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INTERACTION OF BROMIDE AND ORGANIC ANTIFOGGANTS IN DEVELOPMENT

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Abstract

Various levels of bromide and an organic antifoggant, benzotriazole, were combined in a developer and investigated to determine if an interaction existed. Both nitrogen burst agitation and viscous development were used. It was found that benzotriazole is such a strong antifoggant that interaction occurs only at low density levels, and the influence of benzotriazole increases with development time.

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TABLE OF CONTENTS

INTRODUCTION

The function that bromide, an antifoggant, has in the developer is fairly well understood, however the same cannot be said for the organic antifoggants such as benzotriazole. In much of the literature there is little distinction made between bromide and organic antifoggants and there seems to be no knowledge about the interaction of the two when used together in the same developer.

The aim of this thesis is to investigate the interaction of bromide and the organic antifoggant benzotriazole. Originally, the investigation was primarily concerned with microscopic data such as adjacency effects; but due to encountered problems during the course of the year, this was later changed to macroscopic data such as gamma, contrast index, speed, and the base plus fog levels resulting from using different levels of bromide and benzotriazole.

The basic developer used in this investigation consisted of 2 grams per liter of metol, 25 grams per liter of sodium sulfite, and 25 grams per liter of sodium carbonate. Added to this were various levels of bromide and benzotriazole. The levels of metol, bromide, and benzotriazole used in the developer were determined in a preliminary experiment.

THEORETICAL BASIS AND PROCEDURE

Antifoggants are added to the developer to act as a fog restrainer and as an aid toward more uniform development. It has been shown that bromide added to the developer as potassium bromide does this through two different mechanisms.

First, the excess bromide lowers the free silver ion concentration. Second, some of the excess bromide ions are adsorped by the silver bromide crystal.

The mechanisms by which organic antifoggants work, though, are not as well understood. They generally combine with the silver ions, but the change in the pAg is too small to account for the effects. The evidence towards adsorption, however, is conflicting.

Birr in an extensive investigation of adsorption of antifoggants by silver halides could not find a clear relation between the adsorption by silver halide and the photographic activity of 1-phenyl-5-mercaptotetrazole and a group of benzotriazoles.[1] But other studies by Thompson and Rado indicate that adsorption may occur to some extent.[2,3]

A preliminary experiment was made to determine the proper working levels of the metol, bromide and benzotriazole to be used in the developer. This was done using Kodak 5302 Fine Grain Positive orthochromatic film chosen because it is a simple emulsion type with a minimum of addenda. The film was exposed in a sensitometer and processed using various combinations of metol and bromide levels in the developer. The process was then repeated for various combination levels of metol and benzotriazole. The developing process was done using nitrogen burst agitation and for development times of 2, 4, 8, and 16 minutes.

After analyzing the resulting data, it was decided to use the following bromide and benzotriazole levels in the developer along with two grams per liter of metol and the 25 grams per liter of sodium sulfite and 25 grams per liter of sodium carbonate:

Bromide - 0, .4, 1 grams per liter
Benzotriazole - 0, .16, 1 grams per liter

The original plan of attack was to have the film, Kodak 5302, exposed to an edge and then processed in the developer using various levels of bromide and benzotriazole. These edge exposures would then be scanned with the Ansco microdensitometer and the resulting traces analyzed. From the analysis a suitable measurement for the adjacency effect would be computed. Then the influence the various combinations of bromide and benzotriazole levels had on the adjacency effects would be used as a measure for studying the interaction of the two antifoggants.

Attempts were made to obtain an edge by contact printing a National Bureau of Standards edge onto Kodak High Resolution orthochromatic film. Two types of NBS edges, one on a glass substrate and the other on a plastic substrate, were used. In both cases, due to poor contact between the NBS edge and the film, an edge of the desired quality could not be obtained.

Therefore a set of Ronchi rulings were obtained from the Graphic Arts Research Center through Mr. Archer. It was hoped that by using the Ronchi rulings the results of a single microdensitometer scan could be averaged and random error reduced.

The Ronchi rulings target was contact printed onto Kodak 5302 orthochromatic film using an enlarger as an approximate point source. Film was also exposed in a sensitometer and processed along with the Ronchi rulings exposure. The processing was done by nitrogen burst agitation for development times of 2, 4, 8, and 16 minutes.

The film strips containing the Ronchi rulings exposure were then scanned with the Ansco microdensitometer. It was found that no measurable or useful adjacency effects had been created. It was thought that this could be due to the nitrogen burst agitation, therefore it was decided to go to a viscous development.

