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# The stability of reciprocity law failure in color print papers

Victoria L. Carriero

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THE STABILITY OF RECIPROCITY LAW FAILURE  
IN COLOR PRINT PAPERS

by

Victoria L. Carriero

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Bachelor of Science in the School of  
Photographic Arts and Sciences in the  
College of Graphic Arts and Photography  
of the Rochester Institute of Technology

April 1982

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Submitted to the  
Photographic Science and Instrumentation Division  
in partial fulfillment of the requirements  
for the Bachelor of Science degree  
at the Rochester Institute of Technology

ABSTRACT

A study of reciprocity law failure in Kodak Ektacolor 74 and 78 color print papers was carried out by a series of equal energy exposures. Using a color separating filter pack to differentiate the response of RLF of the individual emulsion layers, an acceptable color print is attainable by using these curves to determine exposure and filtration changes.

## ACKNOWLEDGEMENTS

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A special thank you to Bob and Arlene Green from Sentry Color Labs Limited, who generously supplied equipment, materials, and Saturdays for the completion of this thesis. Another thank you to their crew: Linda, Irene, Bob, Ray, George, Don, Peter, Molly, and Jane for their help and tolerance.

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## INTRODUCTION

The reciprocity law for photochemical reactions was formulated by Bunsen and Roscoe in 1862.<sup>1</sup> "They proposed as a general law for photochemical reaction the condition that the mass of the photoproduct from such a reaction is determined by the total exposure involved, that is, the product of the irradiance\* and time, and is independent of the two factors separately."<sup>2</sup> Any deviation from this law is called reciprocity law failure (RLF).

It is of great importance to those who use color photographic materials under varied exposure conditions to be able to compensate for RLF. In custom color printing labs, giant enlargements and murals are common. When making these enlargements, long exposure times are frequently used (over 30 seconds). Hence, RLF is a major problem.

There is no easy solution to this problem as no information is available on RLF for color print papers that would help make corrections for long exposure times.<sup>3</sup> This means that to obtain quality color prints at these longer exposure times, test prints must be made and repeated until the correct color balance and density is achieved. This can take many tries and

\*The term irradiance is used to describe the radiation flux incident on a plan which also has been called intensity. These words for this paper are used interchangeably.



and it consumes valuable time in manpower and throughput, not to mention the costs of wasted paper.

The stability of RLF between emulsion batches of Kodak Ektacolor 74 and 78 papers was investigated so to determine a means of correcting for density loss and color shifts that are inherent at longer exposure times. The ultimate intent here is to determine if these corrections can be made and the accuracy of them.

## BACKGROUND

When the reciprocity law is applied to the photographic process, it specifies only the amount of direct photolytic silver resulting from an exposure.<sup>4</sup> "A given mass of photographic silver can have different efficiencies in initiating development of a photographic material depending upon its location, its state of subdivision, and so on. That the amount of developed density in a processed photographic material should also be independent of irradiance and time individually is thus a condition beyond that originally intended by the Bunsen-Roscoe law."<sup>5</sup> This same terminology however, is used when talking about densities produced in developed photographic emulsions.

In photographic emulsions, the exposure is the product of irradiance and time ( $E=It$ ), but it is not independent of the intensity of exposing light.<sup>6</sup> For example, the density produced by an exposure of 100 meter-candles for 1 second and an exposure of 1 meter-candle for 100 seconds is not equal even though the exposures are equal.

The RLF of a photographic emulsion can be explained in terms of latent image formation. It occurs during either high-intensity, short-time or low-intensity, long-time exposures. Actually, RLF occurs at deviations from the "optimum" exposure time, which is the time that produces the maximum density at

a certain exposure.

"With low-intensity exposures, the efficiency of latent image formation is lowered. Because of the slow release of electrons by the relatively scarce incident photons of light, the latent image can build up only very slowly. During this initial stage of formation the latent image is relatively unstable and may be dissipated by thermal disintegration or chemically induced action. This loss of latent image causes less density to be produced than at more favorable exposure conditions. The photographic emulsion is said to have suffered low-intensity reciprocity failure.

Exposures at high-intensity are inefficient for another reason — the slowness of the migration of silver ions through the crystal to the latent image site. A high-intensity exposure floods the crystal with photo-released electrons. These electrons gather at latent image specks, but the silver ions cannot reach the speck in sufficient quantity to neutralize the electrons. The latent image speck becomes negatively charged, repelling other electrons, and the latent image formation is limited by the slow rate of silver-ion migration. The repelled electrons may be captured by the bromine atoms formed during the exposure. A large number of the photoelectrons are thought to be captured internally in the crystal. Such internal latent image sites are usually unavailable for development, wasting the effect of the exposure that released the electrons. Sites on the surface may not be built up to a developable state even though the sublatent image is stable. High intensity causes a loss in developed density, because the latent images are not built up to sufficient size."

In this study, emphasis will be placed on the low-intensity RLF since this is most common when making prints. Generally, exposure times range from 5-30 seconds when making 8X10 prints. For this experiment, the time will range from .5 to 512 seconds.

In color printing papers, RLF is made complicated by the fact that there are three light sensitive emulsion layers instead of one, as in B&W emulsions. (Figure 1) These are the cyan, magenta and yellow dye-forming layers which are sensitive mainly to red, green and blue light respectively. Each of

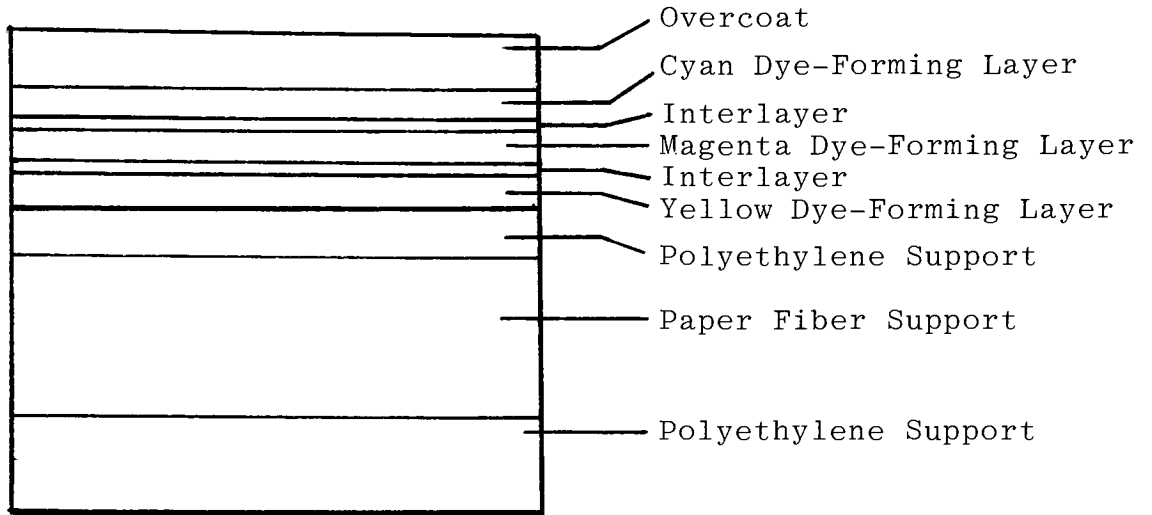


Figure 1. Cross section of Kodak Ektacolor paper.

these emulsion layers suffer from RLF, but the magnitude of the failure varies from layer to layer.<sup>8</sup> When making color prints at different exposure times, not only does the density loss due to RLF have to be accounted for,<sup>but</sup> a color correction will also be needed because of the differential reciprocity failure.<sup>9</sup>

## HYPOTHESIS

The purpose of this thesis is to show that color photographic papers are largely affected by RLF and that this failure differs from one emulsion batch to another. By the use of reciprocity curves that represent the failure in each of the three light sensitive emulsion layers, it is possible to account for the loss of density and color shifts that are inherent at longer exposure times.

## EXPERIMENTAL

The evaluation of the stability of RLF of color print papers will require a series of exposures. The papers will be exposed using a color filter pack consisting of Kodak red, green, and blue wratten color separating filters with neutral density filters to produce high, medium, and low densities. To build the color filter pack, as shown in Figure 2, the color separation filters used are Kodak Wratten #70 red filter, transmitting radiation from 660 - 990 nanometers; the #99 green filter, transmitting radiation from 520 - 590 nanometers; and the #98 blue filter, transmitting radiation from 385 - 495 nanometers.<sup>10</sup> The spectral transmittance of these filters is shown in Appendix I. The red color separating filter was placed in the first column, the green in the second and the blue in the third. To produce the high, medium, and low density patches a 0.6ND filter was placed over the bottom row, a 0.3ND filter on the middle row and zero ND on the top row. The medium density will be called the aim density. To achieve an aim density between .8 - 1.0 across the filter pack, ND must also be placed down the columns because the transmitted radiation through the color separating filters is not equal. The amount of ND used to achieve the aim densities will differ depending on the emulsion because the three light sensitive emulsion layers may vary in speed.

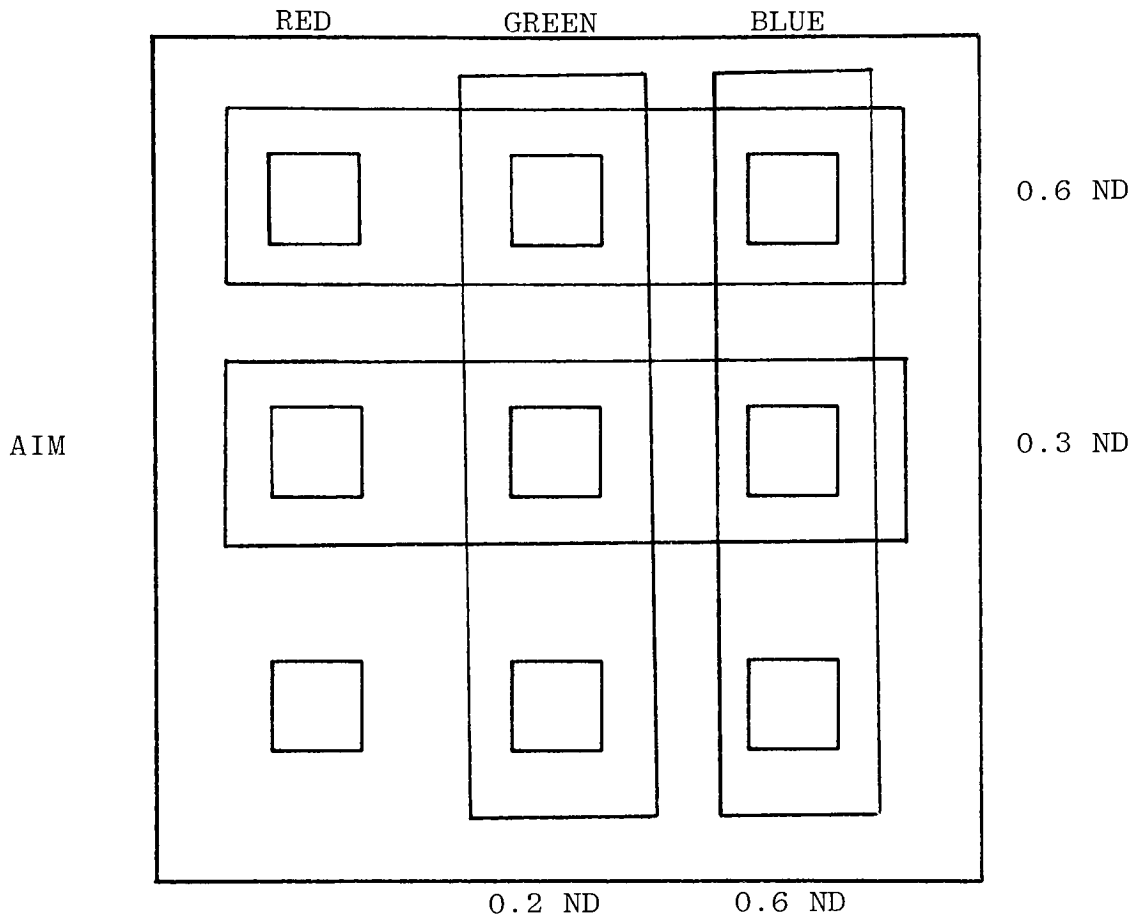


Figure 2. Color Separation Filter Pack.

To run an exposure series, a Super Chromega Enlarger with a 150mm f/5.6 lens at a height of 46.2cm and bellows set at 4cm was used. This set up will be held constant for all exposure series.

For the first exposure series Kodak Ektacolor 74 RC Paper type 2524 emulsion number 109170 was used. The exposure of the paper was held constant. One way of calculating the exposure, E, is shown below:

$$\text{Log } E = \text{Log } I + \text{Log } t - \text{Log } D$$

For the exposures, the lens was set at f/5.6 and the first exposure time was .5 seconds with no neutral density. Neutral density filters were used to change the intensity instead of using the aperture, therefore E and I were held constant and t and D were varied proportionally. The intensity was decreased by one stop increments using 0.3, 0.6, 0.9,...ND placed in a negative carrier as the time was increased by one stop increments, .5, 1, 2, 4,... seconds. A series consisted of 11 exposures ranging in time from .5 - 512 seconds. All 11 exposures were run through a Colenta American 50 inch processor at the same time. The densities produced were read on a MacBeth 924 Transmission/Reflection densitometer.

In order to account for variability of the enlarger and in processing, this series was replicated 5 times. The average and standard deviation of the densities were calculated, then plotted yielding curves representing the response of the red,



green and blue light sensitive emulsion layers due to RLF.

A second exposure series is done with a different emulsion using Kodak Ektacolor 74 RC paper, emulsion number 954230 to test to see if there is stability of the RLF from one emulsion batch to another. Again, 5 replicates were made and the curves were plotted.

To test the stability between the emulsion batches used, the reciprocity curves of one emulsion was normalized to the other. This was done by taking the difference in the densities at each exposure time, adding all the differences and dividing by the total number of exposure times used, which was 11. One curve is then shifted by this value at each point. Using 3 standard deviation error bars on each point, the curves are compared. If both curves overlap, there appears to be no difference in the reciprocity characteristics between these two emulsions. If some of the points do not overlap, then the reciprocity characteristics are different for these two emulsions. This was done for the red, green, and blue emulsion layers.

In order to account for any differences in speed of different emulsion batches, a 4 point test was tried by fitting a third order equation to the reciprocity curves. Using the color filter pack and by choosing four points along the curve, a best fit curve was generated by using program Fit on an Apple computer.<sup>11</sup> The times that were used were 1, 4, 32, and 128 second exposure times. The red, green, and blue curves were tested for accuracy by using exposure times used in the exposure series, and comparing the calculated densities to the

experimental densities.

The method finally used to determine the change in exposure and filtration is described below:

Start with a print of good color balance made at exposure time,  $T_1$ . To produce the same print at another exposure time,  $T_2$ , the reciprocity curves for that emulsion are used. First, obtain the density values for red, green, and blue at both exposure times. These will be  $R_1$ ,  $B_1$ , and  $G_1$  for exposure time  $T_1$  and  $R_2$ ,  $B_2$ , and  $G_2$  for exposure time  $T_2$ . The delta change in the red density will correspond to the change in exposure. When the  $\Delta R$  is multiplied by  $1/\gamma$  of the paper, it yields the change in exposure which is expressed in denominations of stops, .3 equals a 1 stop increase in exposure.

