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THE EFFECTS OF BENZOTRIAZOLE IN A PHOTOGRAPHIC DEVELOPER ON THE COVERING POWER OF AN EMULSION

by

Kenneth A. Carlson

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
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of the Rochester Institute of Technology

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THE EFFECTS OF BENZOTRIAZOLE IN A PHOTOGRAPHIC DEVELOPER ON THE COVERING POWER OF AN EMULSION

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Submitted to the
Imaging and Photographic Science Division
in partial fulfillment of the requirements
for the Bachelor of Science Degree
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ABSTRACT

Benzotriazole in a photographic developer has been determined to increase covering power. This is accompanied by a decrease in photographic speed proportional to the increase in covering power. Benzotriazole decreases the rate of development when measured by mass of silver developed, but may increase the rate of development when measured by density at D-max exposures because of the increase in covering power. The effect of benzotriazole on image color has also been determined. Possible explanations for effects are given.

ACKNOWLEDGEMENT

The author is grateful to Richard J. Byer of the E.I. DuPont Co. who provided valuable consultation and advice throughout the experiment. Without his help, this experiment could not have been carried out effectively.

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I. INTRODUCTION

The covering power of a photographic emulsion is defined as the ratio of density to mass of silver per unit area. This number is interpreted as the reciprocal of the weight of silver per unit area that is required to produce a density of 1.0.

There are many factors that affect covering power, among them;

1.) composition of the developer [1-8].
2.) swelling of the protective colloid, i.e. gelatin [1,9].
3.) drying conditions after processing [10].
4.) undeveloped particle size [2-4].

These four factors affect developed particle size and structure which in turn affect covering power.

Factors relevant to this experiment which affect image color are;

1.) composition of the developer [1,2,3,5,11-15].
2.) swelling of the gelatin layer [1].
3.) particle size [1,3,4,5,16,17,18].

The composition of the developer will affect whether chemical or physical development or a combination of both occurs. In physical development, image silver is formed at a silver/solution interface [19]. Solution-physical development can be accomplished by the addition of a silver halide solvent to a chemical developer. In chemical development, image silver is formed at a silver/silver halide interface [19]. The result of physical development is a compact silver particle giving low covering power [20] and a colored silver deposit [4]. The result of chemical development is the formation of long filaments of silver giving higher covering power [20] and a more neutral silver deposit [4].

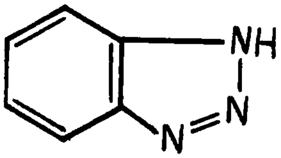

Figure 1. Structural formula of benzotriazole

Some organic compounds in the developer will adsorb to the silver halide crystal during development and cause a change in the developed image structure. It has been shown that benzotriazole (structural formula shown in figure 1.) in the developer covers only 10-15% of the silver crystal surface and that the restraint of physical development is a direct function of the surface area covered and not necessarily dependent on the organic agent that is adsorbed to the surface [21]. Benzotriazole may also accelerate chemical development [14], which in combination with the restraint of physical development may partially explain the blue-black toning effect of benzotriazole. It has also been shown that organic agents adsorbed to the silver crystal surface, through development or otherwise, will change the spectral absorption properties of the silver deposit [22,23].

The amount of swelling of a gelatin emulsion layer affects covering power and the color of the silver deposit. Less mechanical pressure is exerted on the silver halide crystal which promotes expansion of chemically developed crystals and hence, covering power increases [1].

Temperature is one factor which affects emulsion swelling [9]. As developer temperature increases, the emulsion swells more, increasing covering power [1]. If the emulsion is hardened, temperature has less of an effect on swelling and consequently covering power [9]. One would suspect that the amount an emulsion has been hardened would affect the rate of development. It has been shown that the rate of development as measured by mass of developed silver is independent of the amount of hardening before development [1]. The rate of development as measured by developed density, however, decreases with increasing amount of hardening. This means that hardening does not affect the rate of reduction of silver ions, but does affect the expansion of chemically developed silver filaments due to increased mechanical pressure.

Increasing development temperature will increase emulsion swelling which will promote the expansion of chemically developed silver filaments. This should make the developed silver deposit more neutral, but James and Fortmiller [1] have shown experimental evidence to the contrary. They propose that the increase in developer temperature changes the relative amount of solution-physical development which makes the silver deposit more colored as temperature increases.

Blake and Meerkamper [10] have shown that drying conditions after development of a photographic emulsion affect final density and consequently covering power. The two relevant variables with respect to drying are temperature and relative humidity.

Undeveloped particle size also influences covering power. Farnell and Solman [2] have shown that for chemical development, covering power is almost independent of undeveloped grain size in the range of 0.002 to 0.04 μm^2 projected area and is inversely proportional to grain size for grains larger than 0.04 μm^2 projected area. Solman [3] has shown that for physical development, covering power is directly proportional to grain size up to a maximum at about 0.004 μm^2 projected area where covering power becomes inversely proportional to grain size with larger grains. For large particles (greater than 0.04 μm^2 projected area for chemical development and greater than 0.005 μm^2

projected area for physical development), chemical development gives higher covering power than physical development. This is not true for small particles [4].

Image color is also highly dependent on particle size. Increasing particle size shifts the spectral absorption maximum to longer wavelengths and makes the silver deposit less colored [17,18]. Going from a particle diameter of .01 µm to a particle diameter of .08 µm changes the silver deposit transmission color from yellow to blue [5].

Determing the effects of benzotriazole in a developer was the objective of this experiment, and this was done at various concentrations of sodium sulfite to investigate the role of physical development. The comparison was made at constant density. Since benzotriazole is a development restrainer, film samples processed in developers containing high concentrations of benzotriazole required greater exposures for density to remain constant. Five concentrations of benzotriazole were investigated and at three concentrations of sodium sulfite.

The dependent variables investigated were covering power, image color, rate of development, photographic speed, and D-max. Determining covering power was the main objective of this experiment and the other variables were measured to confirm present knowledge and to aid in analyzing covering power data.

DuPont Medical Recording Film (MRF) type 331, a large grain emulsion, was used in this experiment because it has a practical importance since it is currently popular commercially. Medical recording emulsions are intended for transmission viewing, so image color is important. Doctors prefer a "cold-tone" blue-black image color over a "warm-tone" reddish image for X-ray films [26]. It is well known that benzotriazole in a photographic developer will provide a "cold-tone" image. What is not characterized in the literature is the effect that this additive has on covering power.

II. EXPERIMENTAL

Fifteen developers containing various levels of benzotriazole and sodium sulfite were designed to carry out this experiment. All developers had the same basic composition shown in table 1. A matrix describing the various levels of benzotriazole and sodium sulfite added is shown in table 2.

TABLE 1
Basic Developer Formula

metol (N-methyl-p-aminophenol)	2.50 grams
ascorbic acid	10.00 grams
sodium carbonate monohydrate	35.00 grams
potassium bromide	0.200 grams
water to make	1.00 liters

pH = 10.24 ± .02 at 34 °C.

