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The Inhibition of Aerial Fog

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THE INHIBITION OF AERIAL FOG

A THESIS PRESENTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE MASTER OF SCIENCE DEGREE IN
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ROCHESTER INSTITUTE OF TECHNOLOGY, ROCHESTER, N.Y.

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Accepted, May 16, 1969

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INTRODUCTION

Some developing agents, notably alkaline hydroquinone solutions, can give rise to aerial fogging, i.e., the chemical reduction of silver halide into a latent image when a developing agent is oxidized in contact with a suitable photographic emulsion. Traces of copper, an oxidizing catalyst, greatly enhances the formation of this type of fog.

In 1924, E. Fuchs, in an article on aerial fog¹, had attributed the formation of the latent fog to chemiluminescence. Additionally, he found that treatment of the film by desensitizing dyes prevented the formation of aerial fog. This effect of desensitization on chemiluminescence pointed to aerial fog as possibly being light fog. Also in 1924, M.L. Dundon and J.I. Crabtree² in a study of the fogging properties of developers, found pinakryptol green to be the most effective desensitizer tested for preventing aerial fog. Phenosafranine, an isomer of pinakryptol green, was also found to be very satisfactory. T.H. James, in a paper on aerial fogging of photographic emulsions³, had experimentally dis-

¹ E. Fuchs, Phot. Ind., 27, 56 (1924).

² M.L. Dundon and J.I. Crabtree, Brit. J. Phot. 71, 701 (1924).

³ T.H. James, J. Chem. Phys. 11, 183 (1943).

counted the theory of chemiluminescence as the cause of aerial fog. Since hydrogen peroxide is a fogging agent produced in the oxidation reaction of hydroquinone, it was experimentally tested as a cause of aerial fog. The results showed that molecular hydrogen peroxide could not account for the formation of aerial fog. James concluded that a transient intermediate peroxide radical formed during the oxidation of the hydroquinone developer was the most probable cause of aerial fog.

The purpose of this work is to study the formation of aerial fog and to determine how different types of chemical compounds compare in their ability to inhibit or reduce aerial fog. This work will be written in two distinct parts; Part I: The Formation of Aerial Fog, and Part II: Attempts to Inhibit Aerial Fog Formation. Each part will contain the experimental procedure, and a discussion of the results. The conclusions at the end of this report are applicable to both Part I and Part II.

PART I: THE FORMATION OF AERIAL FOG

1. Experimental Procedure and Results

A. Attempts to Induce Aerial Fog

The experimental technique as used by James³ in his study of aerial fogging was modified for use to begin this work. Film strips were immersed in a fogging developer for 40 seconds, removed and suspended in air for 9 minutes, bathed for 15 seconds in a 1% acetic acid stop bath, washed in running water for 5 minutes, and tray processed in full strength DK-50 developer at 70°F for 4 minutes. Using the same fogging developer at pH 10.18 consisting of 5.5 grams of hydroquinone, 12.6 grams of sodium sulfite, 10.6 grams of sodium carbonate, 0.6 grams of potassium bromide, all dissolved in a liter of water, it produced no noticeable aerial fog on the film strips. 5.0 milligrams of copper sulfate was added to the fogging solution to catalyze the aerial fog formation. Noticeable aerial fog was evident, however, the developed fogged film strips appeared blotchy. Since aeration technique was believed to be the possible cause of the blotchiness, various aeration times from 10 seconds through 10 minutes were tried. The overall fog levels increased with aeration time but so did the density range of the blotchiness. Different aeration positions, hanging strips vertically,

laying strips flat with emulsion side up, suspending strips horizontally with emulsion side down, were tried unsuccessfully to produce a uniform fog density across the film strips. 5-6 drops of a 1% saponin solution was added to the fogging agent as a wetting agent but this did not noticeably improve the fogged film strips. No specific density patterns were evident. The blotches appeared to be randomly scattered across the film strips.