Viscous development involves adding a thicking agent, sodium carboxymethylcellulose, to the regular developer. This changes the developer into a gel-like substance. The purpose of this type of development is to reduce agitation to an absolute minimum. The film is then processed by coating the film with the developer. After several trials it was decided to use 25 grams per liter of sodium carboxymethylcellulose. This caused a slight decrease in the pH which was brought up to the original level of the developer by adding sodium hydroxide.

A developer time series experiment involving the various bromide - benzotriazole levels was run using the following procedure. The viscous developer was poured into an 8 x 10 developing tray. The film strips were taped down onto a glass plate, emulsion side up - one strip being exposed to the Ronchi rulings, the other to the sensitometer. The glass plates were then turned over and placed on top of the gel-like developer so the emulsion side of the film was placed in direct contact with the developer. Because it was thought that much longer development times would be needed the processing times were extended to 8, 16, and 32 minutes. This was later reduced to 4, 8, and 16 minutes.

The film exposed to the Ronchi rulings was then scanned with the Ansco microdensitometer and again there were no measurable or useful adjacency effects. Because of the time involved it was decided to use the sensitometric data that had already been obtained. It is now felt that larger adjacency effects could be obtained by reducing the metol level used in the developer and using a sharper target.

RESULTS AND DISCUSSION

There were four factors involved in this experiment: development time, agitation, and the two main factors, the levels of bromide and benzotriazole in the developer. The effects of these four factors in development were measured in four response variables: base plus fog, gamma, contrast index, and speed.

Base plus fog is the smallest density read off the sensi-strips. Gamma is the measure of the slope of the straight-line portion of the density versus log exposure curve. The contrast index is the slope of a straight line joining densities, on the D-log H curve, selected as follows: The minimum density lies on on the arc of a circle having a radius of 0.20 density units. The maximum density lies on the arc of a larger circle concentric to the smaller one and having a radius 2.00 greater than that of the smaller circle.[4] This measure of contrast was facilitated by the use of a contrast index meter. The speed was calculated by using the following equation:

$$S = \frac{0.8}{H}$$

where H is the exposure in lux-seconds needed to get a density of 0.1 above base plus fog.

Two measures of contrast were used because, in some instances, a hard and fixed value for gamma was difficult to obtain. Contrast index provided a number less sensitive to the fluctuations inherent to less than perfect uniformly processed and developed density patches.

The variations in the observed values of base plus fog were attributed largely to the effects of benzotriazole and development time. As expected, longer development times increased the fog level, while greater amounts of benzotriazole decreased the values for base plus fog. At closer inspection, there was evidence of an interaction between the two factors of time and benzotriazole. The nature of the interaction cannot be easily interpreted. The evidence in the present set of data suggest that it is linear in both factors. An increase in development time is accompanied by a corresponding increase in base plus fog; and an increase in benzotriazole levels indicate a corresponding decrease in the base plus fog level (see table I).

The measure of base plus fog was the only response variable to provide any indication that an interaction may have occurred between the two antifoggants, bromide and benzotriazole. Although the individual effect of bromide ceases to be significant at long development times, the joint effect of bromide and benzotriazole becomes significant with increasing time.