To determine the yellow filtration change, the difference in shifts from one exposure time to another is calculated as shown below.

$$\Delta Y = - \left[ (R_2 - B_2) \right] - \left[ (R_1 - B_1) \right] 1/\gamma \times 100$$

The  $\Delta Y$  will be the number of cc units added or subtracted to the pack used at time,  $T_1$ .

The magenta filtration changes are determined the same way:

$$\Delta M = - \left[ (R_2 - G_2) \right] - \left[ (R_1 - G_1) \right] 1/\gamma \times 100$$

The  $\Delta M$  will be the number of cc units added or subtracted to the pack used at time,  $T_1$ .

To test this method of correction, a standard scene was used to make prints. The scene consisted of a grey card and color scale held by a "Shirly" for flesh tones. An initial

time was used to make a reference print. Another print will be made at a longer exposure time using this method to correct for density loss and color shifts due to the RLF.

## RESULTS

The reciprocity curves for Kodak Ektacolor 74 paper, Emulsion I, Emulsion II, and Emulsion III are shown in Appendix II. The aim curves were compared and all three emulsions have the same shape and the three layers show the same trends. It should be noted that the color filter pack was slightly changed when the exposure series was run. A .1 ND was placed over the blue filter to bring the aim densities in range. Therefore, the blue sensitive layer in Emulsion III was significantly faster in speed than the other two emulsions tested.

In the Ektacolor 78 paper, the two emulsions tested had several points which did not overlap with the error bars. The shapes of the three layers are the same but they do not follow the same trends. Also, the speeds of the layers vary quite a bit.

Program Fit was tested using the data from Emulsion I of the 74 paper. Figure 3 shows the accuracy of this program. Four exposure times were used. The times used in the program will depend on the size of the paper being used. For 8x10 inch paper, exposure times of 1, 4, 32 and 128 are a good choice. For larger papers, the 4 points used should take into account the probable times that will be used in actual printing. The largest deviations from the actual to the calculated are the

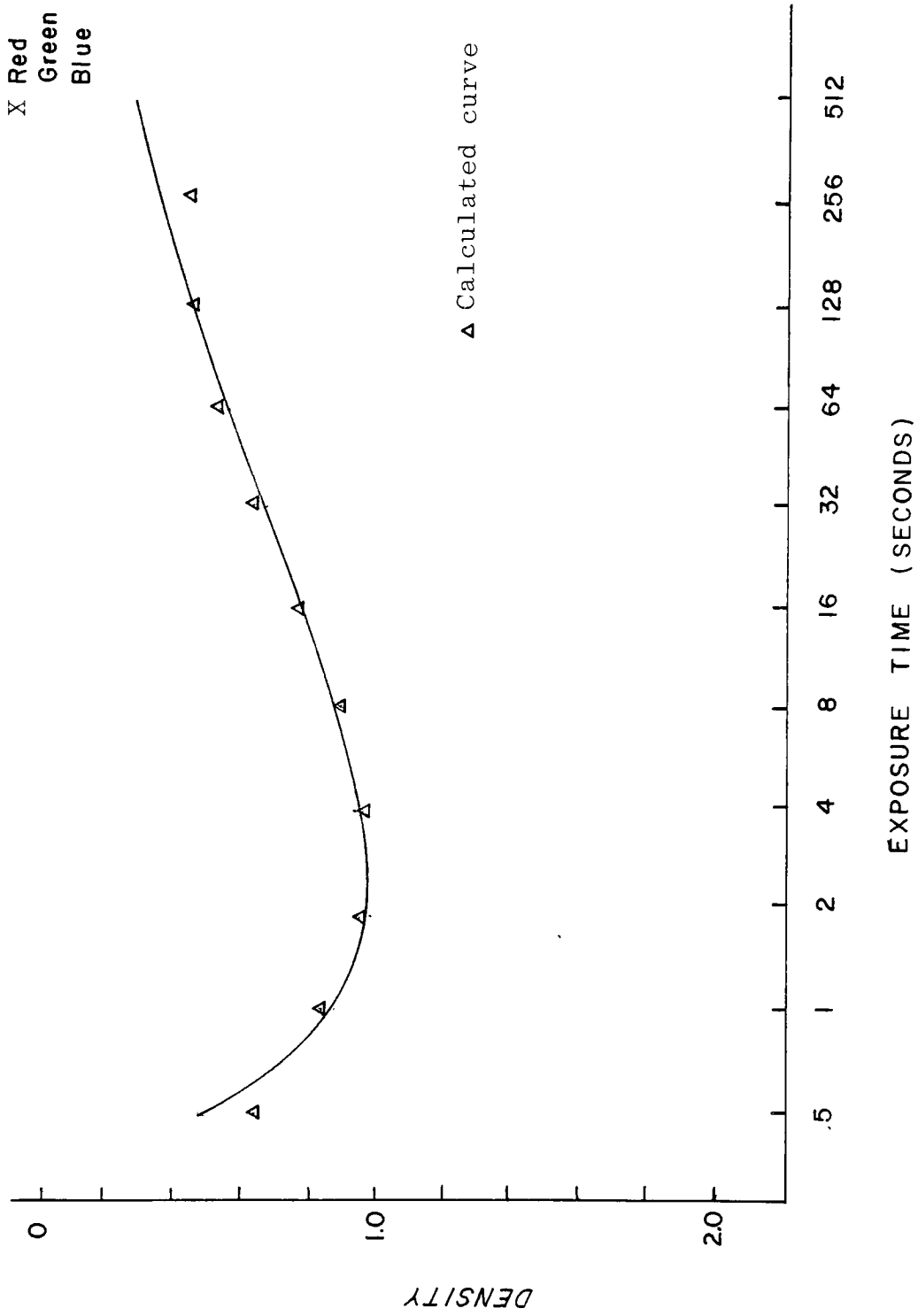


Figure 3a. Red experimental curve compared to red calculated curve.

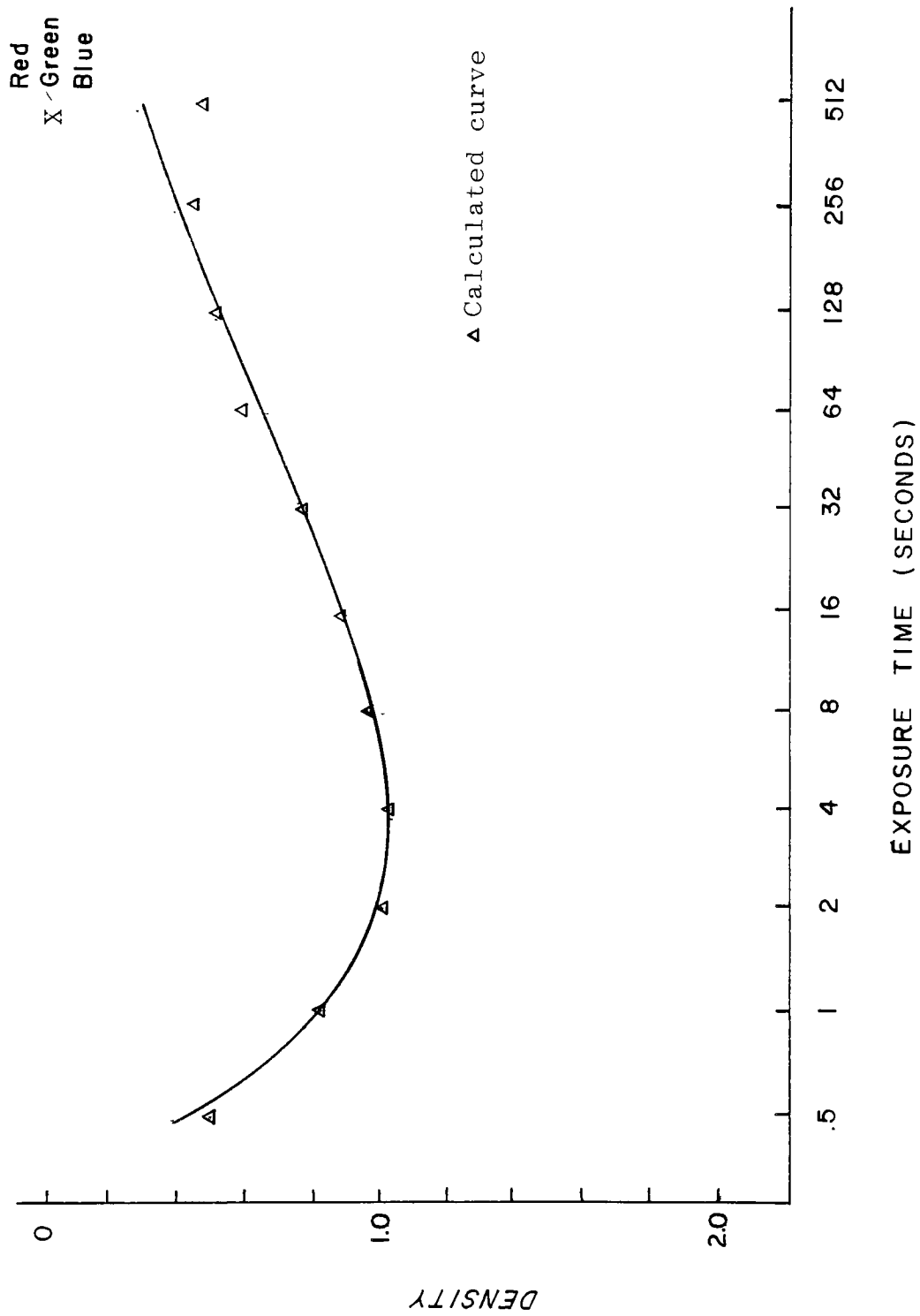


Figure 3b. Green experimental curve compared to green calculated curve.

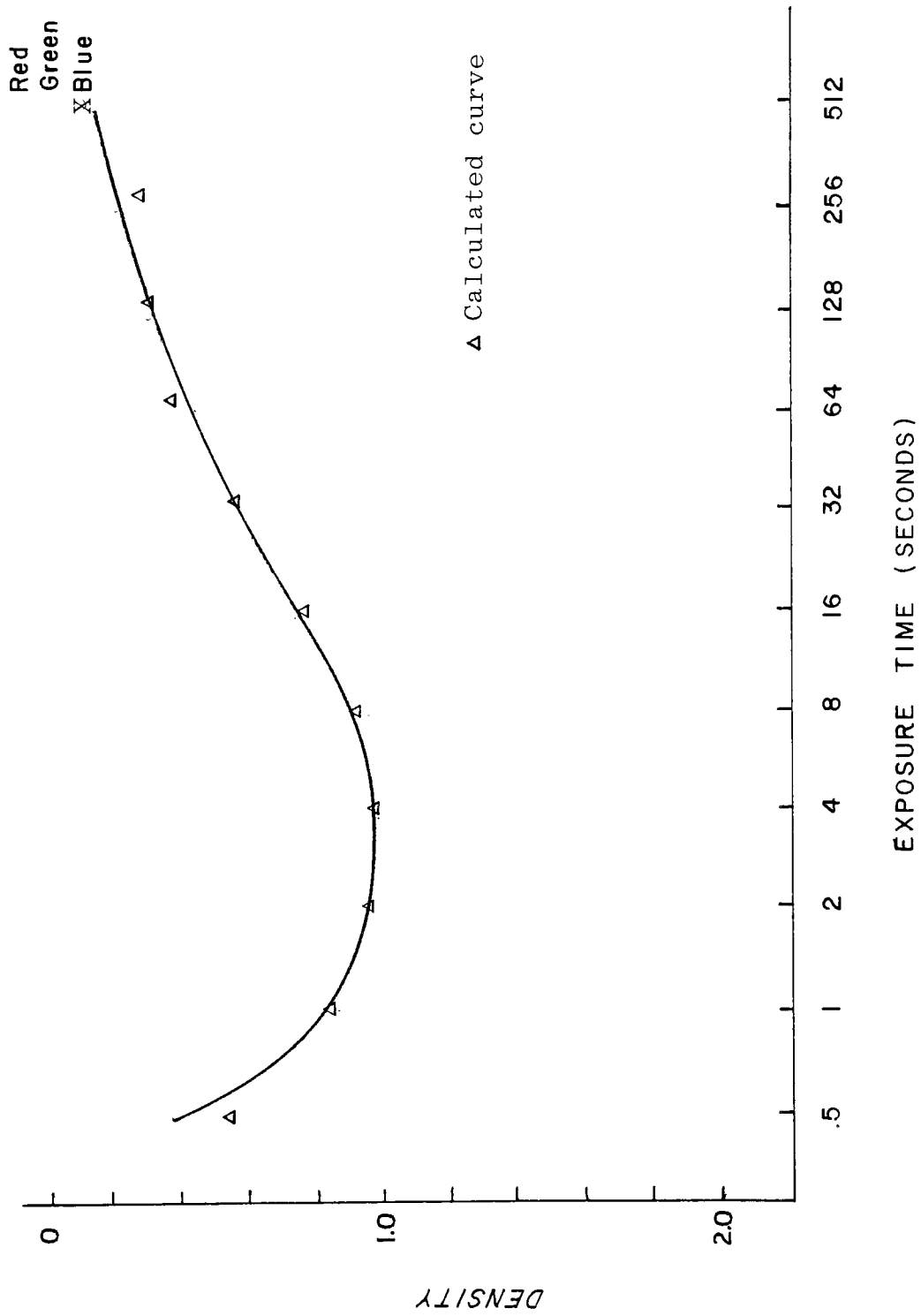


Figure 3c. Blue experimental curve compared to blue calculated curve.

