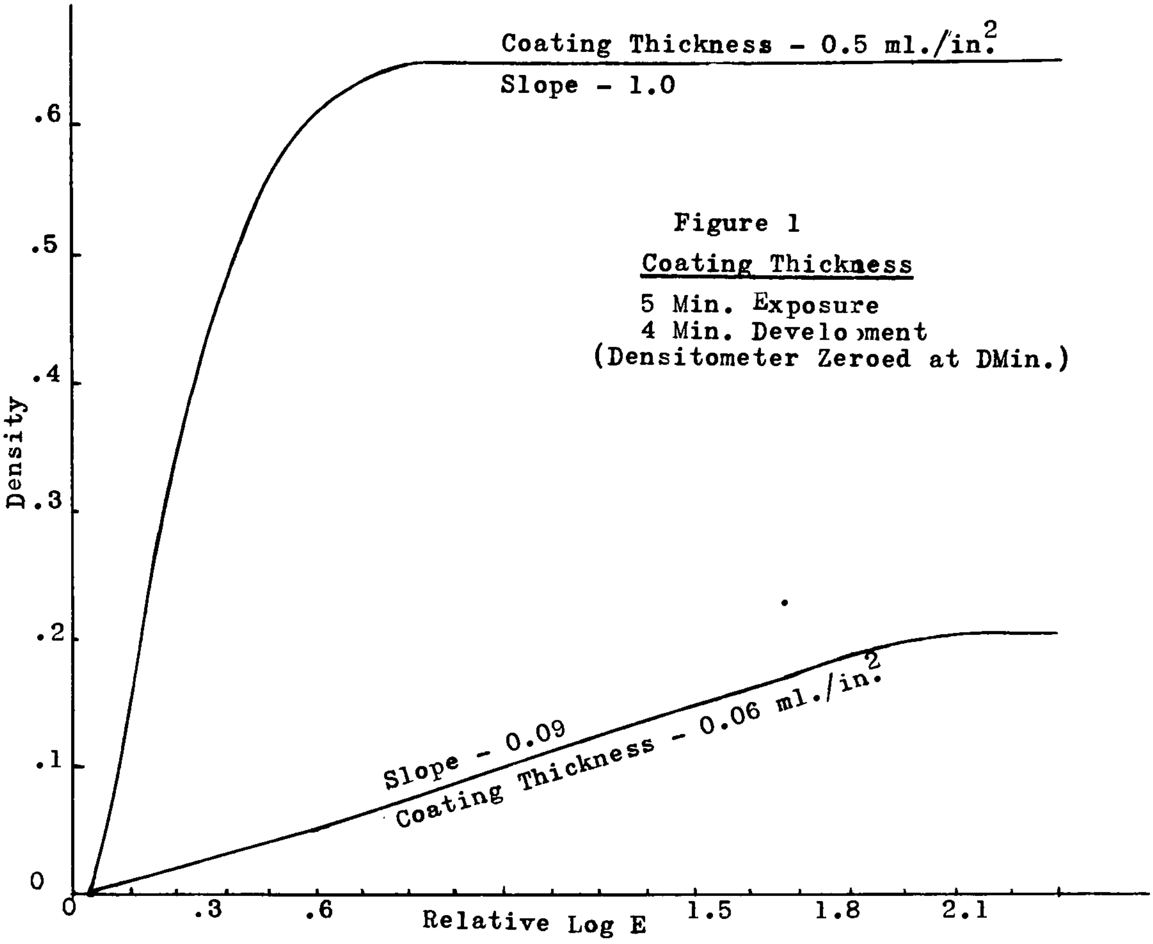


Figure 1

Coating Thickness

5 Min. Exposure
4 Min. Develo)ment
(Densitometer Zeroed at DMin.)

TABLE I

DYE	CONCENTRATION (µmoles/liter emulsion)	MINIMUM DENSITY	MAXIMUM DENSITY	Δ D	(Fixed D) SPEED	SLOPE
Thionin	50	0.22	0.56	0.34	4.2	0.10
	100	.33	.60	.27	132	.09
	200	.13	.28	.15	-	-
Acridine Orange	50	.26	.61	.35	76	.26
	100	.15	.26	.14	-	-
	200	.28	.46	.18	5.0	.04
Erythrosin B	50	.42	.37	.04	-	-
	100	.15	.41	.08	-	-
	200	.28	.49	.06	-	-
Pinacyanol	50	.26	.47	.11	-	-
	100	.30	.41	.11	-	-
	200	.28	.49	.21	3.3	.06
Pyronin B	50	.32	.47	.15	-	-
	100	.16	.22	.06	-	-
	200	.18	.32	.14	-	-
Erythrosin B & Acridine Orange	100	.30	.50	.20	27.5	.10
No Dye	-	.19	.41	.22	1.0	.09