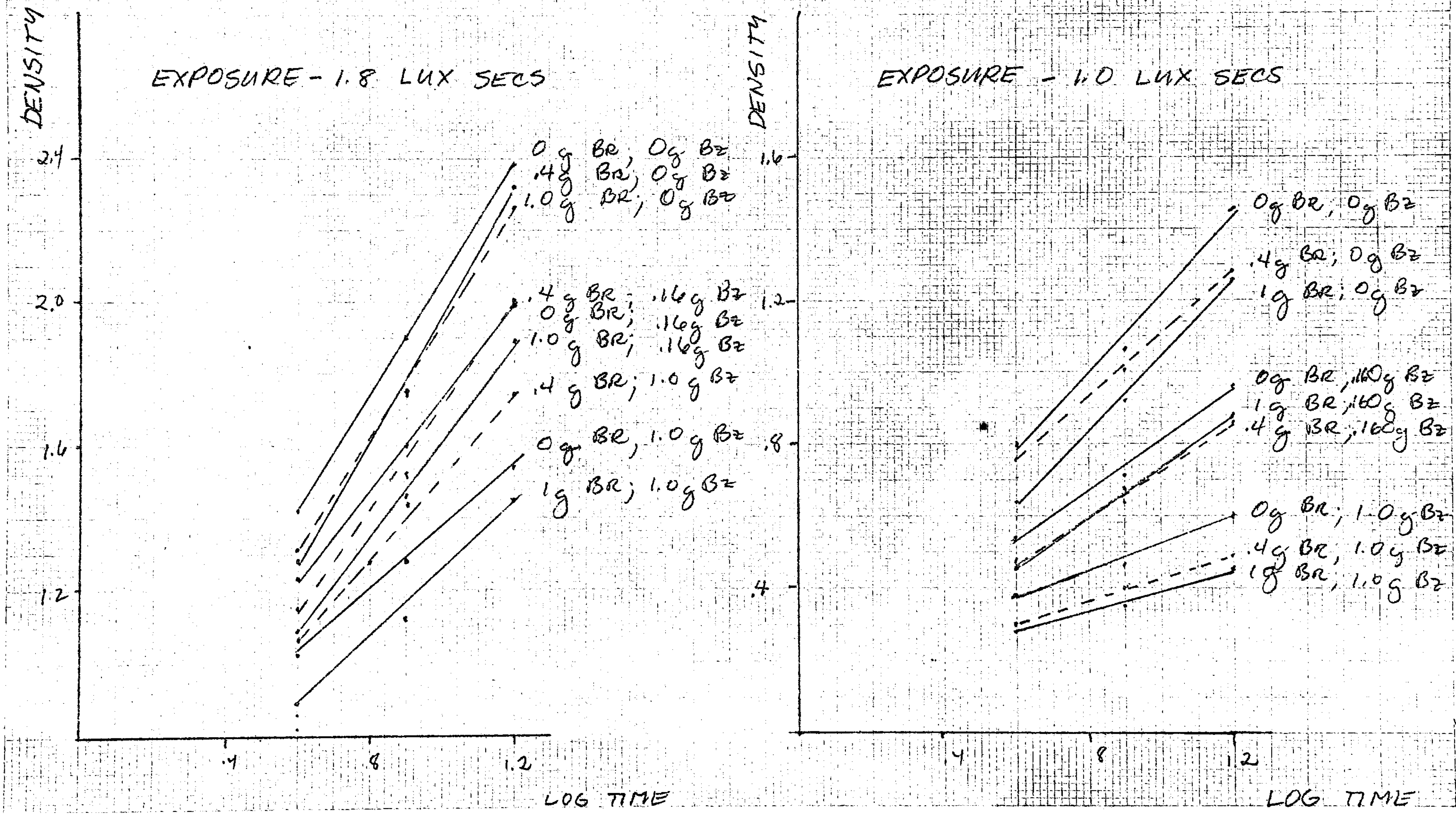
Analysis of the data suggest that the effect of varying the amounts of bromide and benzotriazole are detectable at lower exposure levels. A similar behavior can be observed in the graphs of density versus log time, which also indicate the influence of benzotriazole increases with time (see graph I).

TABLE I

BASE PLUS FOG VALUES

		Viscous		Nitrogen Burst	
Bromide	Benzotriazole	4 min	16 min	4 min	16 min
.4 g	.16 g	.04	.06	.04	.07
	1.00 g	.03	.05	.04	.05
1.0 g	.16 g	.05	.08	.04	.05
	1.00 g	.03	.04	.04	.04

GRAPH I DENSITY VS LOG TIME



Gamma, as a measure of contrast, was not a consistent response variable. This resulted in a large estimate for the error term rendering gamma, as a numerical indicator, insensitive to some effects that were actually present in the treatments. This becomes clearer when the results taken from the analysis of gamma values are compared to those derived from the analysis of contrast index values (see tables II and III).

The inconsistency in the gamma values is due mainly to two unavoidable consequences of the method of obtaining the plots of the density versus log exposure graphs. The first is that not every characteristic curve will have a straight-line portion. The second is that the curves themselves are essentially estimates of discrete density values which are single point estimates if the treatment is not replicated. In this experiment only the viscous developers were replicated. The measure of gamma is therefore susceptible to many subjective interpretations.

The differences found among the gamma values were attributed by numerical analysis to the effects of agitation, development time, and amounts of benzotriazole present in the developer. The obvious influence of agitation and development time on the response variable, gamma, is to increase the observed values. This result was expected as it is known that an increase in agitation or in development time is accompanied by an increae in contrast.