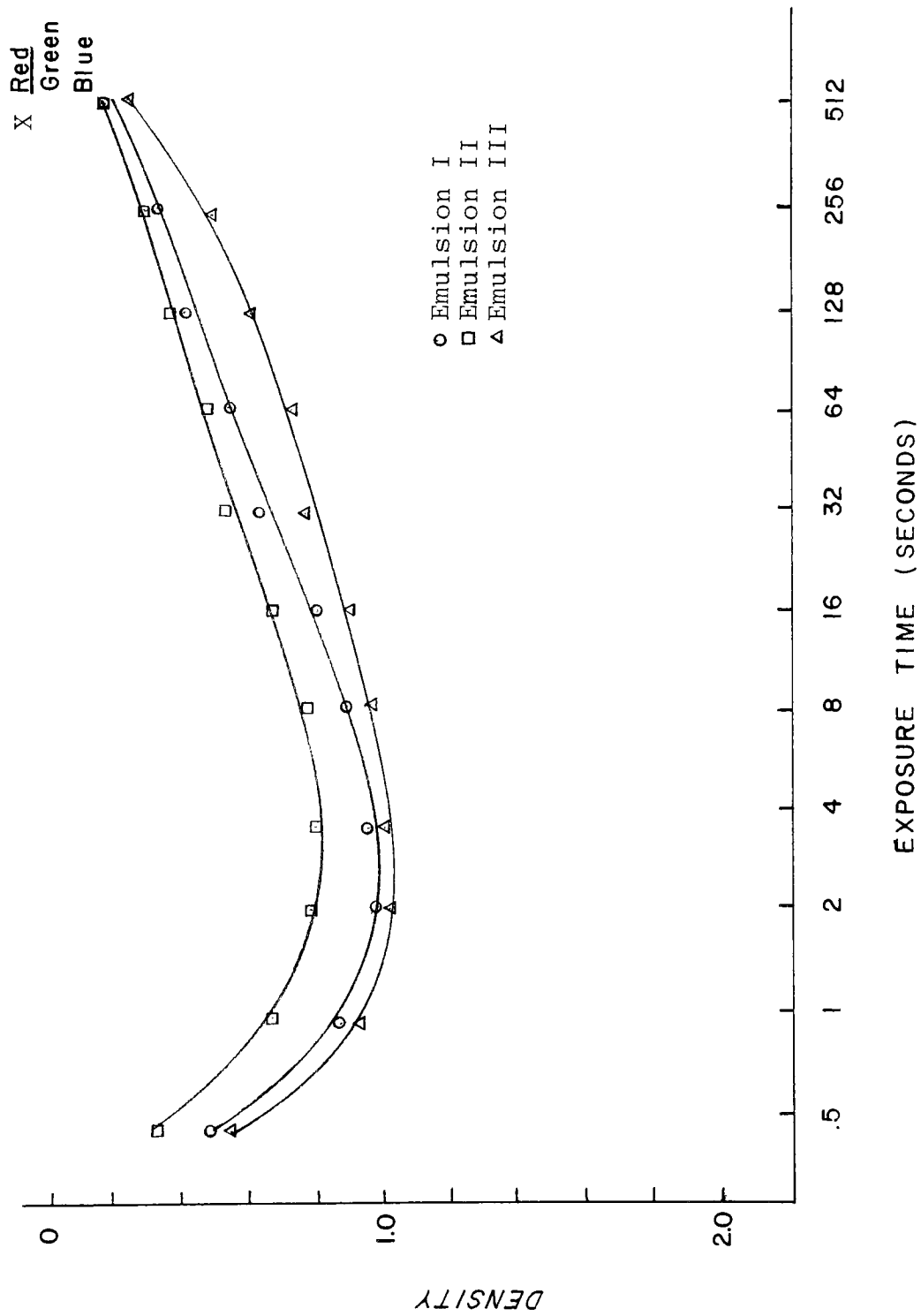


Figure 4a. 74 paper red aim densities.



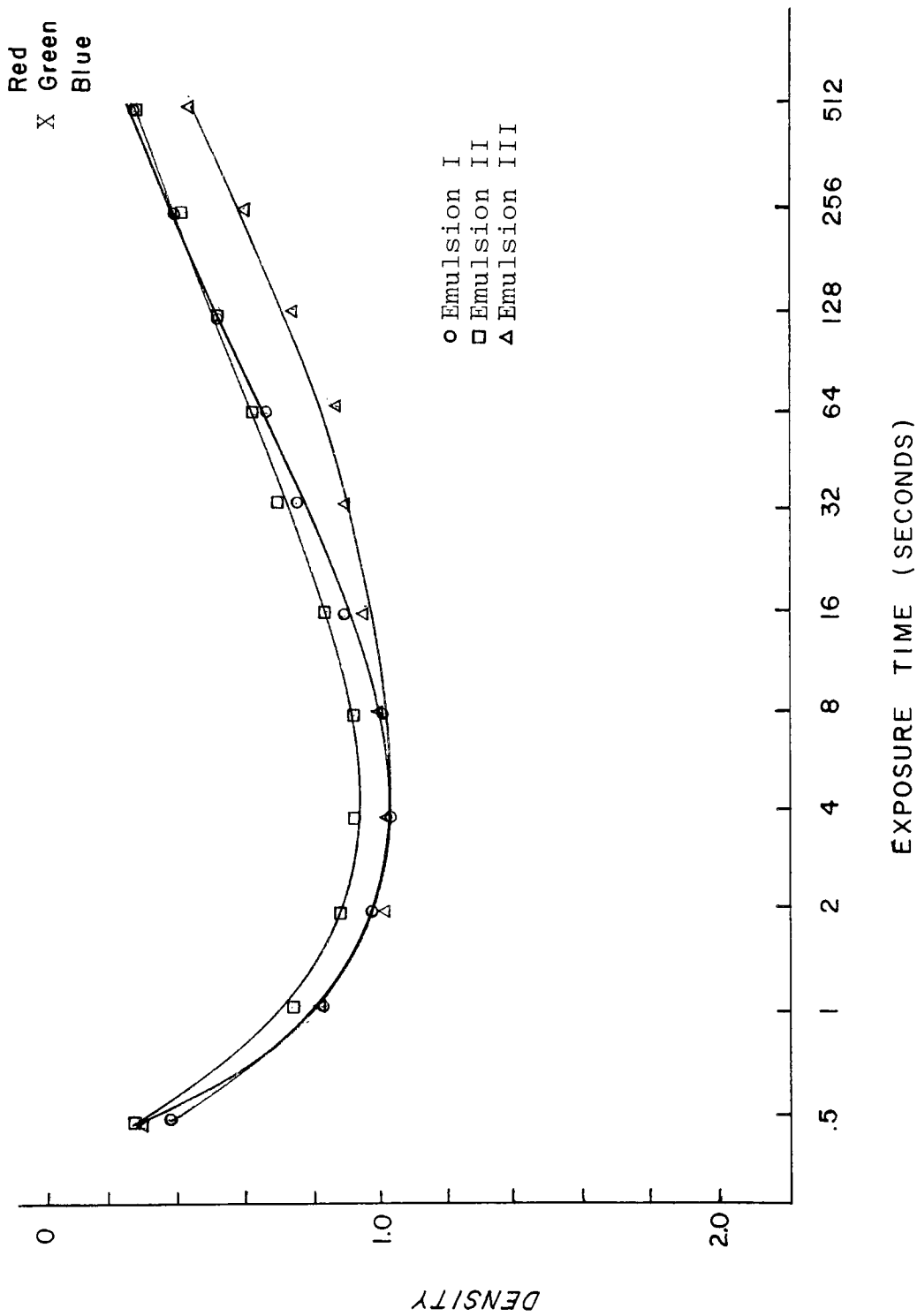


Figure 4b. 74 paper green aim densities.

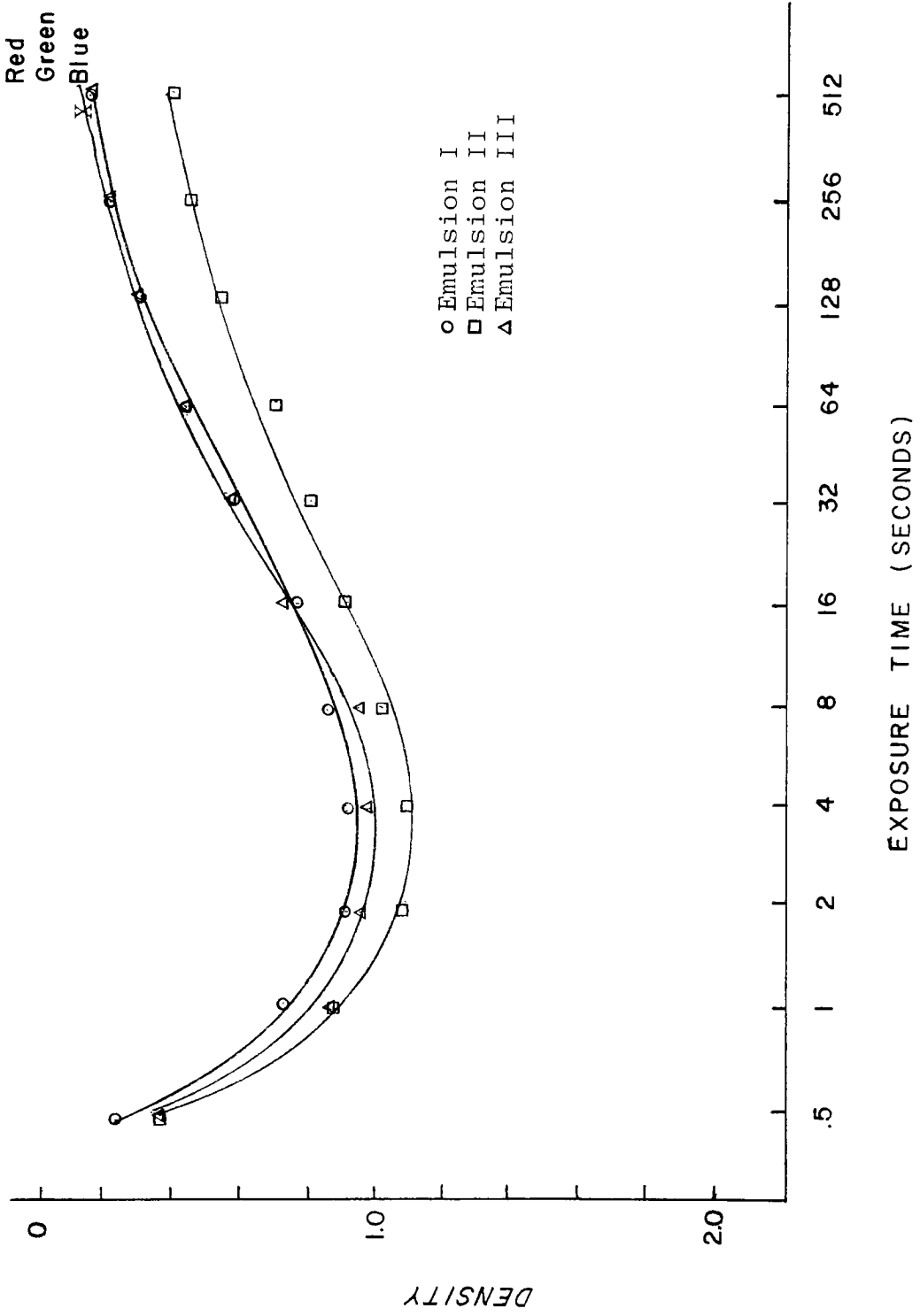


Figure 4c. 74 paper blue aim densities.

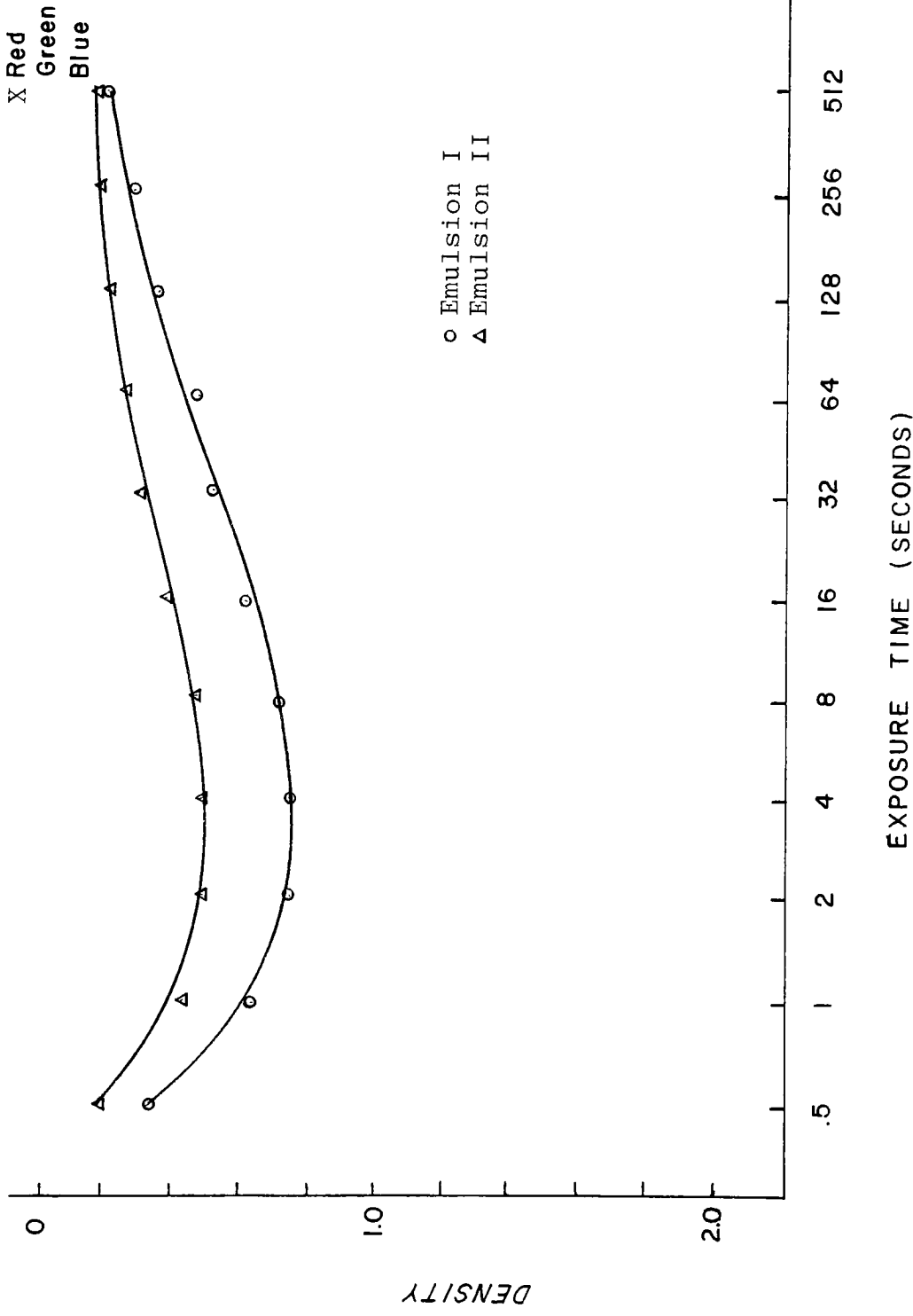


Figure 5a. 78 paper red aim densities.