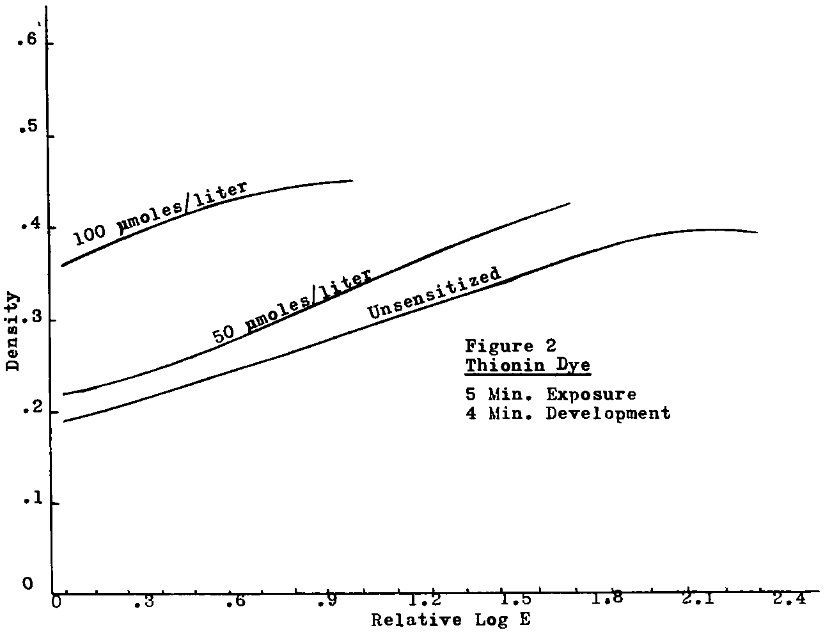


Figure 2
Thionin Dye
5 Min. Exposure
4 Min. Development

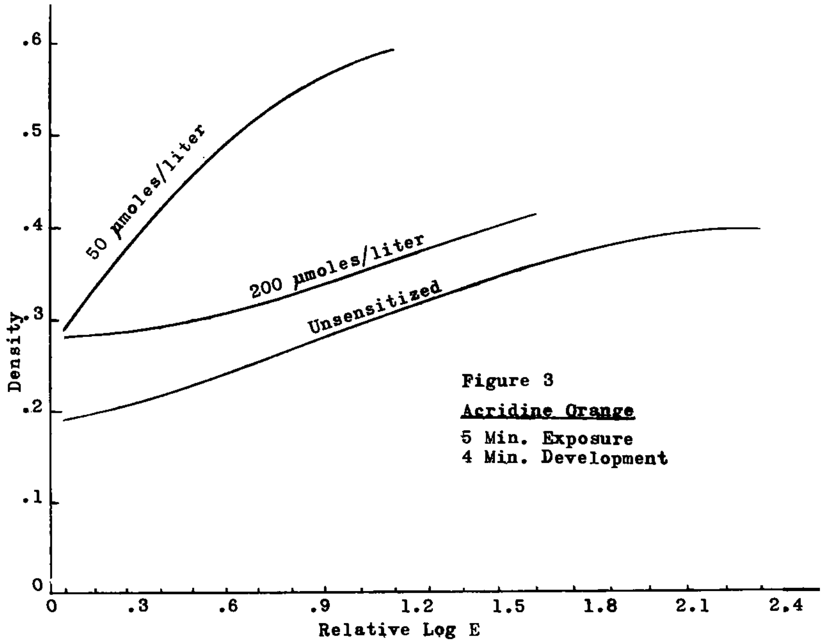


Figure 3
Acridine Orange
5 Min. Exposure
4 Min. Development

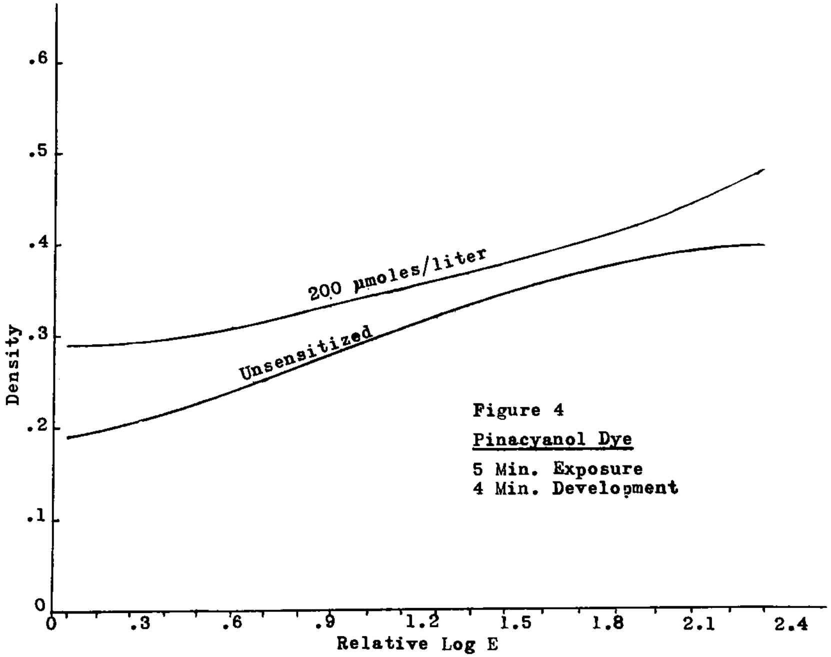


Figure 4
Pinacyanol Dye
5 Min. Exposure
4 Min. Development