TABLE 2
Treatment Combinations

sodium sulfite (g/l)	benzotriazole (g/l) 0	0.1	0.3	0.9	2.7
0	00	01	02	03	04
20	10	11	12	13	14
80	20	21	22	23	24

As an example, developer 00 contains no benzotriazole or sodium sulfite and developer 22 contains 0.3 g/l benzotriazole and 80 g/l sodium sulfite. These concentrations were chosen to provide a range of concentrations that might normally be found in practical developers.

Large batches of the base developer in table 1 were mixed and the appropriate amounts of benzotriazole and sodium sulfite were added to samples of that batch. The pH was readjusted to 10.24 ± .02 pH units at 34^{o}C. The pH measurements were made with a Beckman Research pH meter with a least count of 0.002 pH units.

Sensitometric exposures were made with a tungsten source and a photographic silver step wedge. D-max exposures were made with a 100 watt tungsten source at a distance of 5 feet for 3 minutes. This resulted in an exposure of approximately 5.2 log exposure units greater than the exposure at the speed point. A sensitometric development time series of 15 seconds, 30 seconds, 1 minute, and 2 minutes was done for each developer; exposures necessary to produce densities of 0.7 and 1.2 were determined. Three samples of MRF exposed to produce a density of 1.2 were processed for each developer. Three samples of MRF exposed to produce a density of 0.7 were processed in the ten developers containing the highest and lowest concentrations of sodium sulfite. Details of the processing procedure are given in appendix A.

Density measurements were made with a MacBeth TD-504 transmission densitometer. This instrument measures diffuse density with a 2 mm aperture. A photometric filter was used for all density measurements.

Silver weight analysis for each sample was performed by the E.I. DuPont Co. by X-ray fluorescence, and covering power was calculated from this data. The average precision of the analysis was ± 0.5%.

Image color was determined by measuring spectral densities from 380 nm to 700 nm in 10 nm increments and calculating chromaticity coordinates.

III. RESULTS

TABLE 3
Covering Power at Nominal Density of 0.7

Sodium sulfite conc. (g/l)	Benzotriazole conc. (g/l)	Development time (sec.)	Average density	Sample size	Average CP (m^2/g)
0	0	60	0.76	3	.477
"	0.1	"	0.70	3	.540
"	0.3	"	0.52	3	.580
"	0.9	"	0.57	3	.621
"	2.7	"	0.52	3	.700
80	0	60	0.75	3	.439
"	0.1	"	0.63	3	.482
"	0.3	"	0.88	3	.498
"	0.9	"	0.67	3	.565
"	2.7	"	0.70	6	.958

TABLE 4
Covering Power at a Nominal Density of 1.2

Sodium sulfite conc. (g/l)	Benzotriazole conc. (g/l)	Development time (sec.)	Density	Sample size	Average CP (m^2/g)
0	0	60	1.17	6	.494
"	0.1	"	1.02	3	.534
"	0.3	"	0.94	3	.544
"	0.9	"	0.94	3	.568
"	2.7	"	0.95	6	.750
20	0	60	1.11	3	.484
"	0.1	"	1.05	3	.535
"	0.3	"	1.23	3	.558
"	0.9	"	1.10	3	.588
"	2.7	"	0.98	3	.740
80	0	60	1.12	6	.462
"	0.1	"	1.02	3	.480
"	0.3	"	0.98	3	.501
"	0.9	"	1.18	3	.612
"	2.7	"	1.25	6	.874

TABLE 5
Covering Power at Maximum Density For a Development Time of 60 Seconds

Sodium sulfite conc. (g/l)	Benzotri-azole conc. (g/l)	Development time (sec.)	Density	Sample size	Average CP (m^2/g)
0	0	60	2.72	1	.663
"	0.1	"	3.04	1	.764
"	0.3	"	2.83	1	.689
"	0.9	"	3.18	1	.733
"	2.7	"	2.80	1	.819
20	0	60	2.77	1	.658
"	0.1	"	2.85	1	.674
"	0.3	"	2.85	1	.713
"	0.9	"	2.97	1	.707
"	2.7	"	2.90	1	.786
80	0	60	2.72	1	.630
"	0.1	"	2.79	1	.637
"	0.3	"	2.80	1	.659
"	0.9	"	2.66	1	.675
"	2.7	"	2.25	1	.862

TABLE 6
Covering Power at Maximum Density For a Development time of 30 seconds

Sodium sulfite conc. (g/l)	Benzotri-azole conc. (g/l)	Development time (sec.)	Density	Sample size	Average CP (m^2/g)
0	0	30	2.52	1	.700
"	0.1	"	2.19	1	.693
"	0.3	"	2.43	1	.779
"	0.9	"	2.20	1	.859
"	2.7	"	1.81	1	1.124
20	0	30	2.60	1	.642
"	0.1	"	2.74	1	.717
"	0.3	"	2.43	1	.762
"	0.9	"	2.20	1	.936
"	2.7	"	1.79	1	1.029
80	0	30	2.31	1	.762
"	0.1	"	2.25	1	.760
"	0.3	"	2.18	1	.757
"	0.9	"	1.70	1	1.024
"	2.7	"	1.15	1	1.322

TABLE 7
Image Color

Sodium sulfite concentration (g/l)	Benzotriazole concentration (g/l)	Chromaticity coordinates relative to D65	
		x	y
0	0	0.2902	0.3174
"	0.1	0.2903	0.3180
"	0.3	0.2910	0.3181
"	0.9	0.2920	0.3193
"	2.7	0.2937	0.3216
80	0	0.2900	0.3170
"	0.1	0.2906	0.3176
"	0.3	0.2902	0.3179
"	0.9	0.2914	0.3189
"	2.7	0.2944	0.3223

TABLE 8
Photographic Speed
For Development Time of 60 Seconds

Sodium sulfite concentration (g/l)	Benzotriazole concentration (g/l)	Log photographic speed
0	0	0.658
"	0.1	0.645
"	0.3	0.603
"	0.9	0.510
"	2.7	0.235
20	0	0.789
"	0.1	0.729
"	0.3	0.626
"	0.9	0.527
"	2.7	0.143
80	0	0.787
"	0.1	0.701
"	0.3	0.581
"	0.9	0.192
"	2.7	-0.276

IV. DISCUSSION

A. Covering power at a nominal density of 0.7

A graph of covering power as a function of benzotriazole concentration in the developer is shown in figure 2. This is at a density of approximately 0.7 and for two concentrations of sodium sulfite in the developer. In most cases, covering power increased as benzotriazole concentration increased. Generally, covering power decreases as sodium sulfite concentration increases, and is to be expected since sodium sulfite is a silver halide solvent which increases the relative amount of physical development and consequently decreases covering power.