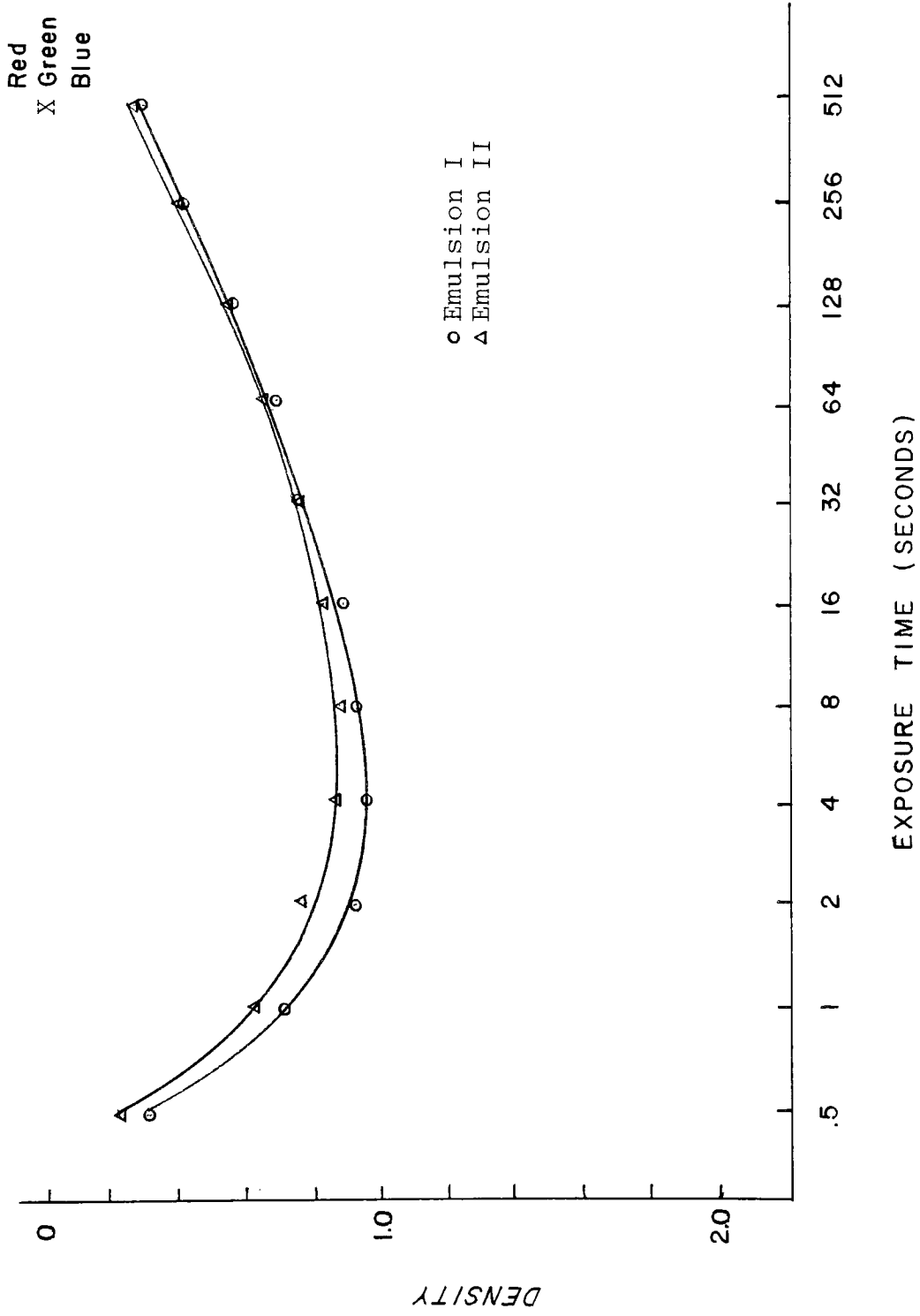


Figure 5b. 78 paper green aim densities.

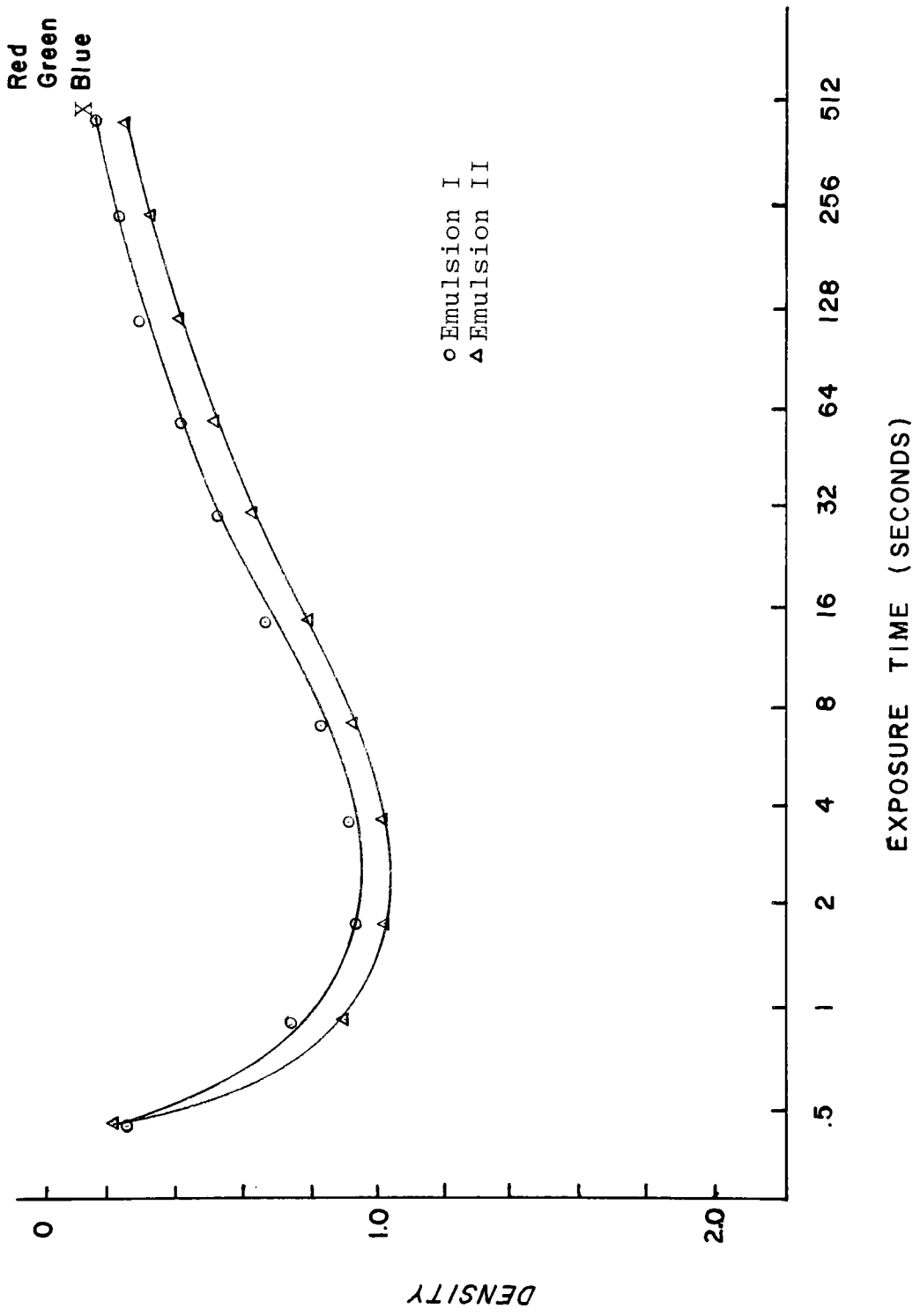


Figure 5c. 78 paper blue aim densities.

extreme points that were not included within the time range. If these points are critical ones, then the 4 exposure times used to fit the curves should be changed.

The results for the method suggested in determining exposure and color corrections are shown in Table 1. This Table indicates the reference print, a print at  $T_2$  without any corrections to demonstrate the reciprocity failure, a print at  $T_2$  with exposure corrections only, and a print at  $T_2$  with both the exposure correction and color correction. The red, green, blue, and visual densities are given.

Table 1. Ektacolor 74 Paper

Exposure Time	no corrections			E corrections			E and color corrections			required filtration			required E change			
	R	G	B	R	G	B	R	G	B	R	G	B		C	M	Y
4	.60	.60	.61	.58	.67	.59	.59	.60	64	.58	.59	.58	0	46	71	reference
8	.54	.55	.56	.54					60	.56	.57	.56	0	47	69	none
16	.48	.52	.47	.49					73	.69	.70	.68	0	49	69	≈1/3 stop
32	.38	.45	.39	.42					72	.66	.67	.66	0	52	67	≈1/2 stop
64	.32	.38	.31	.35	.59	.65	.56	.61	65	.57	.60	.58	0	52	67	1/2 stop

Table 2. Ektacolor 78 Paper

Exposure Time	no corrections			E corrections			E and color corrections			required filtration			required E change			
	R	G	B	R	G	B	R	G	B	R	G	B		C	M	Y
8	.79	.79	.75	.76	.79	.79	.75	.76	79	.79	.75	.76	0	46	62	reference
64	.49	.50	.38	.48	.65	.70	.54	.66	65	.72	.64	.66	0	46	57	1/3 stop

## DISCUSSION

The Ektacolor 74 emulsions do vary in speed, but for the emulsions tested, these variations are within a stop to a stop and a half. They tend to maintain the same characteristics and the cross overs in the red, green and blue curves are fairly constant.

Five prints were made to test this method of correction. The reference point was made at 4 seconds, the others were made at 8, 16, 32 and 64 seconds. The results of the corrections made are visually very close. Comparing the densities of the 4, 8 and 64 second exposure times, the densities are within .02, two density units, which is the tolerance of the densitometer. Careful consideration was taken as to the exact placement for the measurement of these densities. For the 16 and 32 second exposure times, the densities are higher than the reference print made at 4 seconds. This is due to the change in exposure needed to reproduce the print. The 32 second exposure needed almost  $1/3$  stop increase of exposure, and the 64 second exposure needed almost a  $1/2$  stop increase. The exposure was changed by using ND filters that come in  $1/3$  stop increments. If the exposure change was not in these increments, it was rounded to the nearest third of a stop. Both the 16 and 32 second exposures were rounded down, causing a slight in-



crease of exposure.

The RLF in Ektacolor 78 paper is unstable for the two emulsions tested. Emulsion I had aim densities made at the "optimum" exposure time in the .8 to 1.0 density range. Emulsion II ranged from .45 to 1.0 at the same time. This signifies that the emulsion layers vary greatly in speed and make switching from one emulsion to another difficult. By using program Fit, new emulsions can be tested easily.

Two prints, one made at 8 seconds and one made at 64 seconds, were used to test this method of correction. The corrected print was 10 density units lighter than the reference. As explained before, the exposure change was slightly larger than a third of a stop. The correction was made by increasing exposure  $\frac{1}{3}$  of a stop, therefore the final print was slightly lighter than the reference. The color corrections were off by about 2 cc units in cyan and magenta if the density was correct. Visually the two prints were acceptable, noticing only a slight color shift.

One way to reduce the error in exposure corrections would be to use the aperture of the lens along with a color translator for metering the exposure, to determine the exact change in exposure. This would improve the accuracy of the RLF corrections. When changing the filtration on the enlarger, error is also introduced in the exact positioning of the numbers. Other sources for error would be in the calculated reciprocity curves and in processing.

## CONCLUSION

It was found that the RLF in different emulsion batches vary. By testing a new batch of emulsion with 4 exposure times, the densities can be entered into a program to fit a curve close to the actual reciprocity curve. From the curve, red, green and blue densities can be determined for different exposure times. By doing the quick calculation either by hand or by a programmed computer, the exposure and filtration changes are determined. The accuracy of this method is dependent on how precise the exposure correction is, also the precision of the filtration and processing variability.

According to the results, a good to very good approximation of the reference print is attainable by this method. In actual use, a final print with minor corrections of  $\pm 3$  cc units for color can be predicted. With a means of determining exact exposure changes, the visual density of the prints should match the reference print within  $\pm 0.02$  density units.

## References

<sup>1</sup>G. Haist, Modern Photographic Processing Volume 1. John Wiley and Sons, New York, 1979. p. 743.

<sup>2</sup>Mees and James, Theory of the Photographic Process 3rd ed. MacMillan, New York, 1966. p. 133.

<sup>3</sup>Kodak Customer Service, Personal communication.

<sup>4</sup>Mees and James, p. 133.

<sup>5</sup>Mees and James, p. 133.

<sup>6</sup>Haist, p. 744.

<sup>7</sup>Haist, pp. 744-745.

<sup>8</sup>G. Wakefield, Exposure Control in Enlarging. Fountain Press, New York, 1972. p. 187.

<sup>9</sup>Wakefield, p. 187-188.

<sup>10</sup>Kodak Publications B3, Kodak Filters for Scientific and Technical Uses.

<sup>11</sup>R. Quattrini, Program Fit.

<sup>12</sup>Kodak Publications B3, p. 36.

<sup>13</sup>Kodak Publications B3, p. 36.

## APPENDICES

## APPENDIX A

## Kodak Wratten Filters

Kodak Wratten number 96 neutral density filters reduce the intensity of light reaching the film without affecting the tonal rendition of the colors in the original scene.<sup>12</sup> These filters were used in the color filter pack to obtain aim densities in the range of .8 to 1.0. They were also used to reduce the intensity of the exposing light while the time was increased to keep a constant exposure.

The manufacturing tolerance for NO. 96, 75mm square filters is  $\pm .10\%$  of the nominal diffuse density.<sup>13</sup> For the filters used in this thesis, the tolerance was found to be within  $\pm .06\%$  of the nominal diffuse density by direct measurement.

The Kodak wratten filters used in the color filter pack were the 70 red, 99 green, and 98 blue. All three are narrow band, used for separation of the three main emulsion layers.

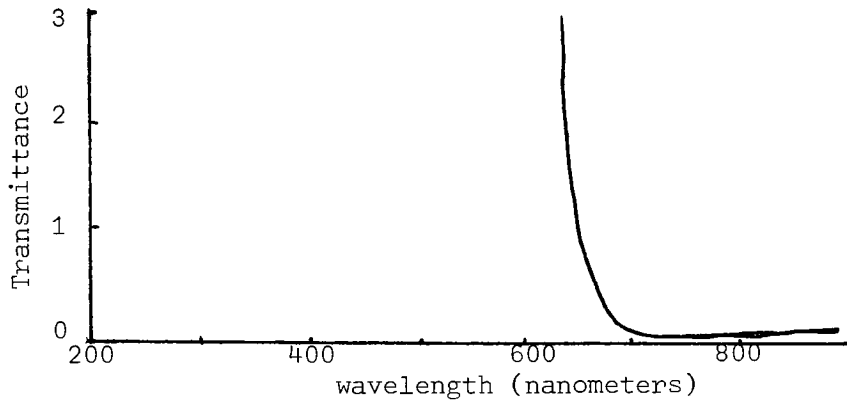


Figure 6a. Dark red, number 70.

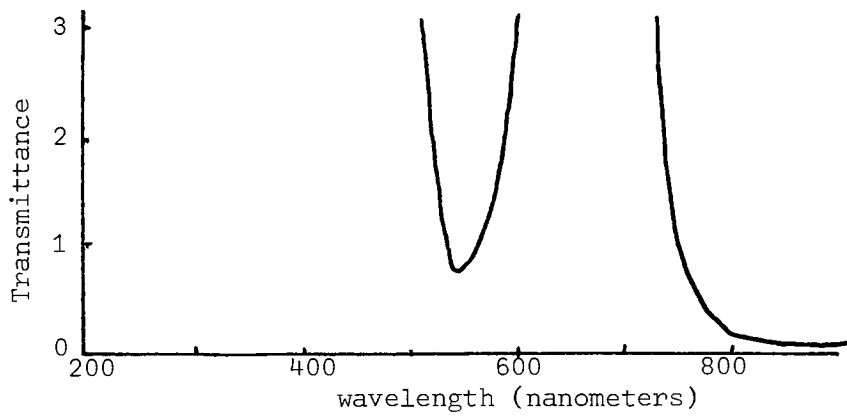


Figure 6b. Green, number 99.