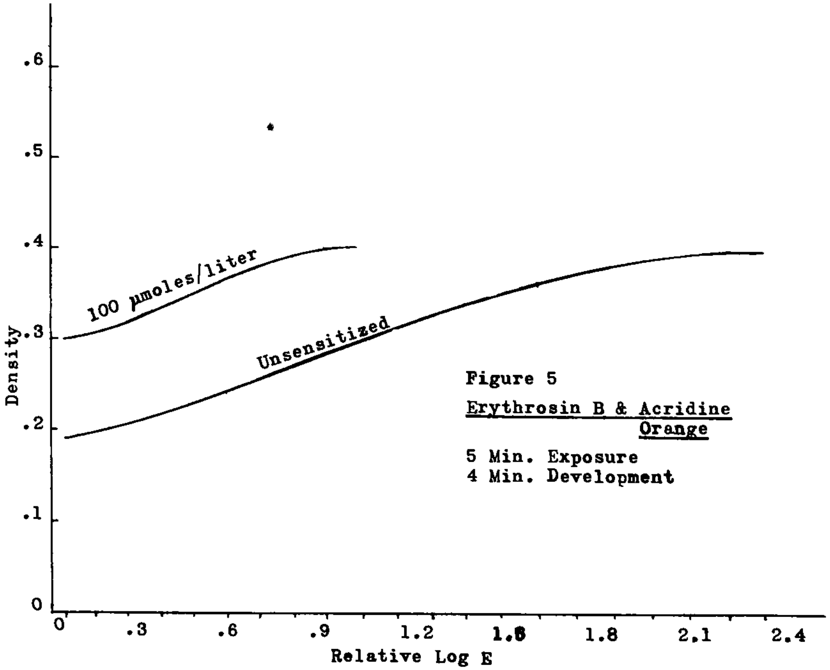
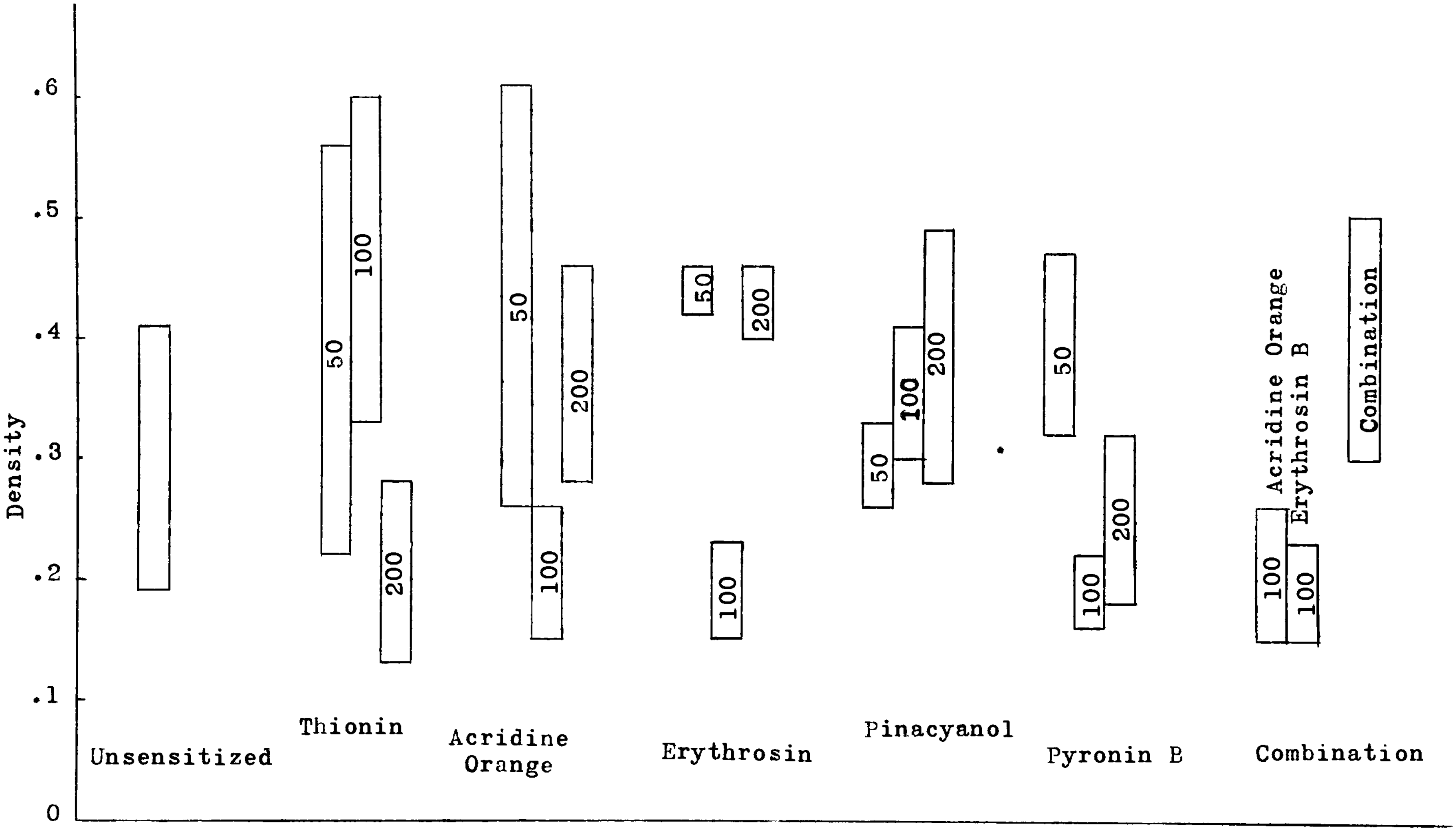


Figure 5
Erythrosin B & Acridine Orange
5 Min. Exposure
4 Min. Development

Figure 6

Density Range vs. Dye Sample

Numbers in Bar indicate
µmoles/liter emulsion



Summary

The appearance of the unexposed emulsion is a bright yellow which turns black on decomposition. The image is therefore a gradation of tones between the bright yellow and black.

From visual examination of the samples, the image quality is relatively poor. The contrast of the image is very low and barely visible on the thin emulsions. The image was more easily seen as the thickness of the emulsion was increased.