TABLE II

GAMMA VALUES

Nitrogen Burst		Time			
Bromide	Benzotriazole	2 min	4 min	8 min	16 min
.4 g	.16 g	1.08	1.61	1.64	1.80
	1.00 g	.90	1.40	1.56	1.89
1.0 g	.16 g	.92	1.35	1.67	1.74
	1.00 g	.80	1.34	1.55	1.80

Viscous		Time				
Bromide	Benzotriazole	4 min	8 min	16 min	32 min	
.4 g	.16 g		.98	1.15	1.33	1st run
		.85	1.15	1.50		2nd run
	1.00 g		1.10	1.37	1.53	1st
		.80	1.10	1.30		2nd
1.0 g	.16 g		.85	1.05	1.33	1st
		.82	1.00	1.35		2nd
	1.00 g		1.10	1.37		1st
		.78	1.05	1.38		2nd

TABLE III

CONTRAST INDEX VALUES

Nitrogen Burst		Time			
Bromide	Benzotriazole	2 min	4 min	8 min	16 min
.4 g	.16 g	.92	1.17	1.20	1.40
	1.00 g	.75	1.10	1.22	1.31
1.0 g	.16 g	.84	1.12	1.27	1.32
	1.00 g	.68	1.02	1.11	1.22

Viscous		Time				
Bromide	Benzotriazole	4 min	8 min	16 min	32 min	
.4 g	.16 g		.78	.97	1.06	1st run
		.75	.92	1.07		2nd run
	1.00 g		.89	1.03	1.17	1st
		.66	.92	1.02		2nd
1.0 g	.16 g		.83	1.04	1.20	1st
		.66	.84	.96		2nd
	1.00 g		.89	.99	1.11	1st
		.64	.86	1.06		2nd

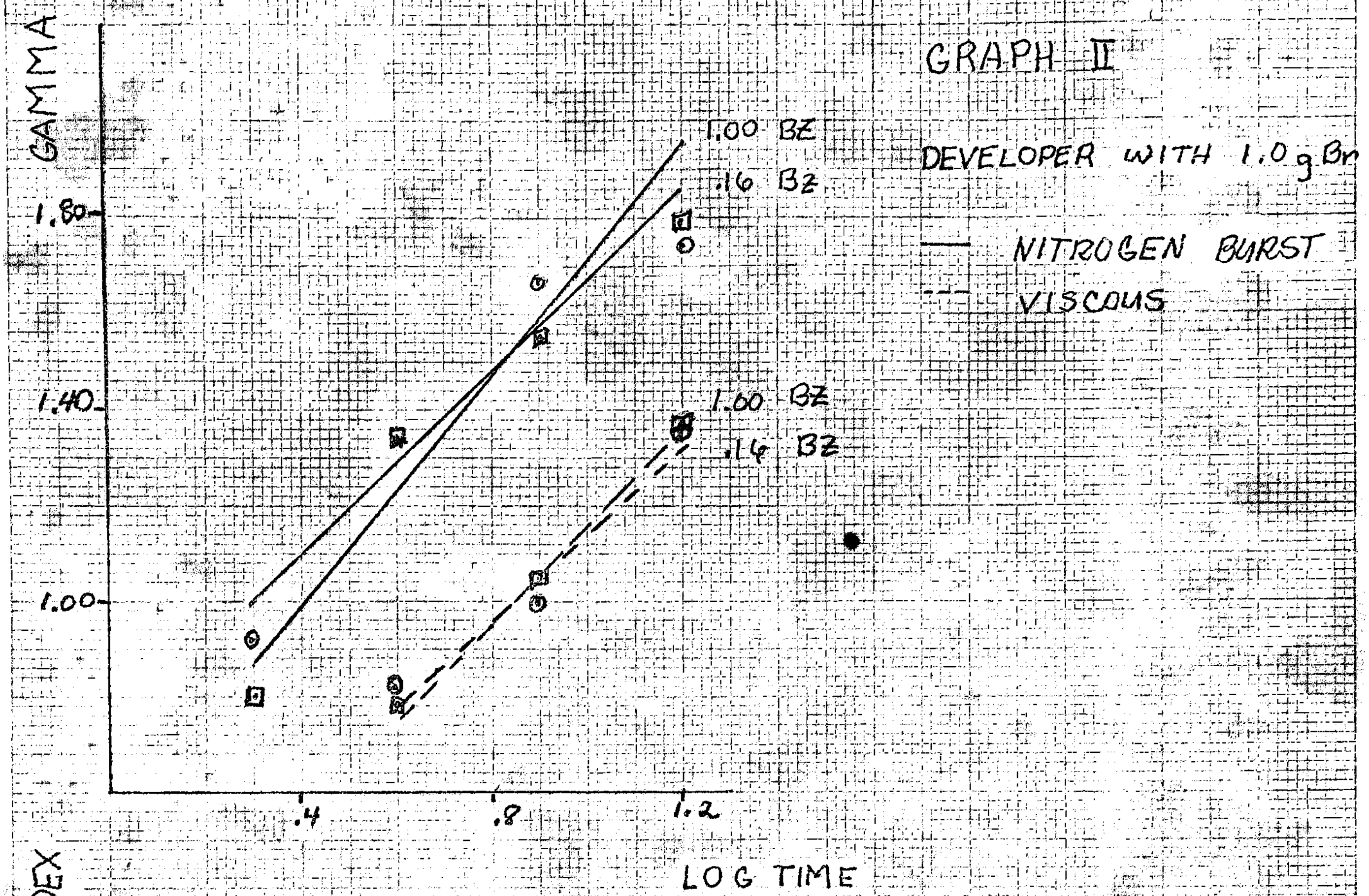
The effect of increasing the benzotriazole level, with full agitation or with none, is evident in the decrease of the gamma values. But it is apparent that, with respect to gamma, the effect of varying levels of benzotriazole is significant at 8 minutes, while not for 16 minutes. But this could be due to the large error term (see table II and graph II).