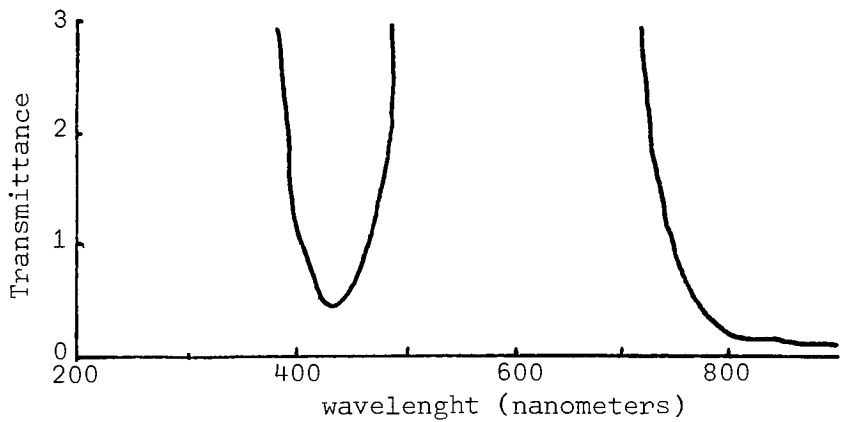


Figure 6c. Blue, number 98.

## APPENDIX B

Reciprocity Curves for 74 and 78 Papers

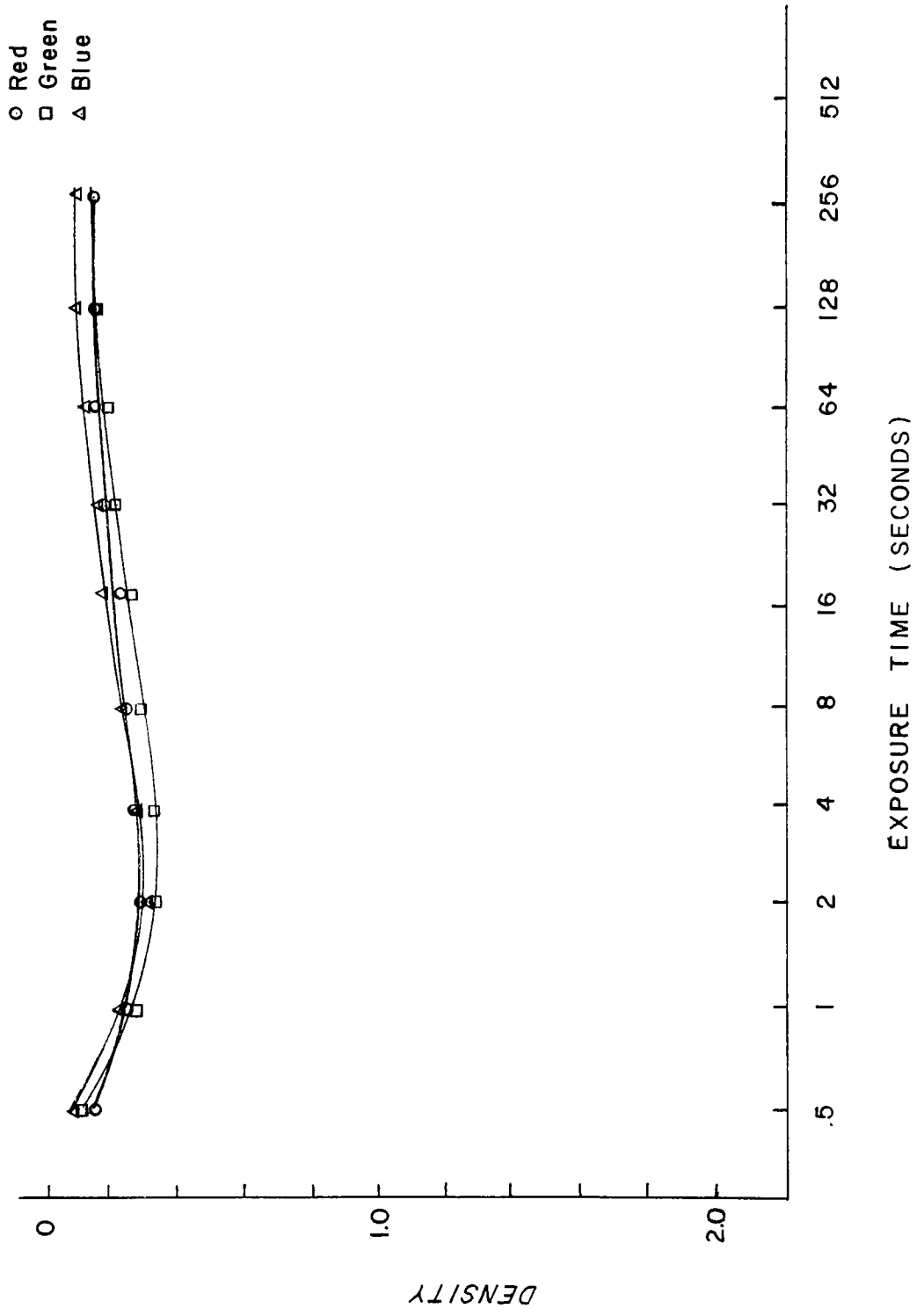


Figure 7a. 74 paper Emulsion I, low densities.



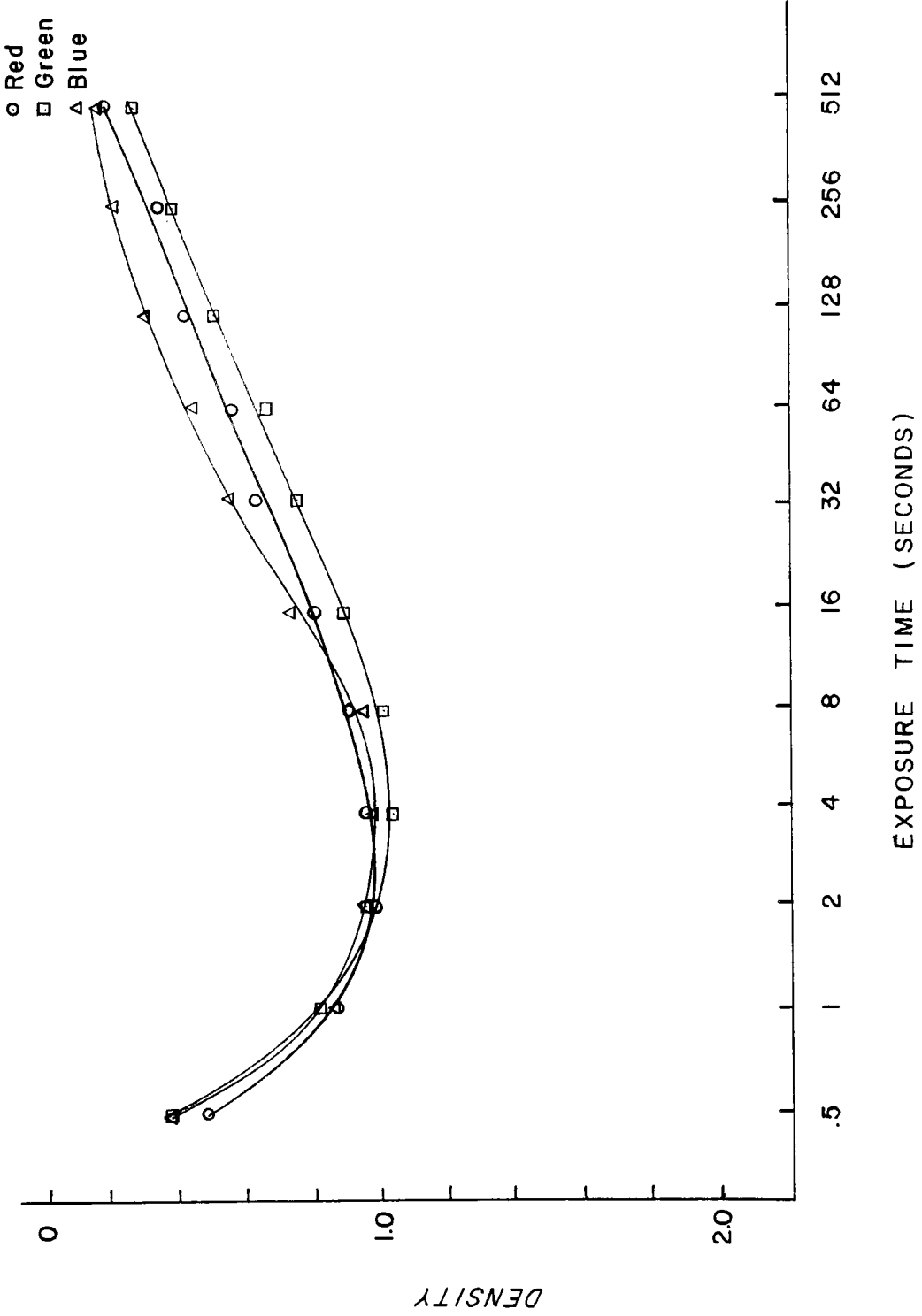


Figure 7b. 74 paper Emulsion I, aim densities.

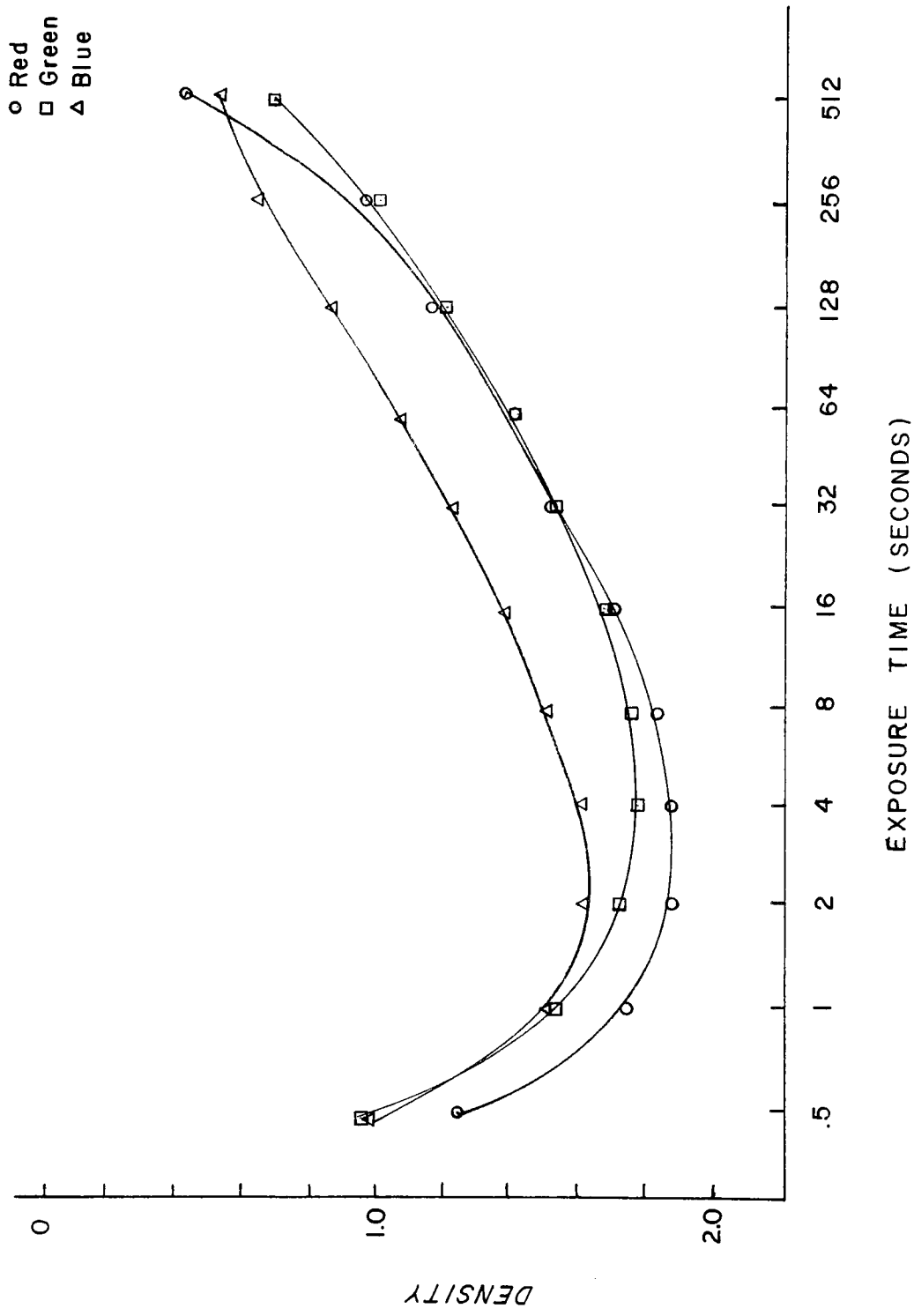


Figure 7c. 74 paper Emulsion I, high densities.