The dye producing the greatest increase in speed at the concentrations tested is Thionin. The dye producing a large increase in both speed and contrast is Acridine Orange.

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1. Van der Meulen, P. A. and Countryman, Robert C., "Photothermography", *Photographic Engineering*, Vol. 4, No. 2 (February 1953).
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3. U. S. Patent 2,095,839
4. British Patent 543,940
5. Brill, Robert H., *Studies of the Optical Sensitization and the Photothermal Decomposition of Mercurous Oxalate*, completed at Rutgers University (Doctorate Thesis), New Brunswick, N. J. August 1955.
6. Gilman, Paul B.,Vaughan, P. A., and Van der Meulen, P. A., "Photothermographic Sensitization of Mercurous Oxalate by Mercurous and Silver Iodides", *Journal Society of Photographic Scientists and Engineers*, Vol. 3, No. 5. (September - October 1959).
7. Van der Meulen, P. A. and Brill, Robert H., "Sensitization of Mercurous Oxalate by Dyes", *Journal Society of Photographic Scientists and Engineers*, Vol.2, No. 3. (October 1958).

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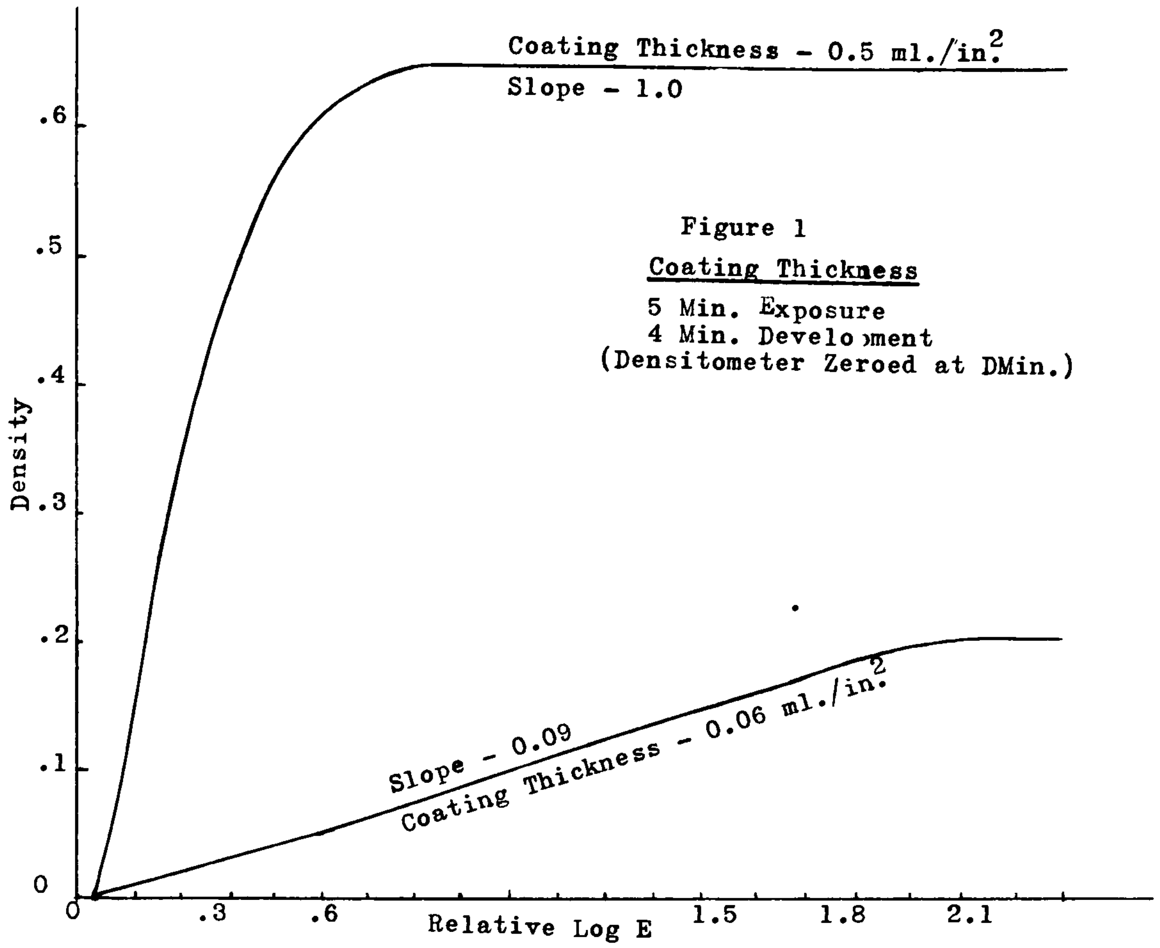