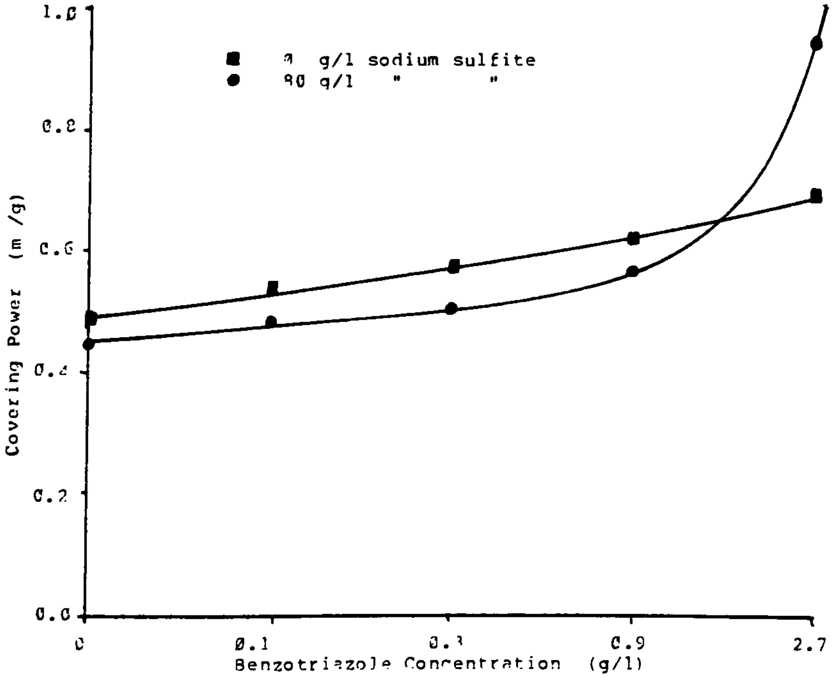

Figure 2. Covering power as a function of benzotriazole concentration at a nominal density of 0.7.

From an analysis of variance (ANOVA) it was determined that benzotriazole does have a significant effect on covering power but sodium sulfite does not (see table 9, appendix B). It was determined that the interaction between the two input variables is significant, however. This can be interpreted to mean that the variability in the data is not enough to mask the effect benzotriazole has on covering power, but the variability is great enough to mask the effect sodium sulfite has, if any. Since the interaction between the two variables was determined to be significant, this means that sodium sulfite in the developer changes the effect benzotriazole has on covering power.

Even though the ANOVA determined that sodium sulfite has no significant effect on covering power, it is obvious from figure 2 that it does have some effect. If the ANOVA is recalculated excluding the developers containing 2.7 g/l benzotriazole (table 10, appendix B), sodium sulfite does have a significant effect on covering power. The ANOVA indicates that there is no significant interaction between benzotriazole and sodium sulfite. Graphically, this means that the curves in figure 2 are parallel. This is why the interaction is insignificant at low benzotriazole concentrations but becomes significant at the highest benzotriazole concentration.

Since the ANOVA indicates there is no interaction between benzotriazole and sodium sulfite in their effect on covering power at low concentrations, it is possible that entirely different mechanisms are responsible for each effect. This changes at high concentrations of benzotriazole and sodium sulfite where the effect of each is interdependent, possibly indicating a common mechanism by which covering power is affected. Benzotriazole forms a salt with silver and it is possible that this has an effect only when the concentration of each is high [27].

B. Covering power at a nominal density of 1.2

The effect is similar at higher densities. Figure 3 shows covering power as a function of benzotriazole concentration for three levels of sodium sulfite in the developer. An analysis of variance tabulated in appendix B shows that, again, benzotriazole has a significant effect on covering power where sodium sulfite does not. The interaction term is also significant. When the developers containing 0.9 and 2.7 g/l benzotriazole are eliminated from the ANOVA, sodium sulfite has a significant effect on covering power and the interaction between benzotriazole and sodium sulfite is no longer significant.

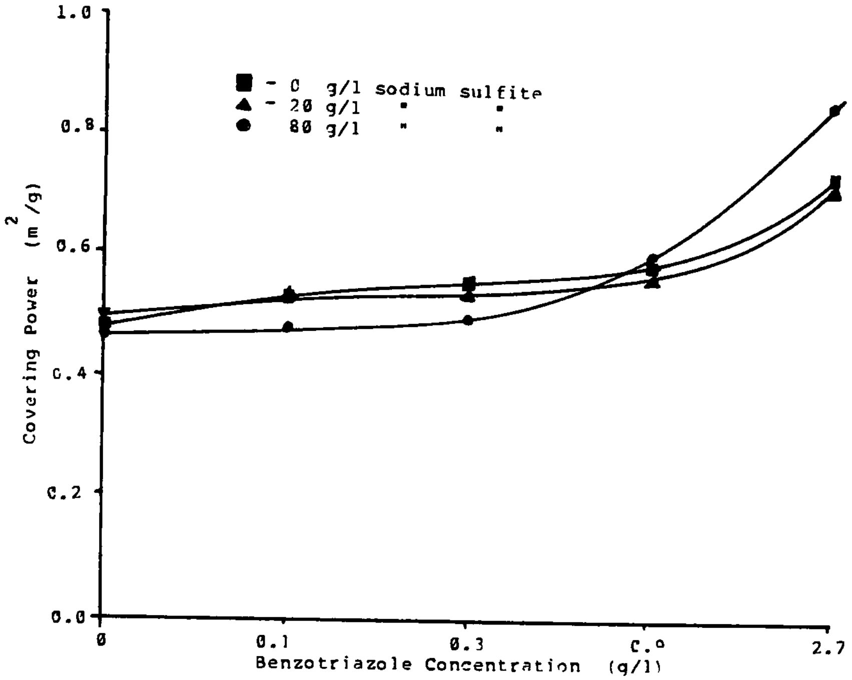

Figure 3. Covering power vs. benzotriazole concentration at a nominal density of 1.2

C. Covering power at maximum density

Figure 4 shows the same relationship at maximum density. This data was not replicated, so an ANOVA was not calculated. The data shows a similar trend as in the lower densities. This trend also occurs at a different development time. Figure 5 shows covering power as a function of benzotriazole concentration for a development time of 30 seconds, where the rest of the data is for a development time of 60 seconds.

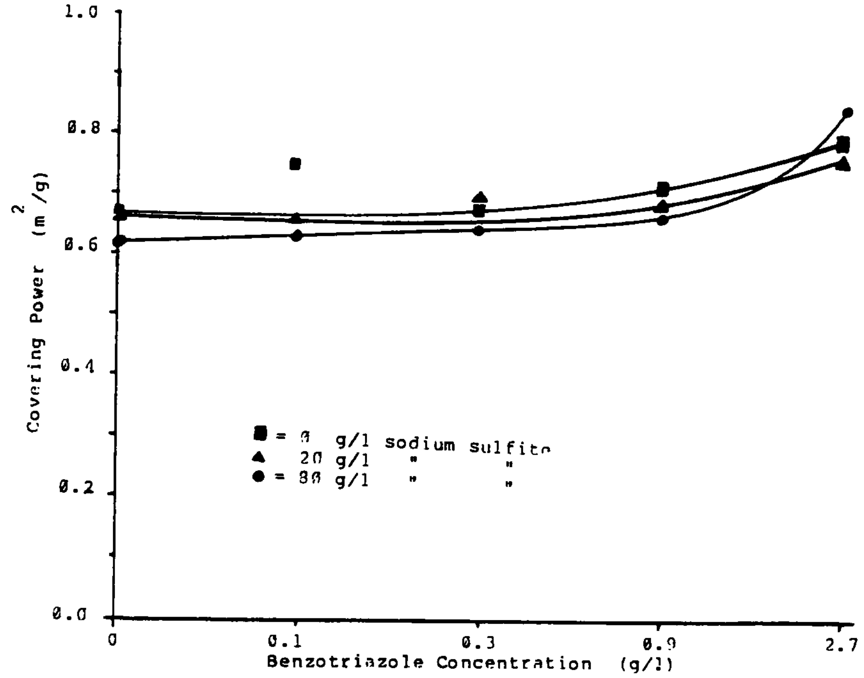

Figure 4. Covering power vs. benzotriazole concentration at maximum density for a development time of 60 seconds.