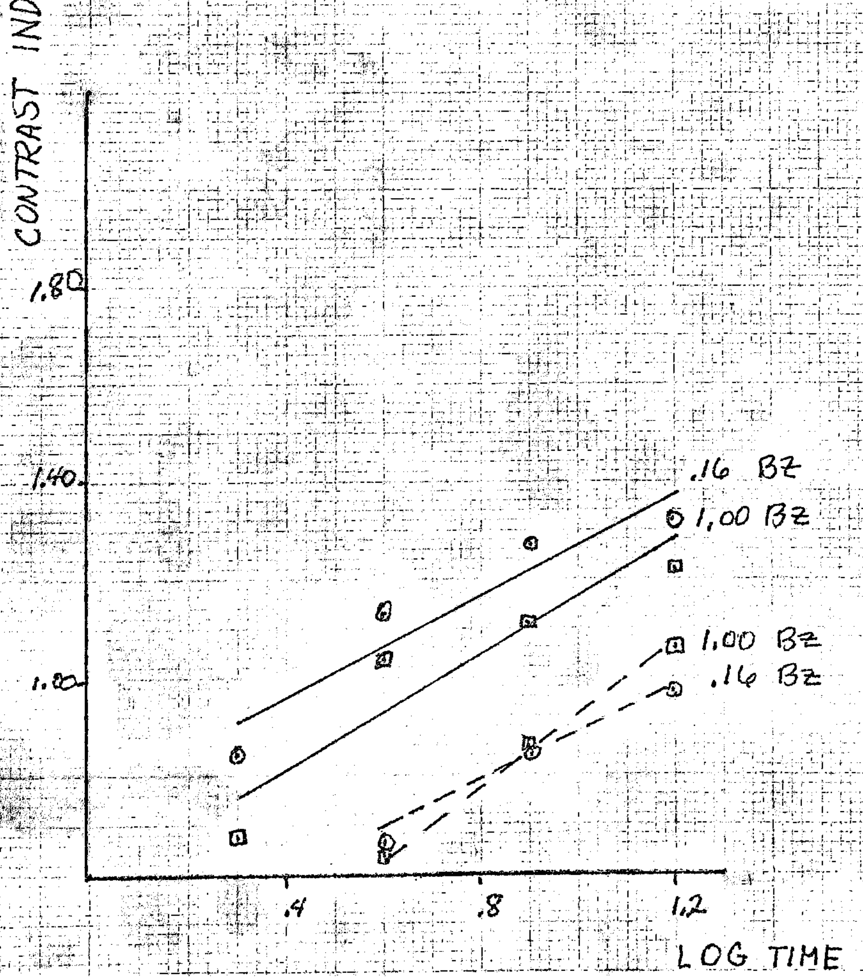
The combination of the antifoggants in the developer did not make any significant difference in the resulting gamma values. This is quite apparent from the characteristic curves of the sensi-strips developed for 4 minutes in each of the following developers:

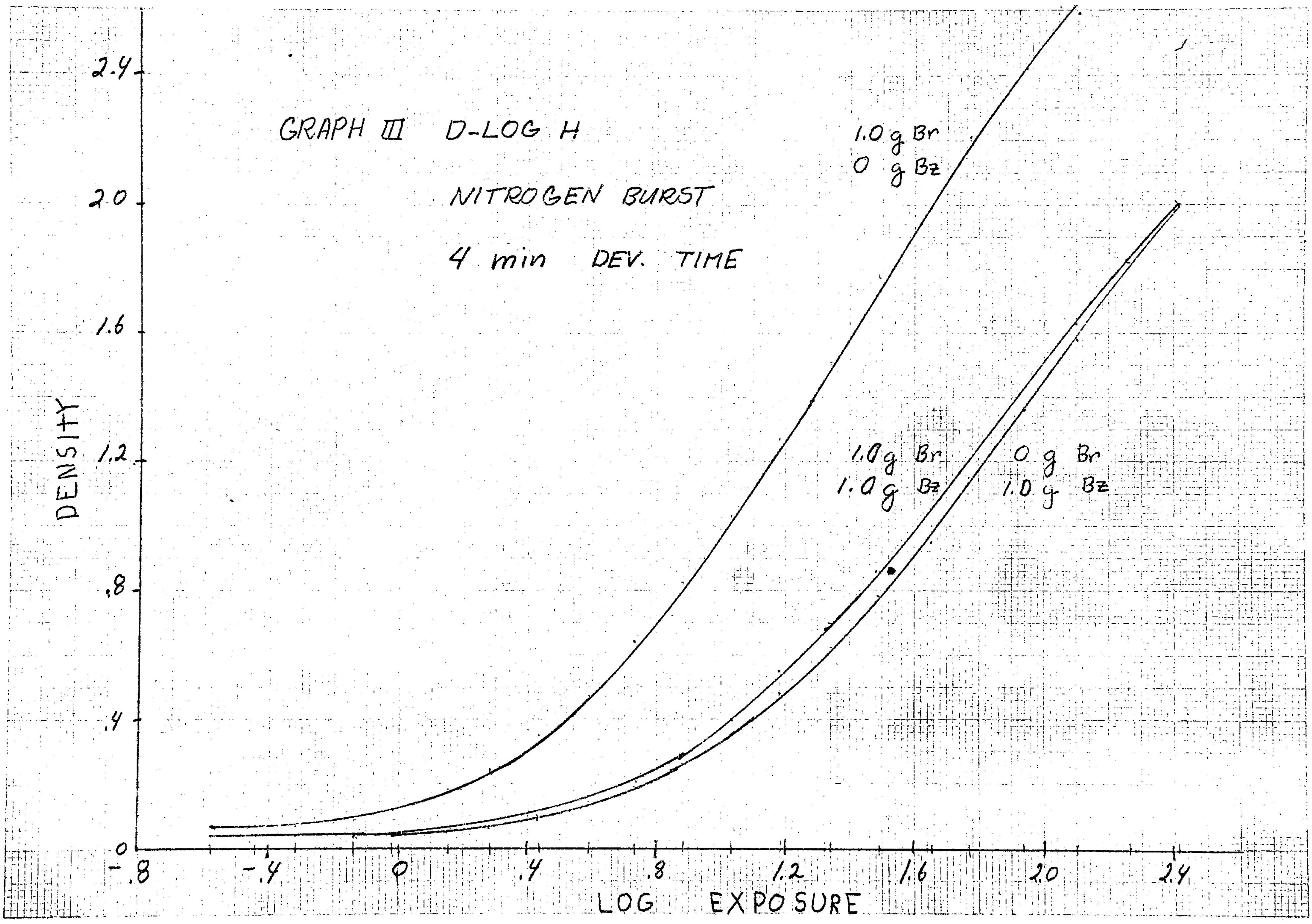
gr/lr Br.	gr/lr Bz.
1.0	0.0
0.0	1.0
1.0	1.0