Figure 1

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Pyronin B	50	.32	.47	.15	-	-
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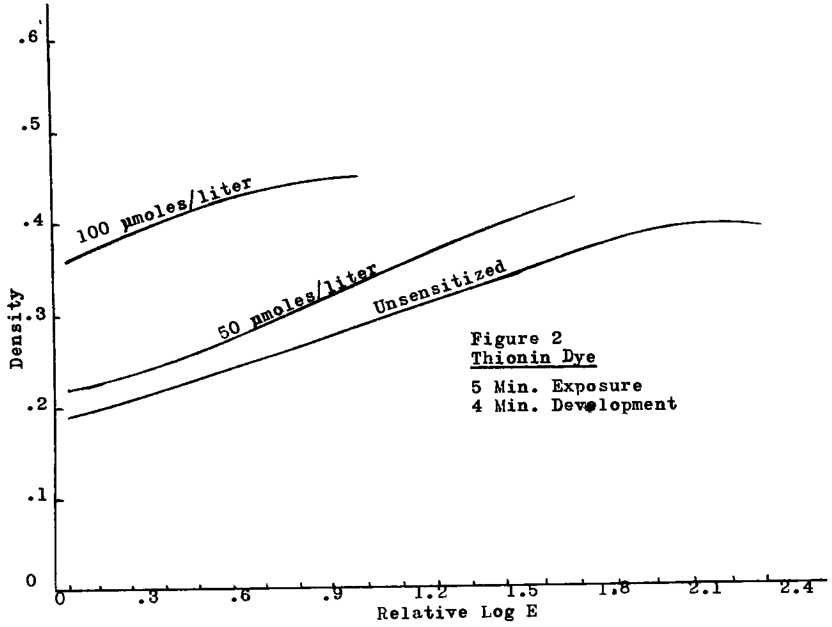