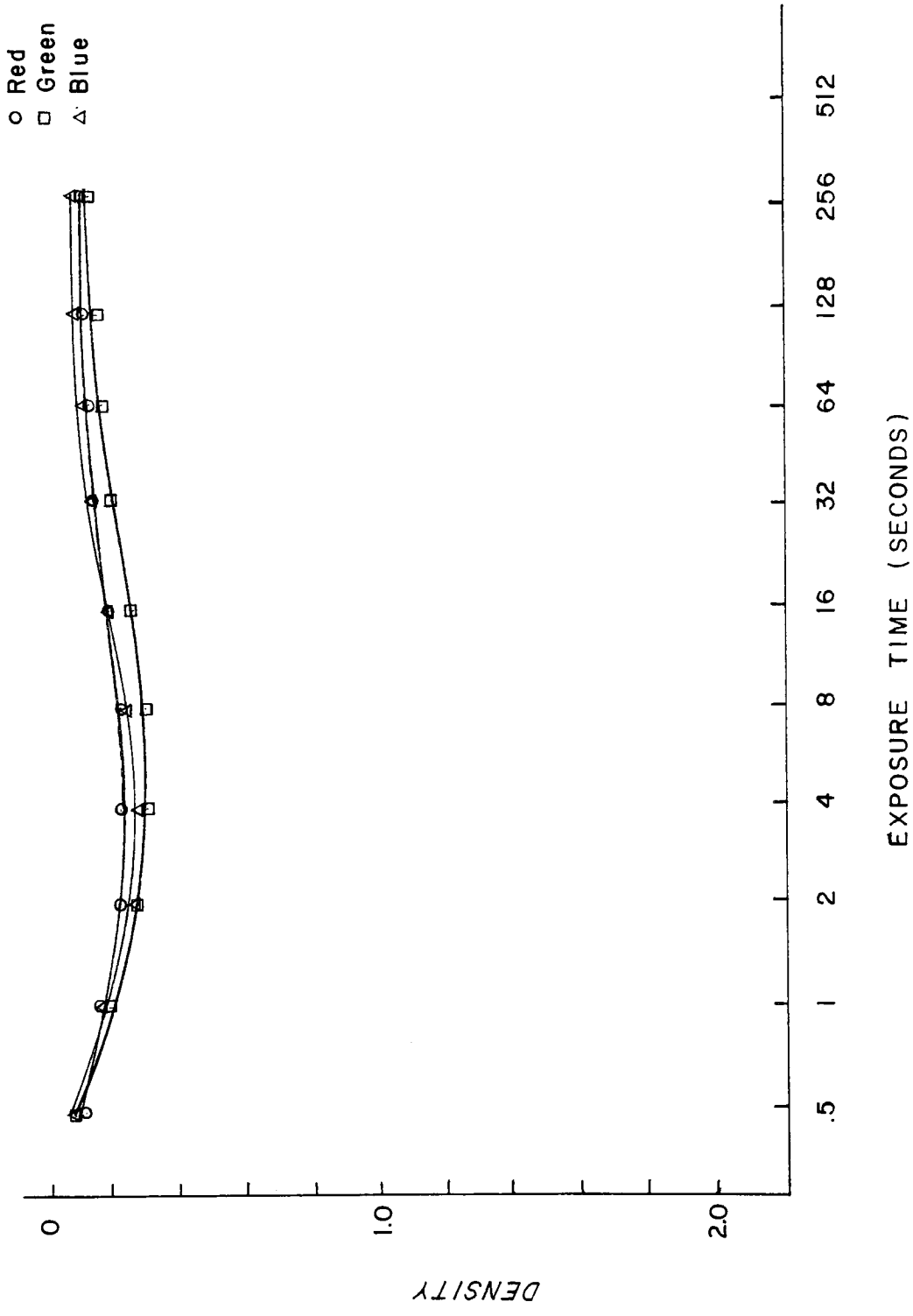


Figure 8a. 74 paper Emulsion II, low densities.

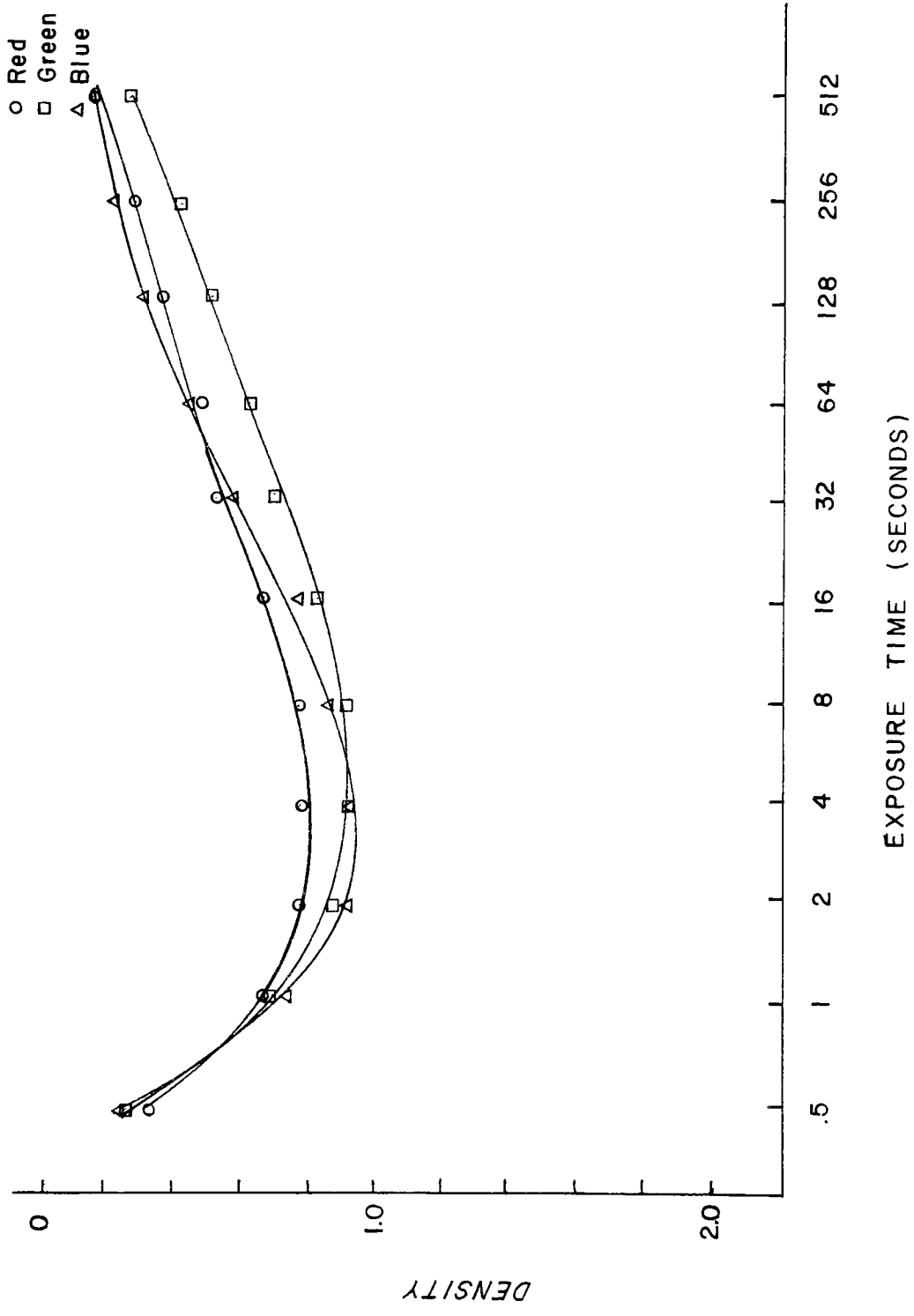


Figure 8b. 74 paper Emulsion II, aim densities.

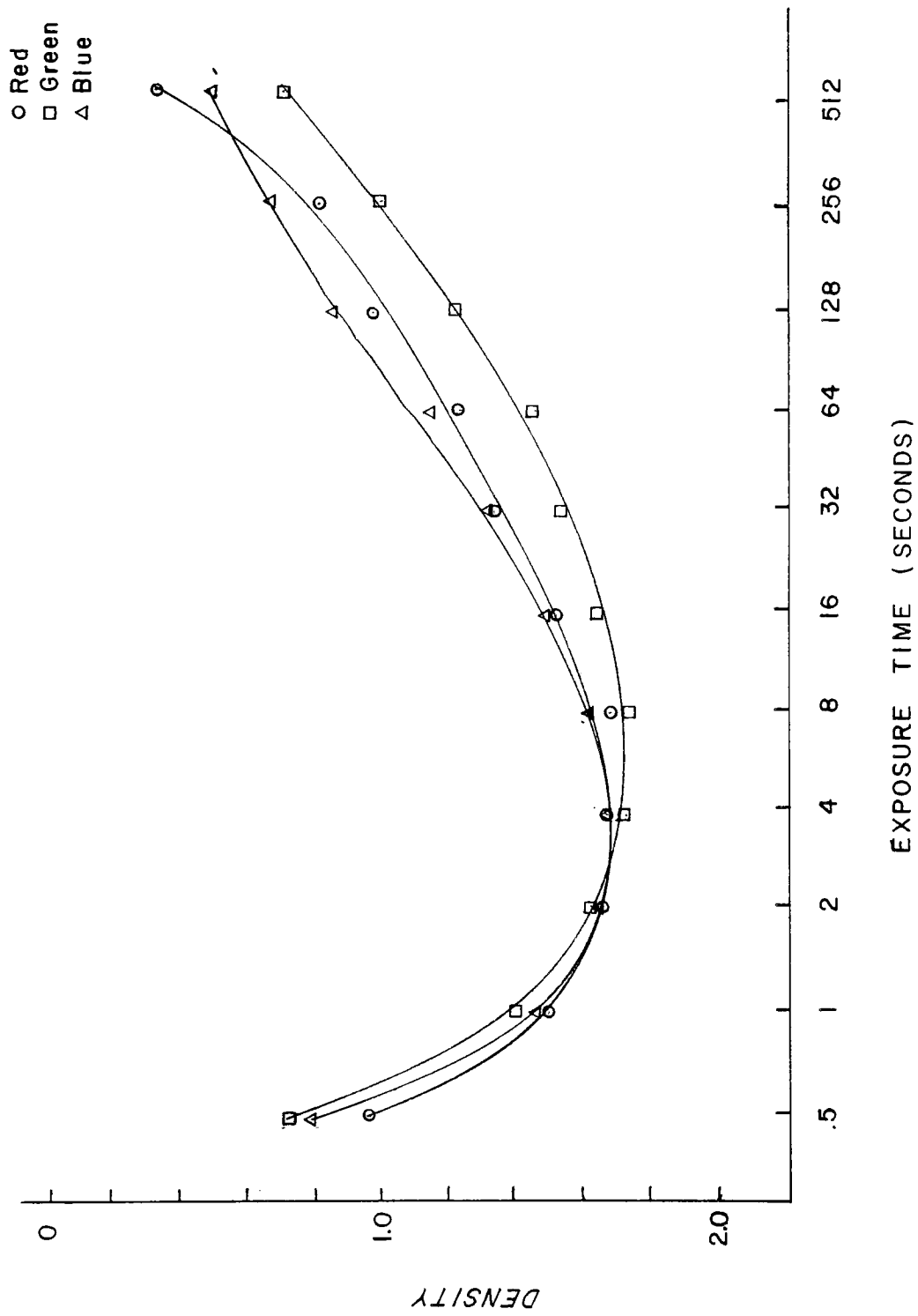


Figure 8c. 74 paper Emulsion II, high densities.

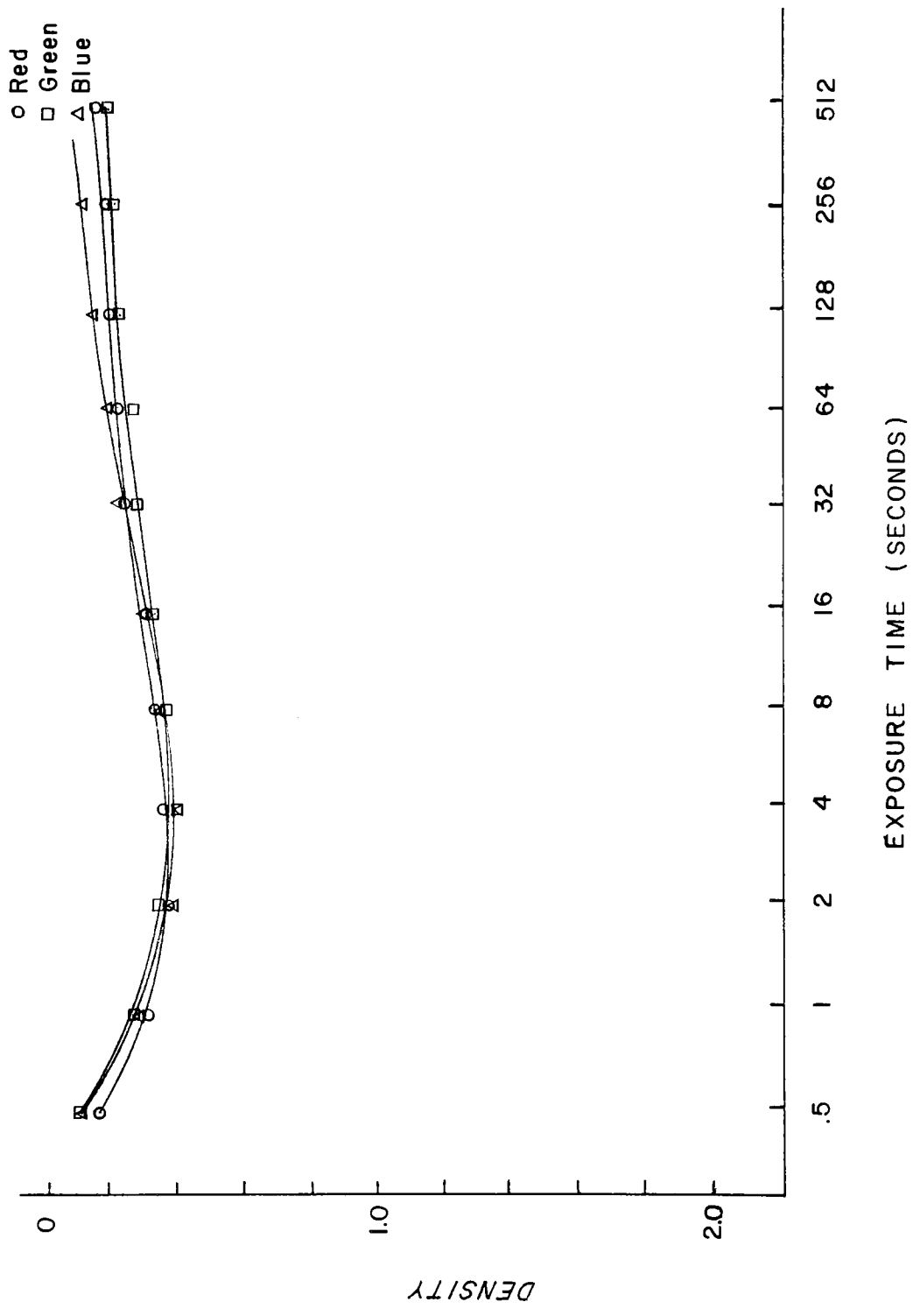


Figure 9a. 74 paper Emulsion III, low densities.