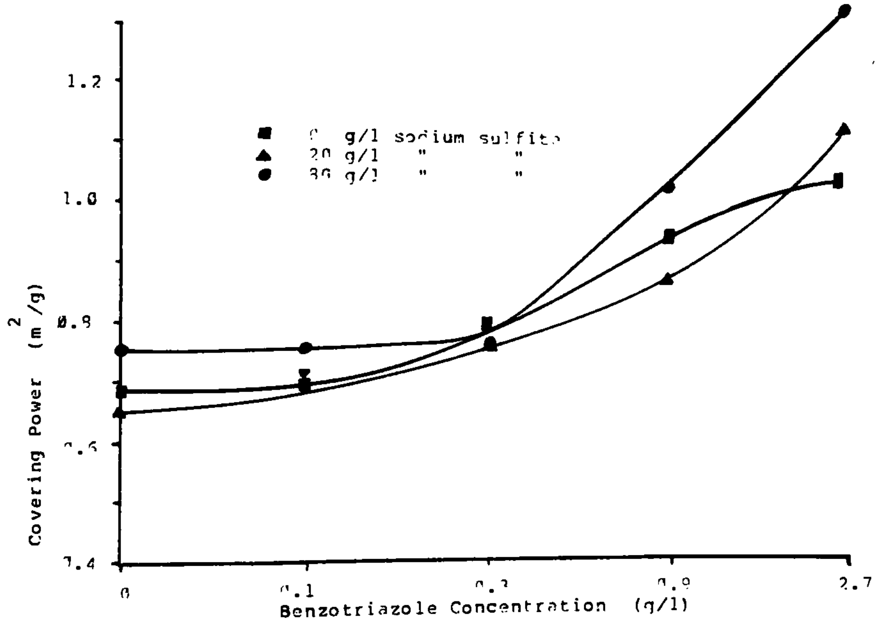

Figure 5. Covering power vs. benzotriazole concentration at maximum density for a development time of 30 seconds.

There are many possible reasons why covering power increases as benzotriazole concentration increases. One possible explanation is benzotriazole's restraint of physical development. Since physical development reduces covering power, benzotriazole in a developer should increase covering power. The series of developers containing no sodium sulfite are low solvent developers which produce almost purely chemical development. Since there is no physical development taking place in these developers, the restraint of physical development by benzotriazole could not be a factor in the increase in covering power seen in figures 2-5 with the 0 g/1 sodium sulfite developers.

D. Photographic speed

In figure 6 the relationship between covering power and log photographic speed is shown. Log photographic speed is inversely proportional to covering power, and the constant of proportionality changes with sodium sulfite concentration. At the highest sodium sulfite concentration, 80 g/1, the relationship is no longer linear near the high benzotriazole, low photographic speed end of the graph. This information may indicate that this experiment should have been carried out at constant exposure rather than constant density.

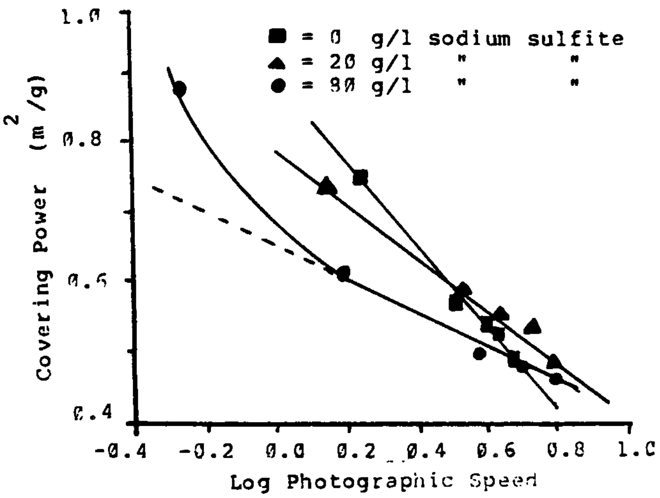

Figure 6. Covering power vs. log photographic speed.

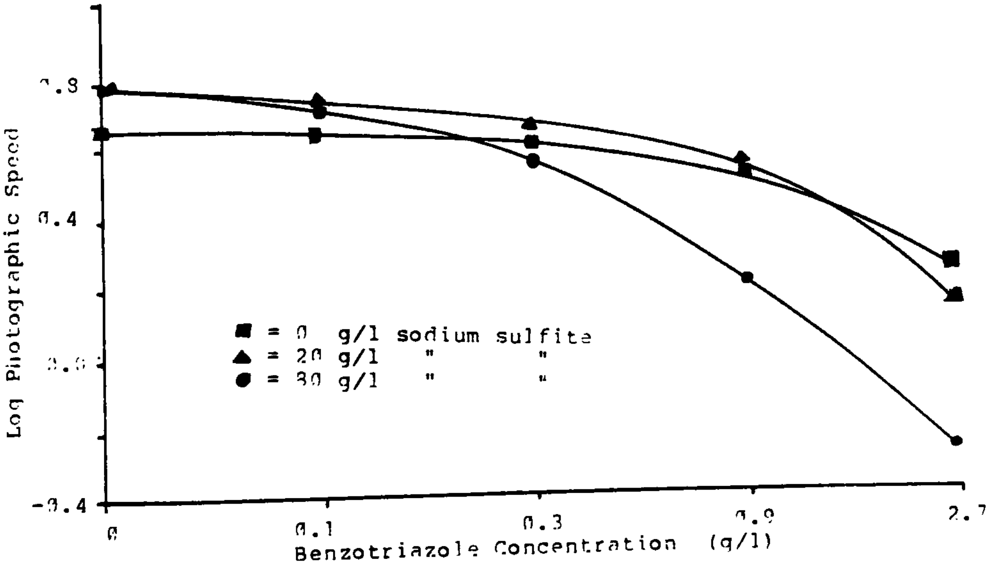

Figure 7. Log photographic speed vs. benzotriazole concentration.

Log speed at a density of 1.0 above base plus fog as a function of benzotriazole concentration in the developer is plotted in figure 7 for three concentrations of sodium sulfite in the developer. Log speed decreases at the high benzotriazole concentrations for the developer containing 80 g/l sodium sulfite. This unusual speed decrease is roughly correlated to the unusual covering power increase in figures 2-5.

A possible explanation for the unusual increase may be the large increase in exposure necessary relative to the exposures necessary to produce the required density at lower benzotriazole concentrations. At higher exposure levels, more grains are made developable and fewer grains are available for solution-physical development. This theory is consistent with figures 2-5. The effect is greatest with developers containing the highest sodium sulfite levels, that is those producing the most physical development. The effect becomes less apparent with developers containing less sodium sulfite, or those producing less physical development.