Figure 2
Thionin Dye
5 Min. Exposure
4 Min. Development

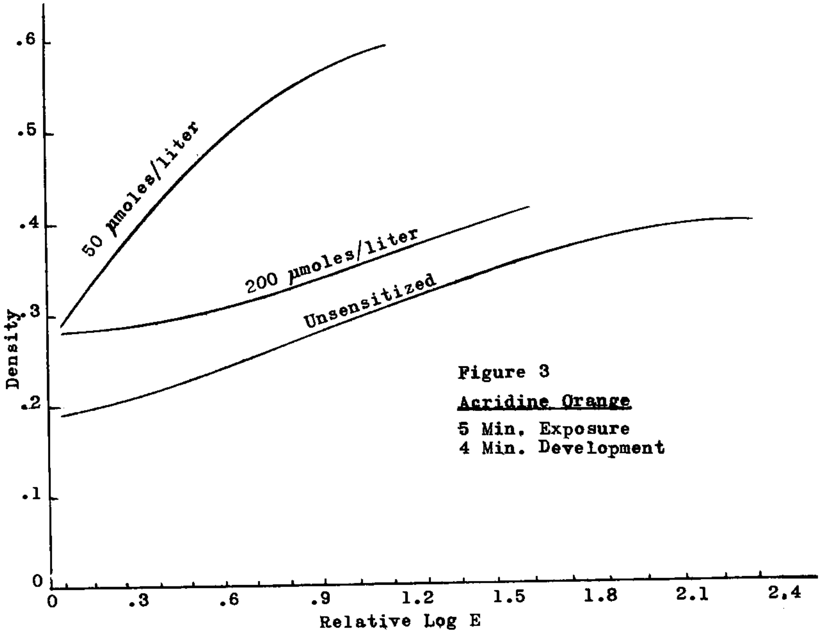

Figure 3
Acridine Orange
5 Min. Exposure
4 Min. Development

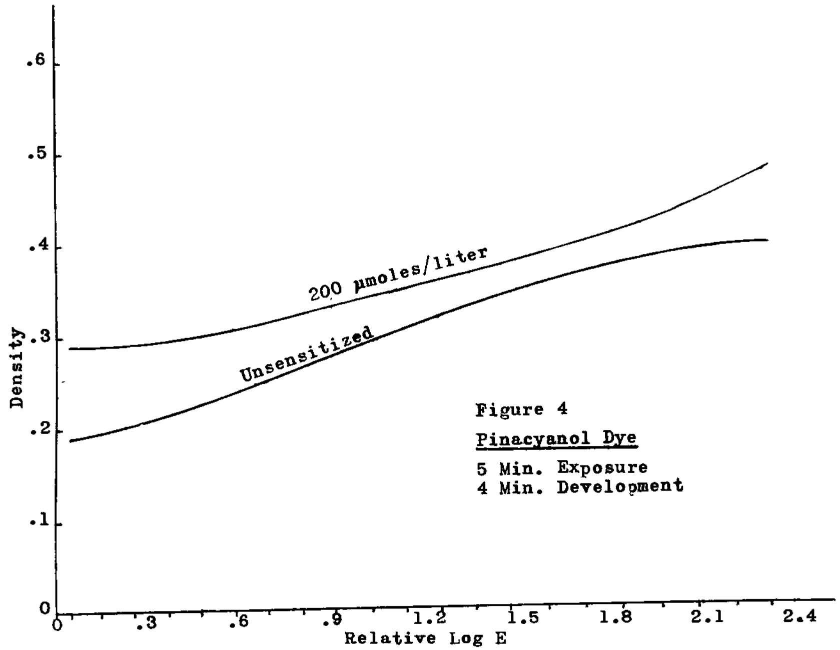

Figure 4
Pinacyanol Dye
5 Min. Exposure
4 Min. Development

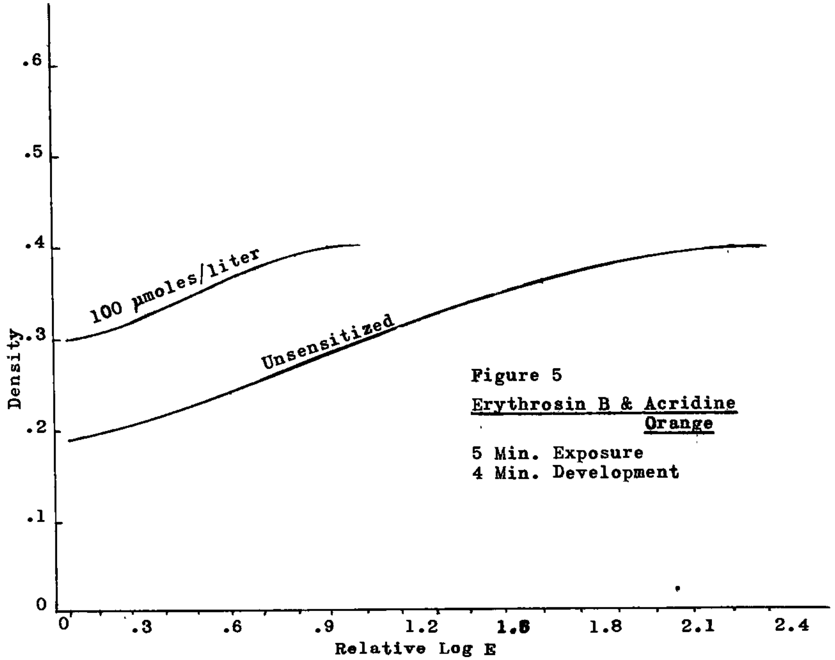

Figure 5
Erythrosin B & Acridine Orange
5 Min. Exposure
4 Min. Development

Figure 6

<u>Density Range vs. Dye Sample</u>

Numbers in Bar indicate
μmoles/liter emulsion