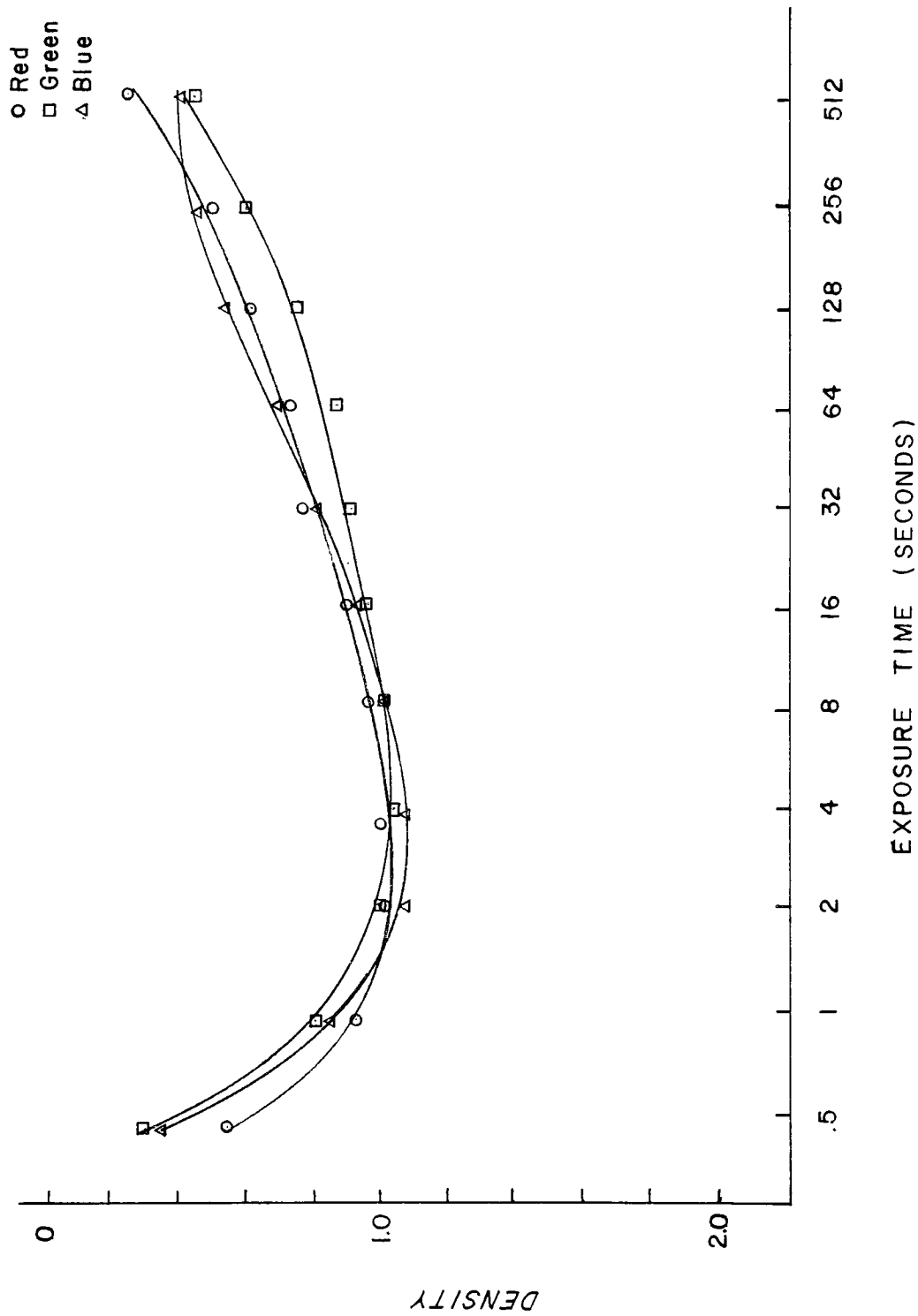


Figure 9b. 74 paper Emulsion III, aim densities.

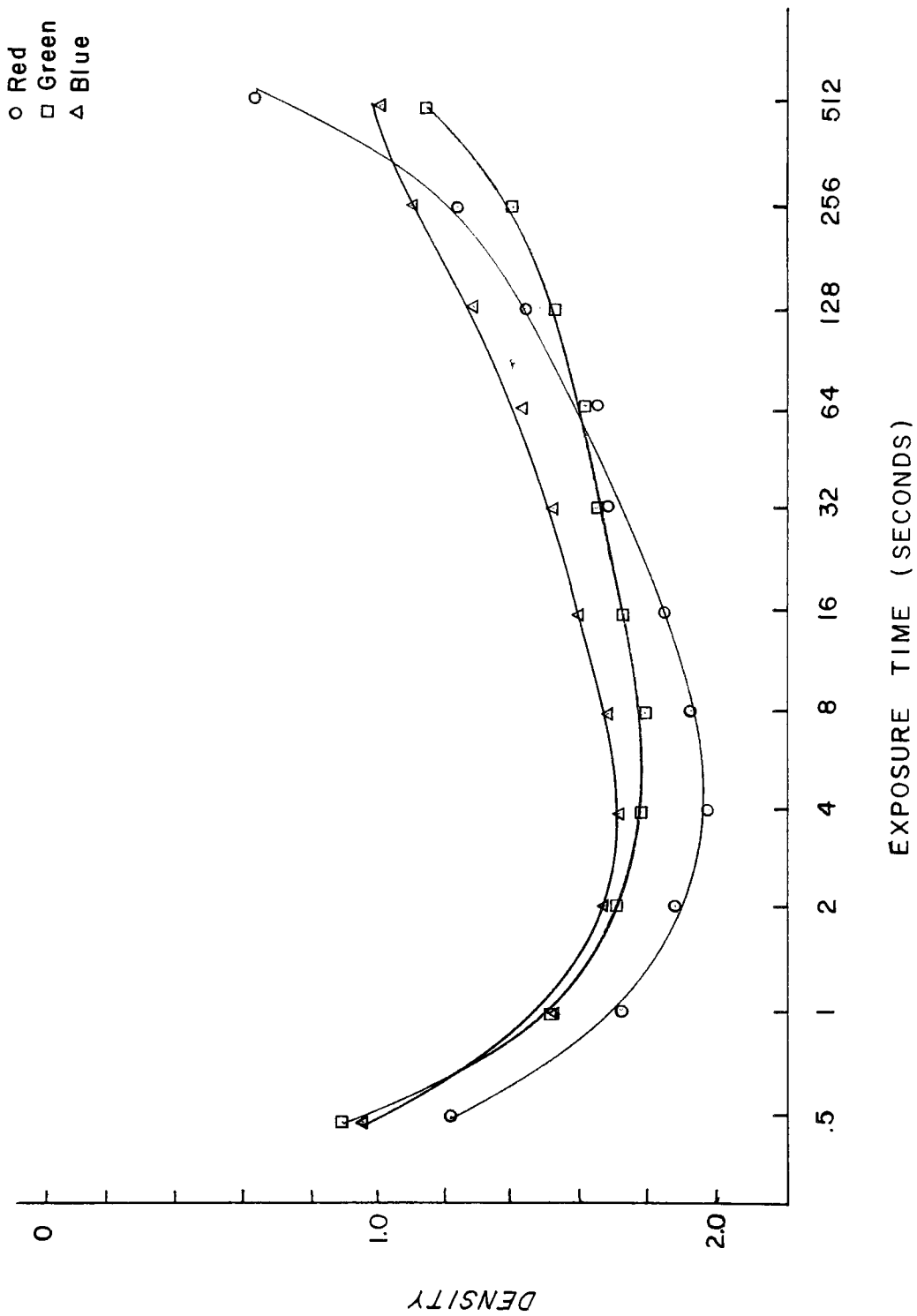


Figure 9c. 74 paper Emulsion III, high densities.



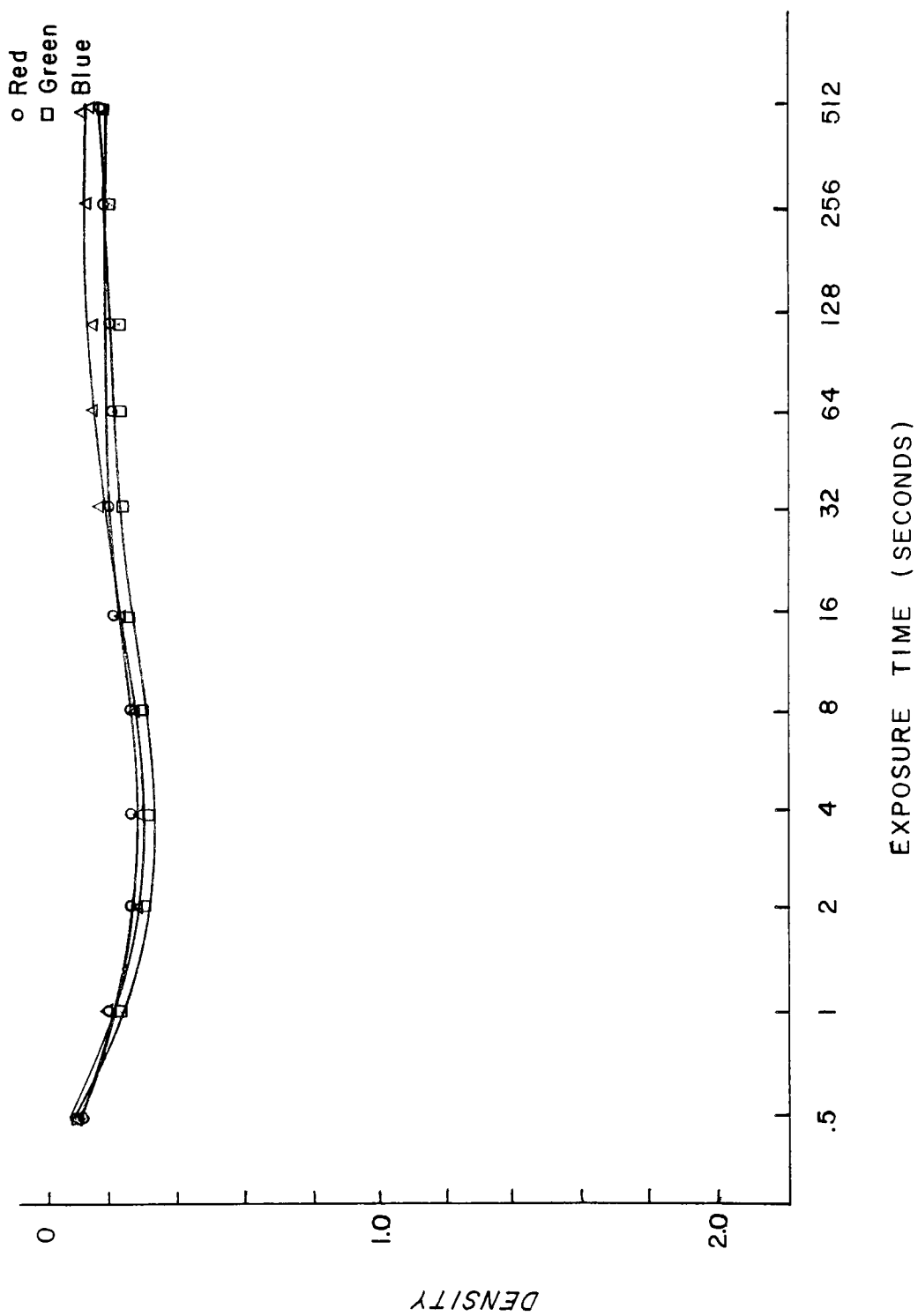


Figure 10a. 78 paper Emulsion I, low densities.

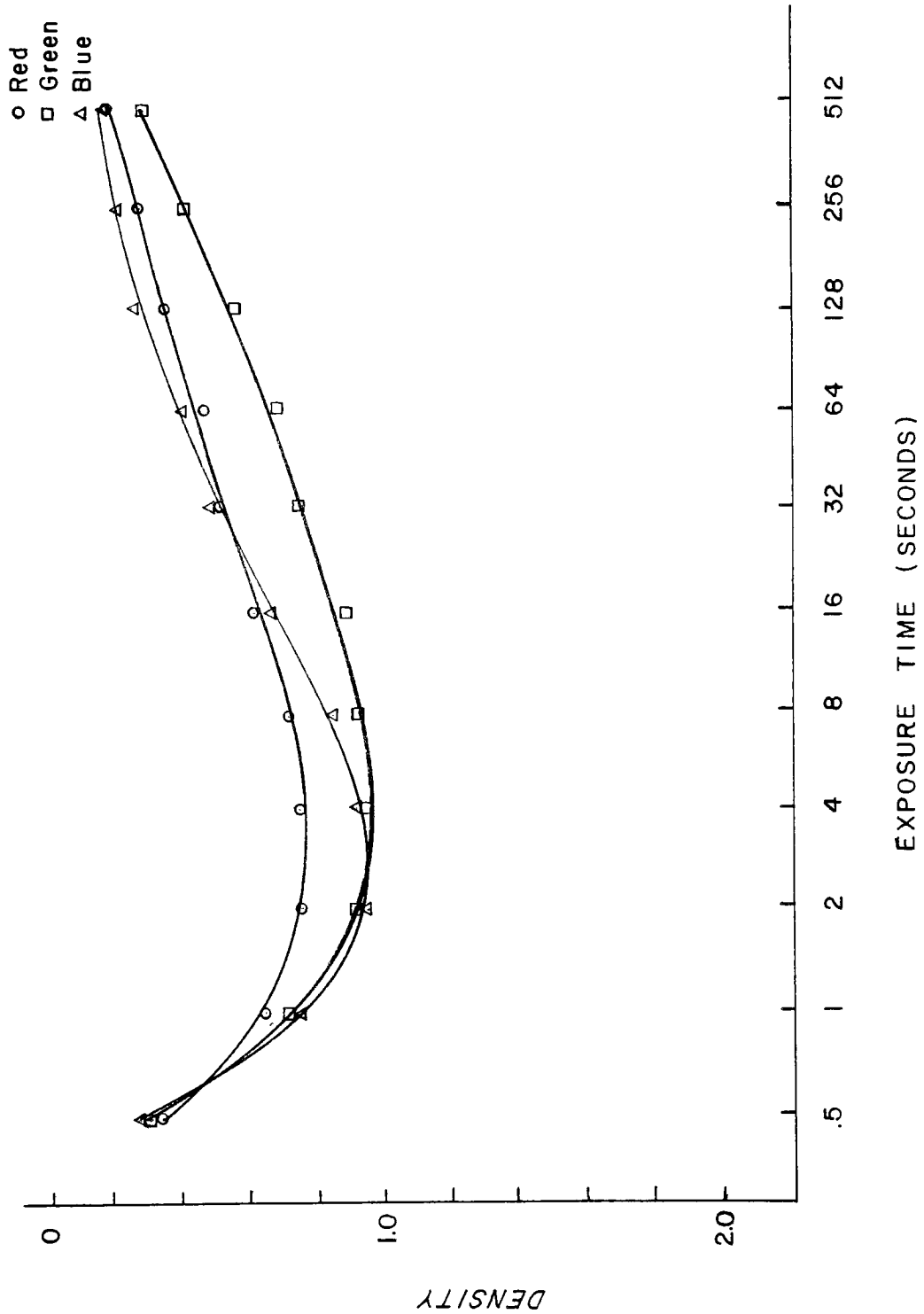


Figure 10b. 78 paper Emulsion I, aim densities.