E. Image color

Benzotriazole in a developer is known to alter image color. Since the base of MRF is tinted blue, changes in the color of the emulsion layer could erroneously change the photometric density measured which in turn would affect the covering power calculated. To determine if any change in the color of the emulsion layer significantly affected density measurements, spectral transmittances of film samples were measured at wavelengths from 380 nm to 700 nm in 10 nm increments and chromaticity coordinates calculated relative to D_{65}, a standard daylight source. Sample calculations are given in appendix C. Chromaticity coordinates were calculated and plotted in figure 8 for MRF samples processed in developers containing the highest and lowest concentrations of sodium sulfite. Benzotriazole did affect image color as expected, but sodium sulfite did not. Sodium sulfite increases the relative amount of solution-physical development which will change the morphology of the developed silver and consequently alter image color. It is possible that the changes in sodium sulfite concentration are small enough not to make a detectable difference in image color.

If the lines from the source to the film samples are extended to the edge of the chromaticity diagram, the dominant wavelengths determined change from approximately 483 nm to approximately 486 nm as benzotriazole level changes from 0 g/l to 2.7 g/l. In this same interval, purity changes from 0.1 to 0.075. These are small changes and do not significantly change the visual density measured. Visual color determinations were made and a human observer could not distinguish any color difference. It is concluded that benzotriazole has no visual effect on image color under the conditions of this experiment.

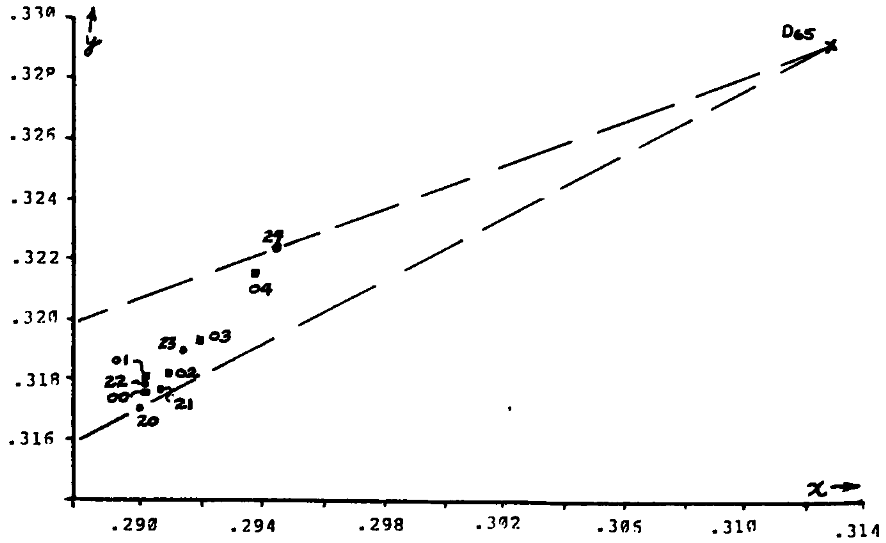

Figure 8. Chromaticity coordinates of samples. (Numbers indicate treatment combinations; see table 2.)

F. Covering power as a function of density

In figures 9 and 10 it can be seen that covering power generally increases as density increases. Farnell [6] gives three reasons for this:

a.) Average developable grain size decreases with increasing exposure. Covering power increases as grain size decreases.

b.) More grains become developable, decreasing the number of grains available for physical development.

Any physical development will decrease covering power.

c.) Latent-image speck size increases and the factorial spread of speck sizes decreases, reducing the spread of induction periods. Since the grains begin to develop more nearly together, less silver is available from the less readily developable grains for solution-physical development of the more readily developable grains.

Another possible explanation for the increase in covering power as density increases is the increase in packing density of the particles. Solman [3] has shown that covering power increases as mass of silver per unit area increases.

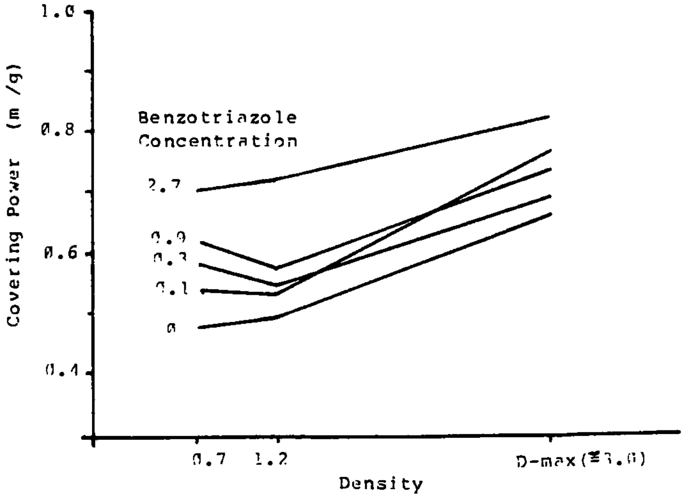

Figure 9. Covering power vs. density for 0 g/l sodium sulfite developer.

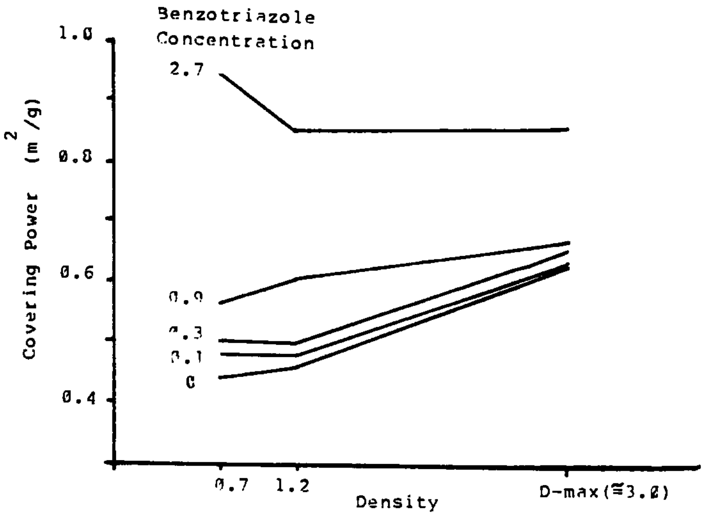

Figure 10 Covering power vs. density for 80 g/l sodium sulfite developer.

G. Rate of Development

Since benzotriazole is a development restrainer, it should be expected that less silver is developed in a given period of time when benzotriazole is added to the developer. This is the case in figure 11. At a D-max exposure, mass of silver per unit area stays approximately the same to the middle concentrations of benzotriazole and then decreases at the higher benzotriazole concentrations. Since benzotriazole increases covering power, density developed in a given period of time may increase as benzotriazole concentration increases. In figure 12, maximum density increases up to the middle concentrations of benzotriazole and then decreases at the higher benzotriazole concentrations. For this reason, rate of development measured in terms of developed density may increase as benzotriazole concentration increases.