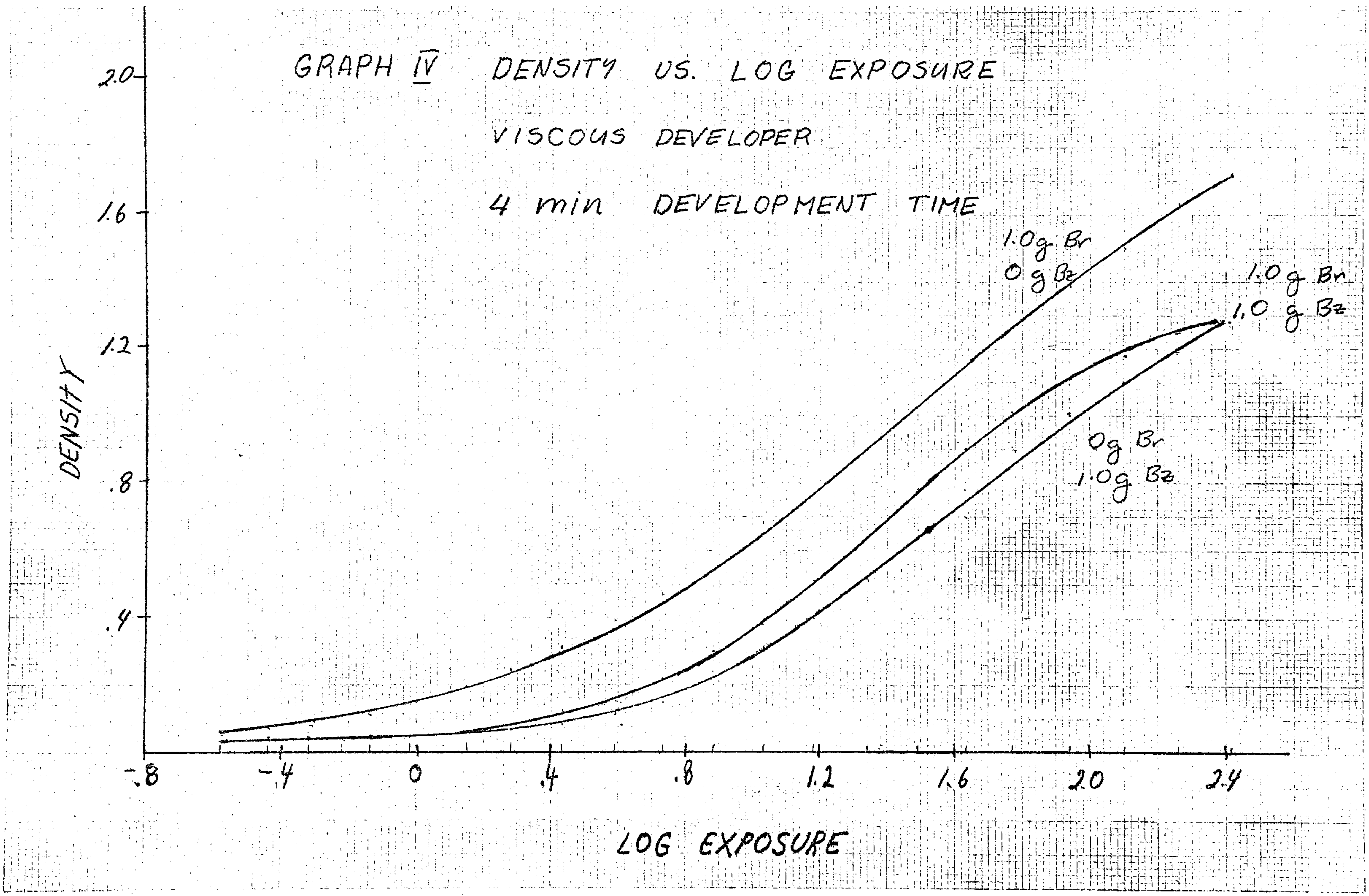
These were processed by nitrogen burst agitation (see graph III). Agitation, however, does make a difference in the results as is evident in the characteristic curves of sensi-strips processed in viscous developers with the same amounts of bromide and benzotriazole (see graph IV). The effect of the combination of bromide and benzotriazole becomes significant at l w density levels.