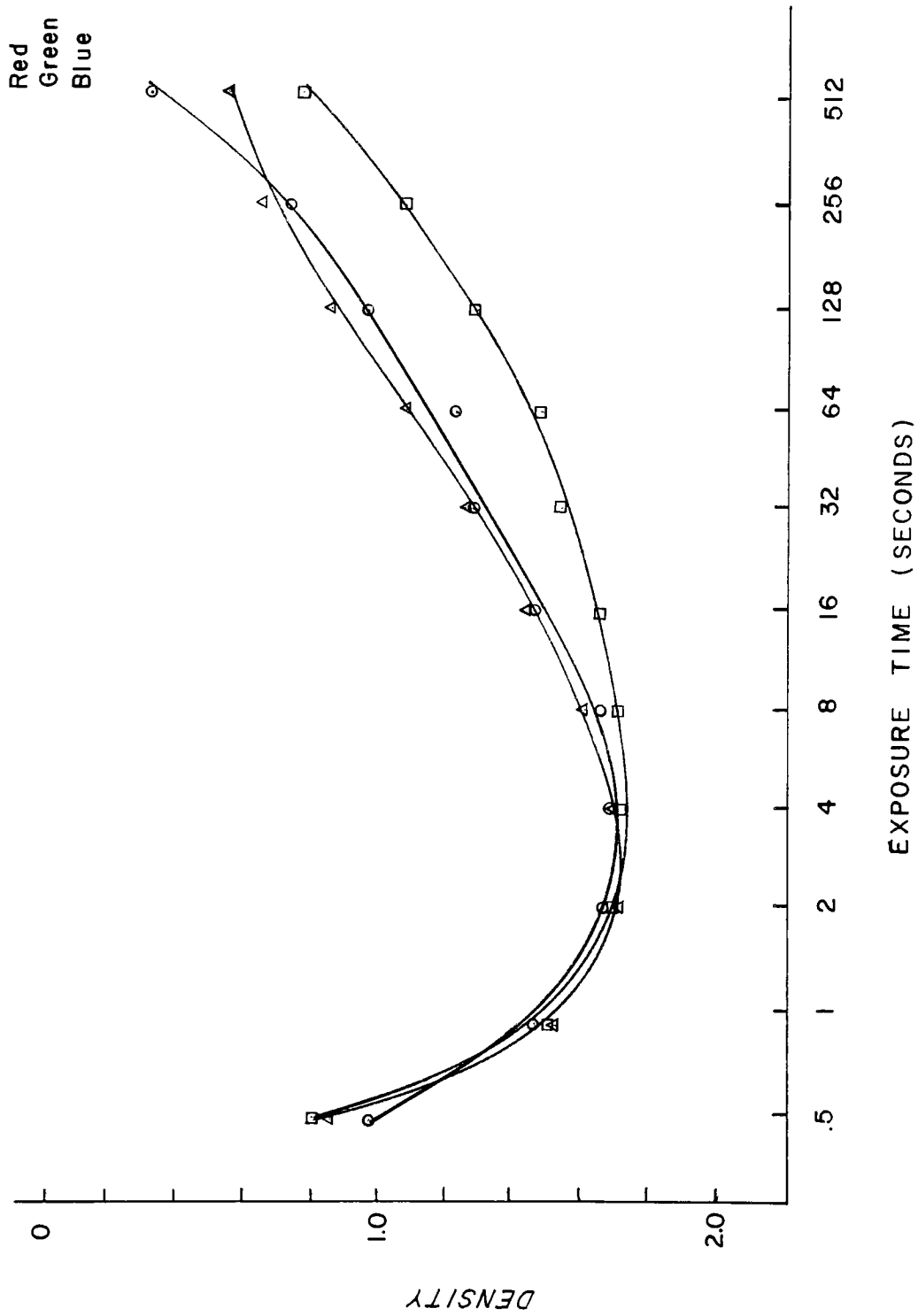


Figure 10c. 78 paper Emulsion I, high densities.

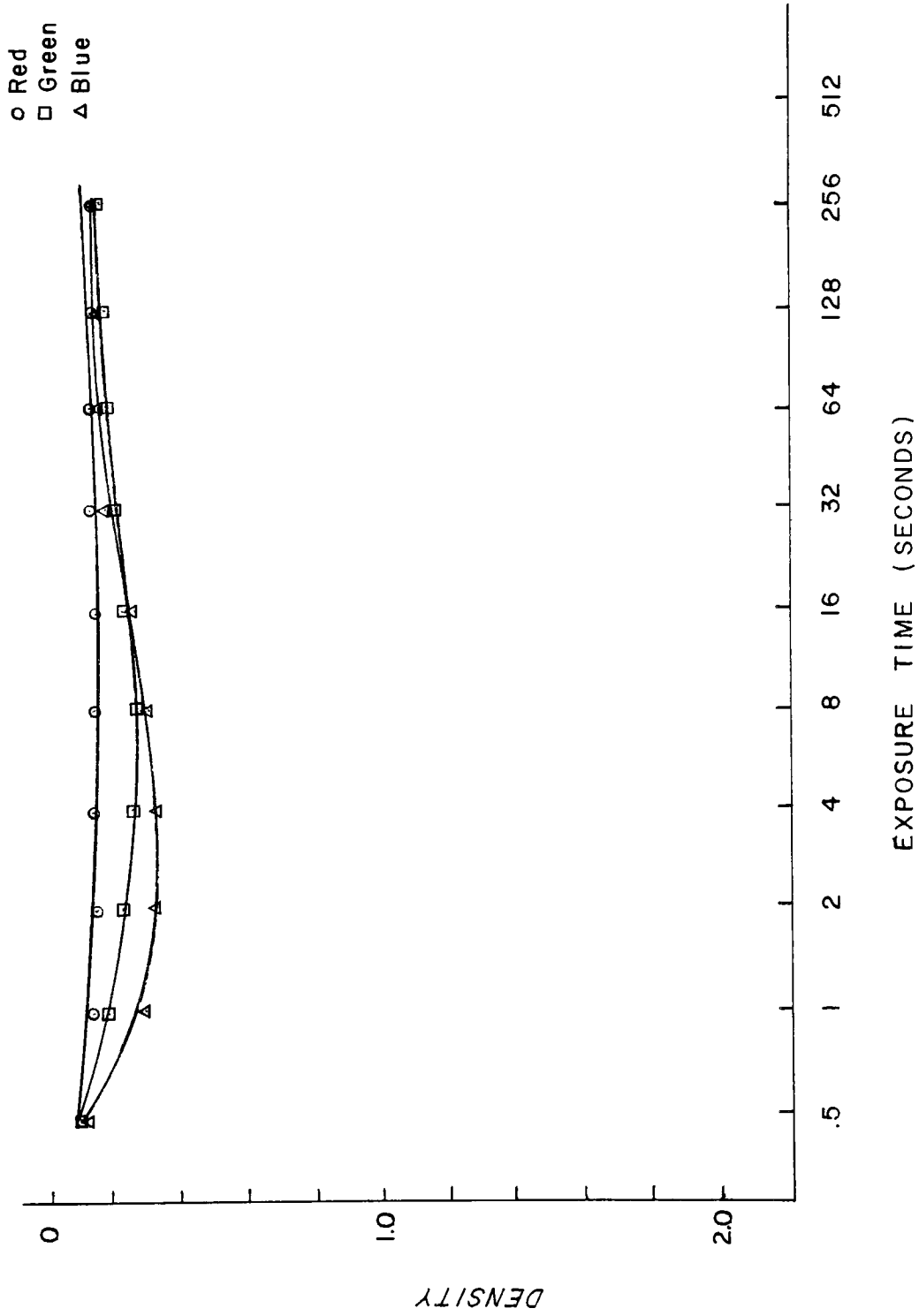


Figure 11a. 78 paper Emulsion II, low densities.

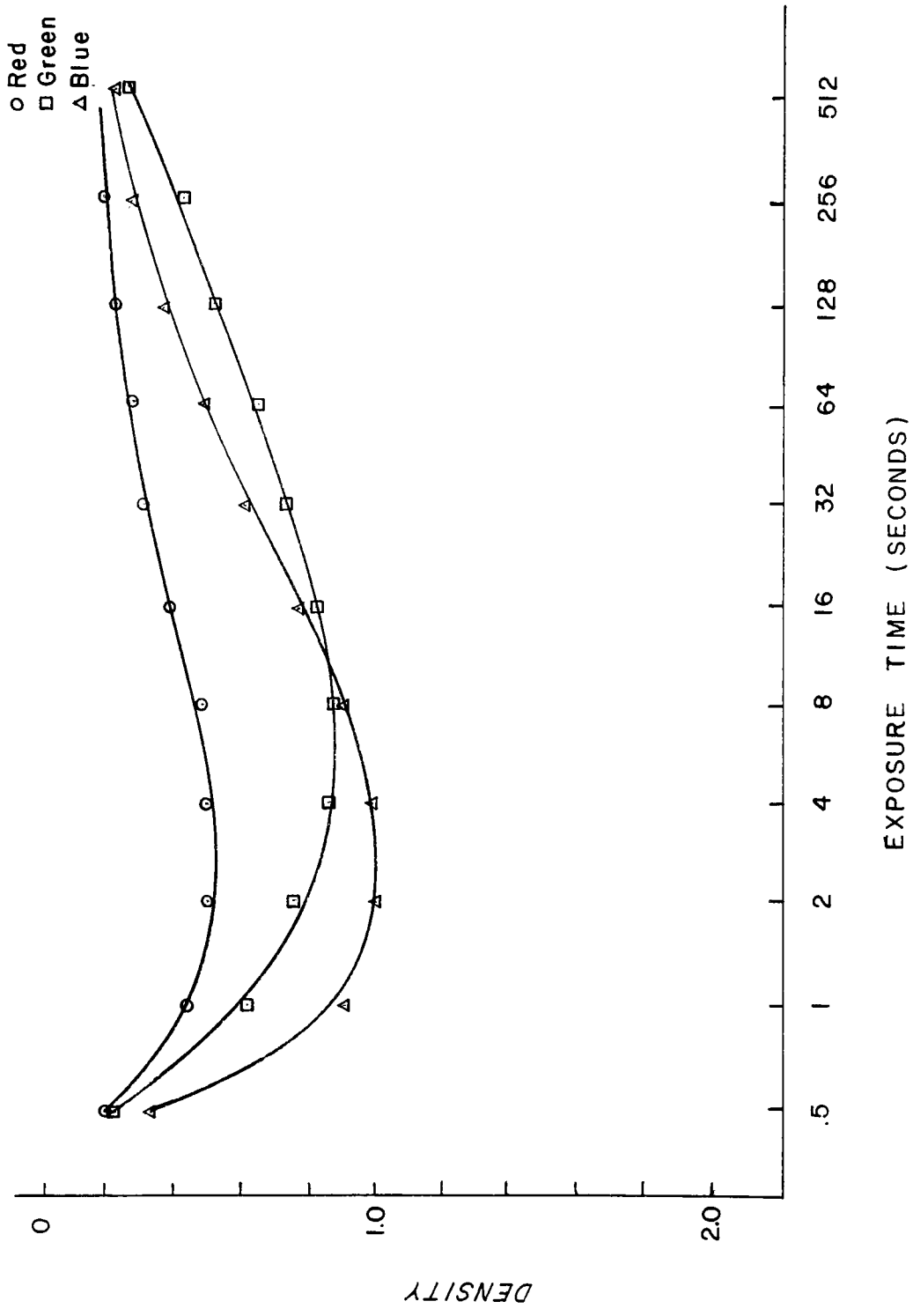


Figure 11b. 78 paper Emulsion II, aim densities.

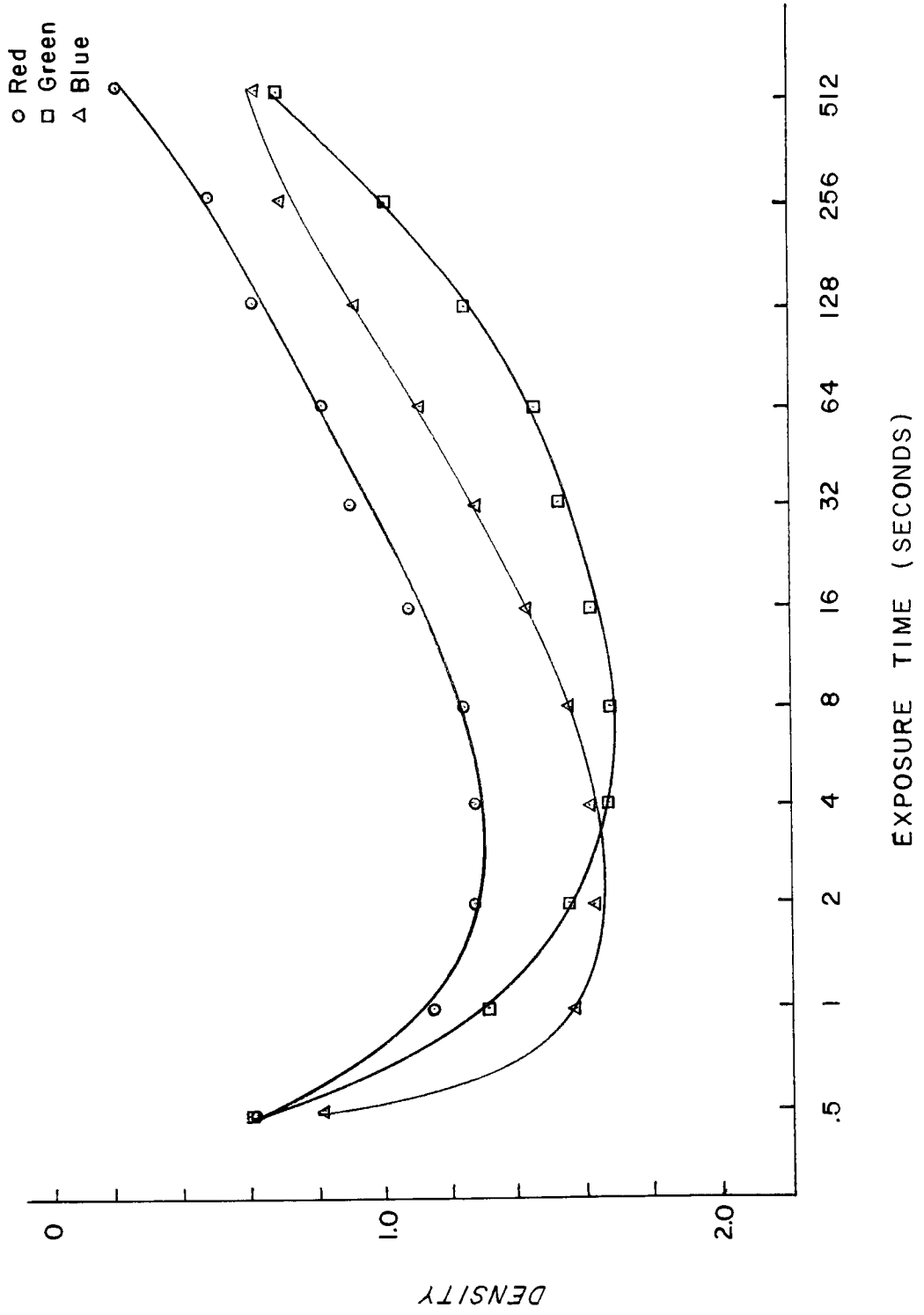


Figure 11c. 78 paper Emulsion II, high densities.

## VITA

Vicki was born in Cherry Hill, New Jersey and graduated with honors from Delran High School in Delran, New Jersey. She began her studies in Photographic Science at Rochester Institute of Technology in Septmeber 1978. Between her junior and senior year she was employed by Digital Equipment Corporation as a Process Engineer and plans on returning for a permanent position upon graduation.