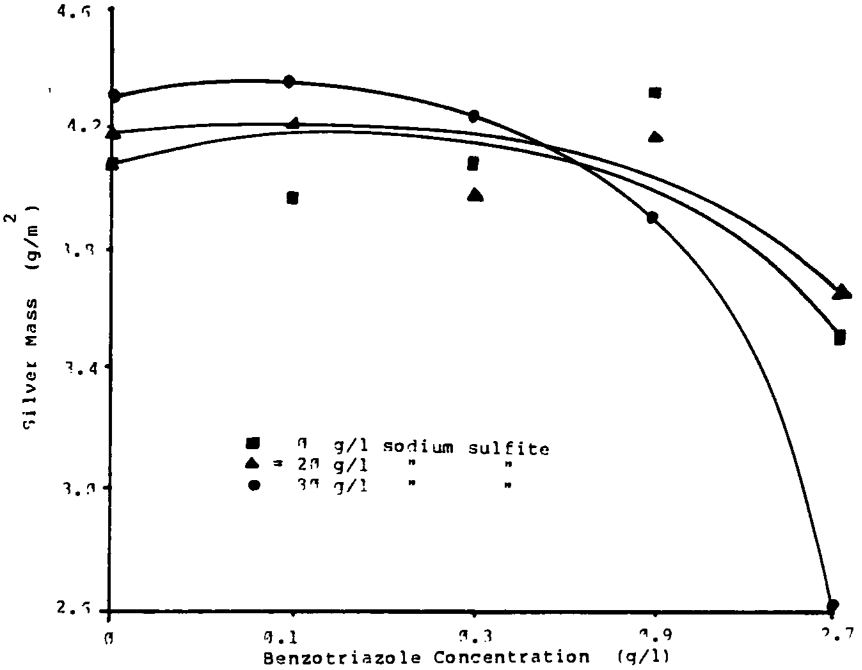

Figure 11. Mass of developed silver per unit area vs. benzotriazole concentration.

In figure 13, time of development required for a density of 1.2 is plotted as a function of benzotriazole concentration. Log exposure was -0.25, an exposure at the beginning of the shoulder of the sensitometric curve. At low benzotriazole concentrations, little effect on rate of density formation is seen. At higher concentrations of benzotriazole, rate of density formation is significantly slower. The greatest effect occurs in developers containing 80 g/l sodium sulfite.

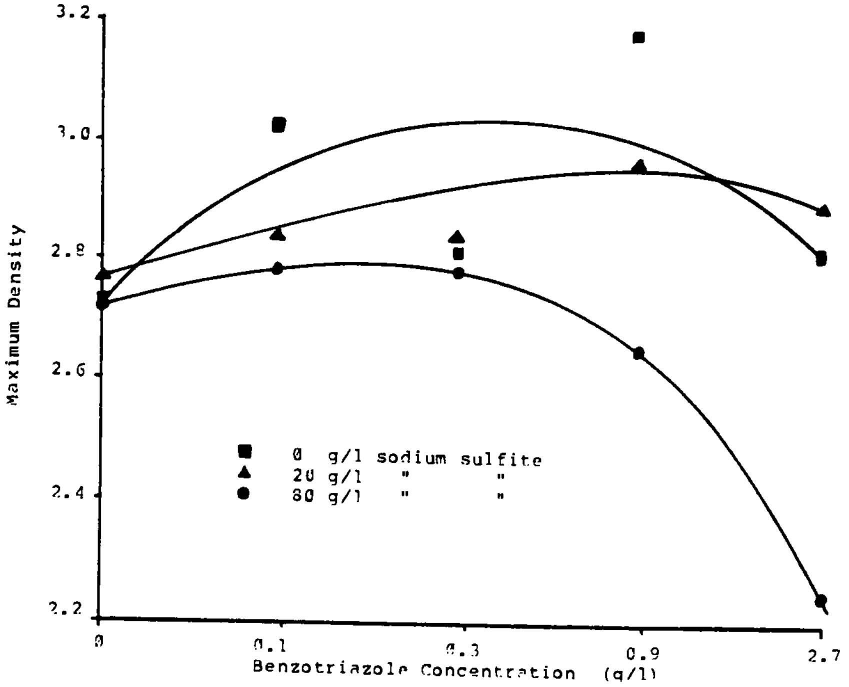

Figure 12. Maximum density vs. benzotriazole concentration.

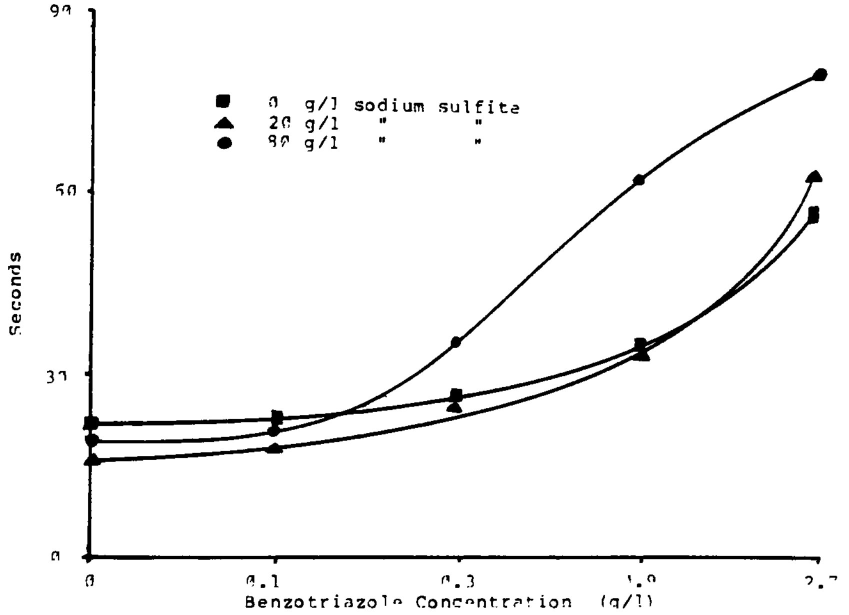

Figure 13. Rate of density formation: Time required to develop a density of 1.2 vs. benzotriazole concentration.

Sensitometric curves of MRF are plotted in figures 14 and 15 for developers at three levels of benzotriazole and two levels of sodium sulfite. Benzotriazole reduces density in the toe of the curve and for the middle benzotriazole concentration, increases density in the shoulder of the curve. At the highest benzotriazole concentration, densities in all regions of the curve are lower.