As a whole, contrast index was more indicative of the main effects than was gamma. It provided roughly the same information obtained from the numerical analysis of gamma values, attributing the variations observed in the


GRAPH II
DEVELOPER WITH 1.0 g Br
NITROGEN BURST
VISCOUS
GAMMA
1.80
1.40
1.00
1.00 BZ
.16 BZ
1.00 BZ
.16 BZ
.4
.8
1.2
LOG TIME


CONTRAST INDEX
1.80
1.40
1.00
.16 BZ
1.00 BZ
1.00 BZ
.16 BZ
.4
.8
1.2
LOG TIME


GRAPH III D-LOG H
NITROGEN BURST
4 min DEV. TIME
1.0 g Br
0 g Bz
1.0 g Br
1.0 g Bz
0 g Br
1.0 g Bz
DENSITY
2.4
2.0
1.6
1.2
.8
.4
0
-.8
-.4
0
.4
.8
1.2
1.6
2.0
2.4
LOG EXPOSURE


GRAPH IV DENSITY VS. LOG EXPOSURE
VISCOUS DEVELOPER
4 min DEVELOPMENT TIME
1.0g Br
0 g Bz
1.0 g Br
1.0 g Bz
0g Br
1.0g Bz
2.0
1.6
1.2
.8
.4
DENSITY
-.8
-.4
0
.4
.8
1.2
1.6
2.0
2.4
LOG EXPOSURE

data to the same factors - viz. agitation, development time, and benzotriazole. However, the numerical analysis of the contrast index values yielded up more readily the fact that the joint effects of benzotriazole with the rate of development and agitation are significant. This was suspected but the numerical analysis of gamma values failed to indicate this because of the large error term.

The joint effect of benzotriazole and time with respect to contrast is linear in both factors (see table III). Increase in time results in an increase in contrast. Increase in the amount of benzotriazole results in a decrease in contrast. The effect of benzotriazole becomes significant at development times of 8 and 16 minutes for the viscous development. Again, with respect to this measure of contrast, no significant interaction occurs between bromide and benzotriazole when combined in the developer.

The numerical analysis of speed as the response variable is more difficult to interpret than the other response variables; because, strictly speaking, speed is not independent of contrast, one of the response variables. However, because contrast was not treated as a factor in this experiment, there is no way at present of gauging the strict validity of applying univariate statistical tests on the variance observed among the speed values. To insure, in a limited fashion, the validity of the following statements no effect will be considered significant unless it is significant at an alpha risk of .01.

An analysis of variance on speed values rendered significant the effects of development time and benzotriazole. The combined effects of development time and agitation with benzotriazole were also considered significant. This is all consistent with the information obtained from the study of contrast index and gamma. Again, the addition of bromide in the developer did not make any significant difference in the resulting values for speed (see table IV).

The analyses on variance for all four response variables suggest that bromide and benzotriazole behave differently in development. The addition of benzotriazole into a developer containing bromide overshadows whatever effect bromide may have had, particularly on contrast. The effects of benzotriazole and bromide are more detectable at low densities. This is obvious with the observed values for base plus fog. As development time increases or when agitation is employed the effect of bromide becomes insignificant compared to that of benzotriazole. However, as the density continues to build up with time, the effect of the benzotriazole level ceases to be a significant factor in the resulting contrast and speed values.

TABLE IV

SPEED VALUES

		Viscous		Nitrogen Burst	
Bromide	Benzotriazole	4 min	16 min	4 min	16 min
.4 g	.16 g	.85	1.50	1.58	1.73
	1.00 g	.80	1.10	1.35	1.70
1.0 g	.16 g	.82	1.00	1.35	1.75
	1.00 g	.78	1.05	1.25	1.50

CONCLUSIONS

In considering these conclusions one must remember that they pertain only to the bromide and benzotriazole levels used in this investigation. It is evident that when benzotriazole and bromide are combined in the developer the former, benzotriazole, is the stronger of the two antifoggants. Also, benzotriazole has an increasing effect on the developed density levels with increasing development time. This is more evident at the lower exposure levels.

FOOTNOTES

[1]E. J. Birr, *Z. Wiss. Photo*, *47*, 72 (1952) as quoted in C. E. Kenneth Mees and T. H. James, *The Theory of the Photographic Process.* (New York: MacMillian Co., 1966) p. 345.

[2]Thomas Thompson, "Action of Organic Stabilizers on a Photographic Emulsion," *Photographic Science and Engineering*, Vol. 18, no. 6 (Nov.-Dec. 1959) p. 272.

[3]A. Rado. *Z. Wiss. Photo, 56,* 141 (1962) as quoted in C. E. Kenneth Mees and T. H. James, *The Theory of the Photographic Process*. (New York: MacMillian Co., 1966) p. 346.

[4]*SPSE Handbook of Photographic Sciences and Instrumentation*, Edited by Woodlief Thomas, Jr. (New York: John Wiley & Sons) 1973, p. 821.

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