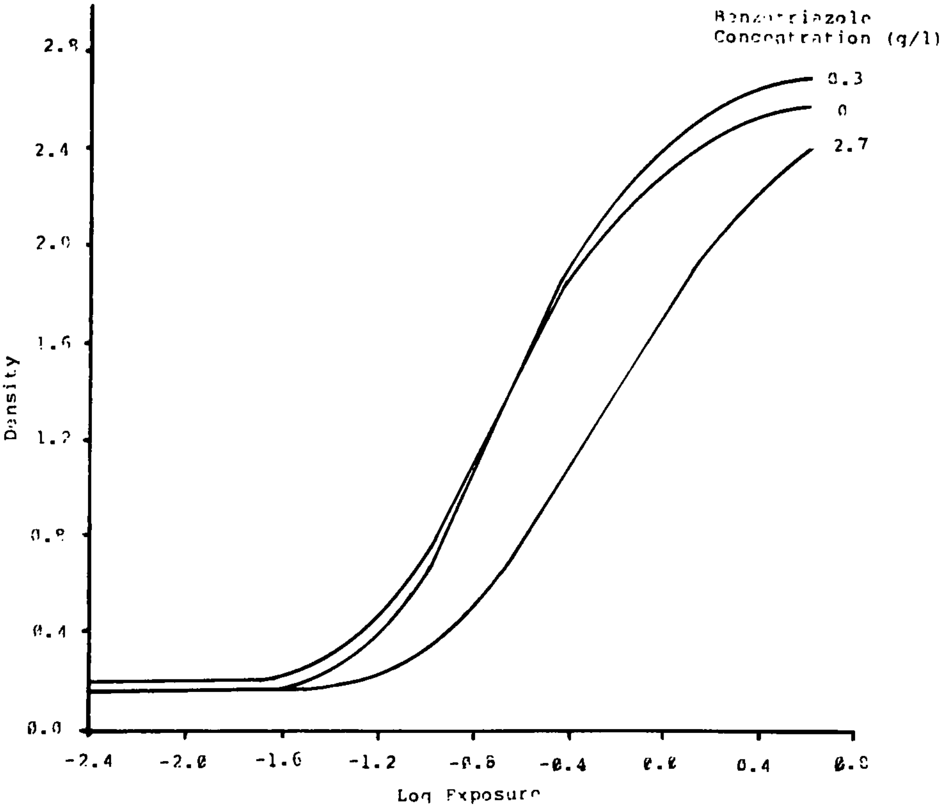

Figure 14. Sensitometric curves for MRF processed in developers containing 0 g/l sodium sulfite.

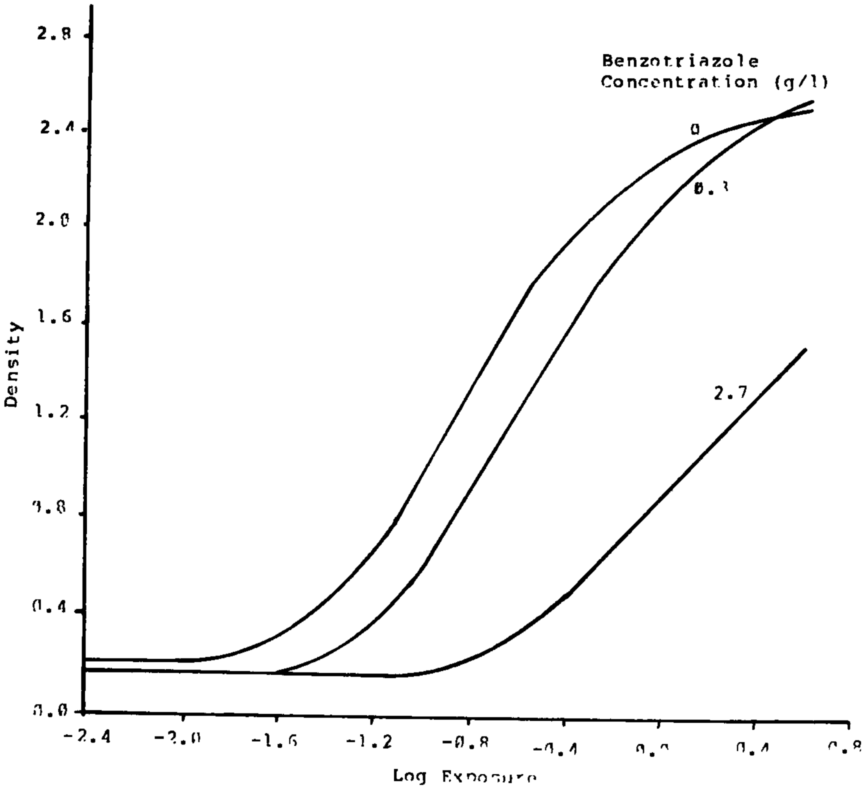

Figure 15. Sensitometric curves for MRF processed in developers containing 80 g/l sodium sulfite.

H. Future Work

Unusual covering power increases begin to occur with developers containing 80 g/l sodium sulfite, the highest silver halide solvent level in this experiment. This is close to the highest concentration of sodium sulfite that is normally used in developers. Future work may include repeating this experiment at higher silver halide solvent levels in the developer, possibly using thiocyanate or thiosulfate compounds. Benzotriazole may be a very effective covering power increasing agent in developers containing high concentrations of silver halide solvents such as monobaths. The covering power obtained with monobaths is typically very low because of the large relative amount of physical development.

This experiment could also be carried out at constant exposure rather than constant density. Figure 6 indicates a linear relationship between exposure and covering power independent of benzotriazole concentration. The exposure given a film sample rather than developed density may be a more significant variable with respect to covering power.

Another possibility for additional experimentation would be to compare the effects of reduced emulsion grain size with the effects of benzotriazole in a developer. Reducing grain size in a large grain emulsion will produce effects similar to those produce by adding benzotriazole to the developer, covering power will increase but photographic speed will decrease. Reducing emulsion grain size may be a more effective method of increasing covering power than adding benzotriazole to a developer when high photographic speed is important such as in X-ray emulsions.

V. CONCLUSIONS

1.) Benzotriazole in a developer will increase covering power. The increase is greater when the developer contains a relatively high concentration of the silver halide solvent sodium sulfite.

2.) The increase in covering power with benzotriazole concentration is inversely proportional to the log photographic speed.

3.) Covering power increases as density increases.

4.) Benzotriazole in a developer measurably affects image color, but under the conditions of this experiment did not have a visually significant effect.

5.) Benzotriazole reduces the rate of development when measured by mass of silver developed. The reduction in the rate of development is increased when the developer contains a silver halide solvent. If rate of development is measured by the rate of density formation at a D-max exposure, benzotriazole may increase the rate of development because of the increase in covering power.

6.) The increase in covering power by benzotriazole and the decrease in covering power by sodium sulfite are caused by different mechanisms at low concentrations. At higher concentrations, the effect of each substituent is interdependent indicating a common mechanism. This was determined by analysis of variance.

VI. REFERENCES

1. T.H. James and L.J. Fortmiller, "Dependence of Covering Power and Spectral Absorption of Developed Silver on Temperature and Composition of the Developer.", Phot. Sci. Eng., 5, 297 (1961).

2. G.C. Farnell and L.R. Solman, "The Covering Power of Photographic Silver Deposits. I. Chemical Development.", J. Phot. Sci., 18, 94 (1970).

3. L.R. Solman, "The Covering Power of Photographic Silver Deposits. II. Physical Development.", J. Phot. Sci., 18, 136 (1970).

4. L.R. Solman, "The Covering Power of Photographic Silver Deposits. III. Comparison of Chemical and Physical Development.", J. Phot. Sci., 18, 179 (1970).

5. T.H. James and W. Vanselow, "The Influence of Development Mechanism on the Color and Morphology of Developed Silver.", Phot. Sci. Eng., 1, 104 (1958).

6. G.C. Farnell, "The Consequences of Solution Effects in Conventional Developers.", J. Phot. Sci., 21, 145 (1973).

7. T.H. James and W. Vanselow, "The Rate of Solution of Silver Halide Grains in a Developer.", Phot. Sci. Tech., 2, 135 (1955).

8. J.C. Barnes, "Mechanism of Development in Monobaths Containing Thiosulfate Ion.", Phot. Sci. Eng., 5, 204 (1961)

9. D.A. Nepela, "Effect of Development Temperature on Covering Power of a Developed Silver Image.", Phot. Sci. Eng., 5, 305 (1961).

10. R.K. Blake and B. Meerkamper, "Developed Image Structure.", J. Phot. Sci., 9, 14 (1961).

11. J.D. Kendall, "Phenidone: a New Commercial Developing Agent.", Brit. J. Phot., 1/30/53 p.56.

12. J.C. Barnes, G.J. Johnston, and W.J. Moretti, "The Chemistry of Monobaths: Effect of Thiosulfate Ion Upon Image Structure.", Phot. Sci. Eng., 8, 312 (1964).

13. K. Futaki, Y. Ohyama, and T.I. Iwasaki, "Influences of Some Addition Agents on the Color of Developed Silver From Liquid Photographic Emulsions.", Phot. Sci. Eng., 4, 97 (1960).

14. K. Futaki and Y. Ohyama, "The Influence of Some Addition Agents on the Rate of Development of Liquid Photographic Emulsion.", Phot. Sci. Eng., 4, 257 (1960).

15. Y. Ohyama and K. Futaki, "Observation on Fine Structure of Developed Silver in the Presence of Added Tone Modifiers.", Phot. Sci. Eng., 7, 84 (1963).

16. C.R. Berry and D.C. Skillman, "The Color And Covering Power of Silver Particles.", J. Phot. Sci., 17, 145 (1969).

17. D.C. Skillman and C.R. Berry, "Spectral Extinction of Colloidal Silver.", J. Opt. Soc. Am., 63, 707 (1973).

18. E. Klein and H.J. Metz, "Color of Colloidal Silver Sols in Gelatin.", Phot. Sci. Eng., 5, 5 (1961).

19. H.J. Metz, "On the Mechanism of Photographic Development.", J. Phot. Sci., 20, 111 (1972).

20. G. Haist, Modern Photographic Processing, Vol. 1, Wiley and Sons, New York, 1979, p.753.

21. R.J. Newmiller and R.B. Pontius, "The Adsorption of Development - Restrainers to Silver and Their Effects on Physical Development.", Phot. Sci. Eng., 5, 283 (1961).

22. L.G. Schulz, "An Interferometric Method for the Determination of the Absorption Coefficients of Metals, with Results for Silver and Aluminum.", J. Opt. Soc. Am., 41, 1047 (1951).

23. L.G. Schulz, "Optical Constants of Silver, Gold, Copper and Aluminum. I. The Absorption Coefficient k.", J. Opt. Soc. Am., 44, 357 (1954).

24. I. Miller and J. Freund, Probability and Statistics for Engineers, 2nd. ed., Prentice-Hall, New Jersey, 1977, p.152.

25. ANSI standard PH2.9-1974

26. R.J. Byer, E.I. DuPont Co., Rochester,NY, personal communication, 1/10/84

27. H. Roberts, Rochester Institute of Technology, personal communication, 4/5/84

VII. APPENDIX A

Processing Procedures

1.) Film samples were developed in a 11 cm X 14 cm tray containing 500 ml of developer at a depth of 3 cm at 34°C. ± 1°C. with constant agitation for the specified length of time ± 2 seconds.

2.) Sample was rinsed in Kodak SB-1 stop bath at 30°C. ± 2° C. for 15 seconds ± 5 seconds with constant agitation.

3.) Sample was fixed in Kodak F-5 fixer at 30° C. ± 2° C. with constant agitation for twice the clearing time, which was 30 seconds ± 5 seconds.

4.) Sample was washed in running water at 34°C. ± 1°C. for 5 minutes ± 30 seconds.

5.) Sample was dried at 66° C. Temperature and humidity assumed constant.

VIII. APPENDIX B

TABLE 9
Analysis of Variance For a Nominal Density of 0.7

SOURCE OF VARIANCE	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F VALUE	* TEST F VALUE
benzotriazole concentration	48.380	4	12.095	122.35	2.87
sodium sulfite concentration	0.006	1	0.006	0.06	4.35
interaction	11.271	4	2.818	28.50	2.87
error	1.977	20	0.099		
total	61.634	24			

TABLE 10
Analysis of Variance For a Nominal Density of 0.7 Excluding Developers Containing 2.7 g/l Benzotriazole.

SOURCE OF VARIANCE	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F VALUE	* TEST F VALUE
benzotriazole concentration	5.730	3	1.910	108.61	3.24
sodium sulfite concentration	2.030	1	2.030	115.44	4.49
interaction	0.145	3	0.048	2.75	3.24
error	0.281	16	0.018		
total	8.186	23			

* From statistical tables.

TABLE 11
Analysis of Variance For a Nominal density of 1.2

SOURCE OF VARIANCE	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F VALUE	* TEST F VALUE
benzotriazole concentration	0.487	4	0.122	587.57	2.69
sodium sulfite concentration	0.001	2	0.001	2.56	3.32
interaction	0.051	8	0.006	30.23	2.27
error	0.006	30	0.000		
total	0.545	44			

TABLE 12
Analysis of Variance For a Nominal density of 1.2 Excluding Developers Containing 2.7 g/l Benzotriazole

SOURCE OF VARIANCE	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F VALUE	* TEST F VALUE
benzotriazole concentration	0.056	3	0.019	134.80	3.01
sodium sulfite concentration	0.005	2	0.002	17.86	3.40
interaction	0.011	6	0.002	13.06	2.51
error	0.003	24	0.000		
total	0.075	35			

* From statistical tables

TABLE 13

Analysis of Variance For Nominal Density of 1.2 Excluding Developers Containing 0.9 and 2.7 g/l Benzotriazole

SOURCE OF VARIANCE	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE	F VALUE	* TEST F VALUE
benzotriazole concentration	0.014	2	0.007	51.37	3.55
sodium sulfite concentration	0.012	2	0.006	43.62	3.55
interaction	0.001	4	0.000	2.31	2.93
error	0.002	18	0.000		
total	0.029	26			

* From statistical tables

IX. APPENDIX C

Calculations for Chromaticity Coordinates

$$X = \sum_{380}^{700} S(\lambda)\bar{x}(\lambda)T(\lambda)\Delta\lambda$$

$$Y = \sum_{380}^{700} S(\lambda)\bar{y}(\lambda)T(\lambda)\Delta\lambda$$

$$Z = \sum_{380}^{700} S(\lambda)\bar{z}(\lambda)T(\lambda)\Delta\lambda$$

$$x = \frac{X}{X+Y+Z}$$

$$y = \frac{Y}{X+Y+Z}$$

$$z = \frac{Z}{X+Y+Z}$$

Where:

$S(\lambda)$ = Source spectral power distribution

$\bar{x}(\lambda),\bar{y}(\lambda),\bar{z}(\lambda)$ = Spectral tristimulus values

$T(\lambda)$ = Spectral transmittance of sample

$\Delta\lambda$ = Wavelength increment

X,Y,Z = Tristimulus values

x,y,z = Chromaticity coordinates

X. VITA

Kenneth Carlson was born in Sharon, Pennsylvania in May, 1962. He graduated from High School in June, 1980 with honors and now attends the Rochester Institute of Technology, Rochester, New York. This thesis concludes his undergraduate college study.