Two types of film were tried in the attempts to produce a uniform fog level across the strips, KODAK Aerial Recon Duplicating Film Type 8427, and KODAK Fine Grain Release Positive Type 5302. Both types exhibited the blotchiness. For identical fogging conditions the Type 5302 showed a lower level of fog and a more uniform fog density at that level than the Type 8427. After 1 minute immersion in the fogging solution followed by a 5 minute aeration time, the average densities were a low of 0.98 to a high of 1.31 for the Type 8427 and a low of 0.72 to a high of 0.86 for the Type 5302. Comparing Type 8427 at approximately the same fog level as Type 5302 given above, the density spread of the Type 8427 was from 0.60 to 0.84 density. The remainder of the experimentation was conducted using Type 5302.

In order to keep the film strips immersed in the fogging solution during the hydroquinone oxidation process, a device was constructed to bubble air through

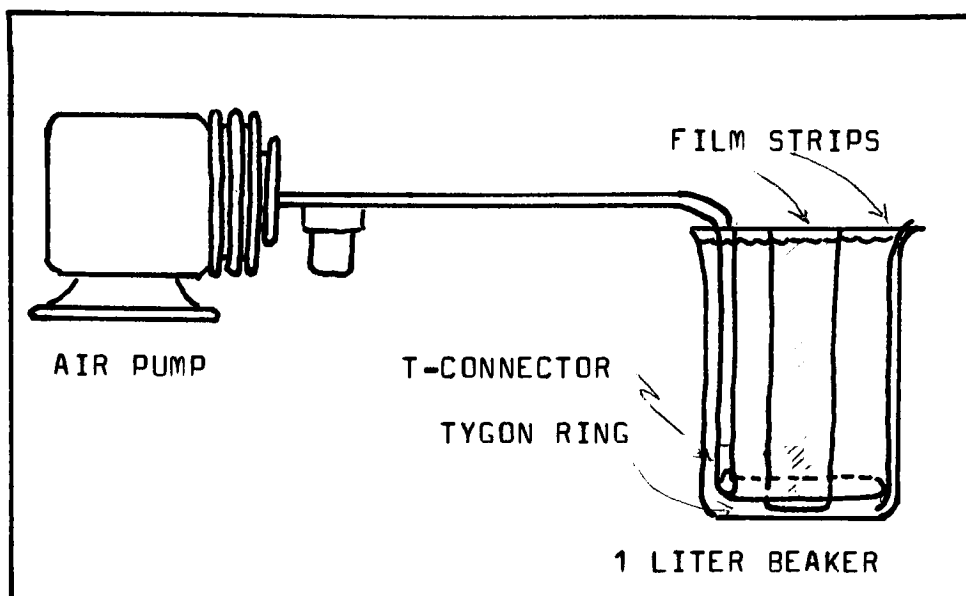


FIGURE I. DIAGRAM OF OXIDATION DEVICE

the fogging solution. The apparatus consists basically of an air pump, tygon plastic tubing, and a one liter beaker (see Figure I). A ring was formed using tygon tubing since it is chemically inert to the reagents used. Many small holes were drilled into the tubing to allow the air to escape into the solution. The holes were drilled with a #60 drill bit and were spaced approximately 1 centimeter apart. This ring was placed in the bottom of the beaker and connected to the air pump via a T-connector and additional tygon tubing. The ring was constructed of sufficient circumference to barely exert pressure against the inside wall of the beaker. The tops of the film strips were secured to the beaker rim with black plastic tape. The bottom of the film strips

were inserted between the ring and the inside wall of the beaker, thus preventing the film strips from moving during the bubbling process. Four 35mm film strips $5\frac{1}{2}$ inches long can be secured around the 1 liter beaker this way.

After the strips were secured in place, one liter of aerial fogging solution was poured into the beaker, simultaneously starting the pump. This device provided an aerial fog density of sufficient uniformity at various fog levels to conduct the remaining experimentation. The standard deviation of density for a given strip varied from a low of 0.0087 to a high of 0.0211 for strips ranging in fog levels of from 0.32 to 0.93; the mean standard deviation was 0.0147.

B. Factors Affecting Aerial Fog Density

(1) Copper Sulfate

Since traces of copper in a hydroquinone solution are known to catalyze the formation of aerial fog, various amounts of cupric sulfate were added to the basic fogging developer (page 3). Fogging times (time of pumping air into the fogging solution using the oxidation device) of 2, 4, 6, and 8 minutes were tested. Various concentrations of from 0 through 20 milligrams of copper sulfate per liter of fogging solution were tried. As can be seen in Figure II, when plotting aerial fog density vs the

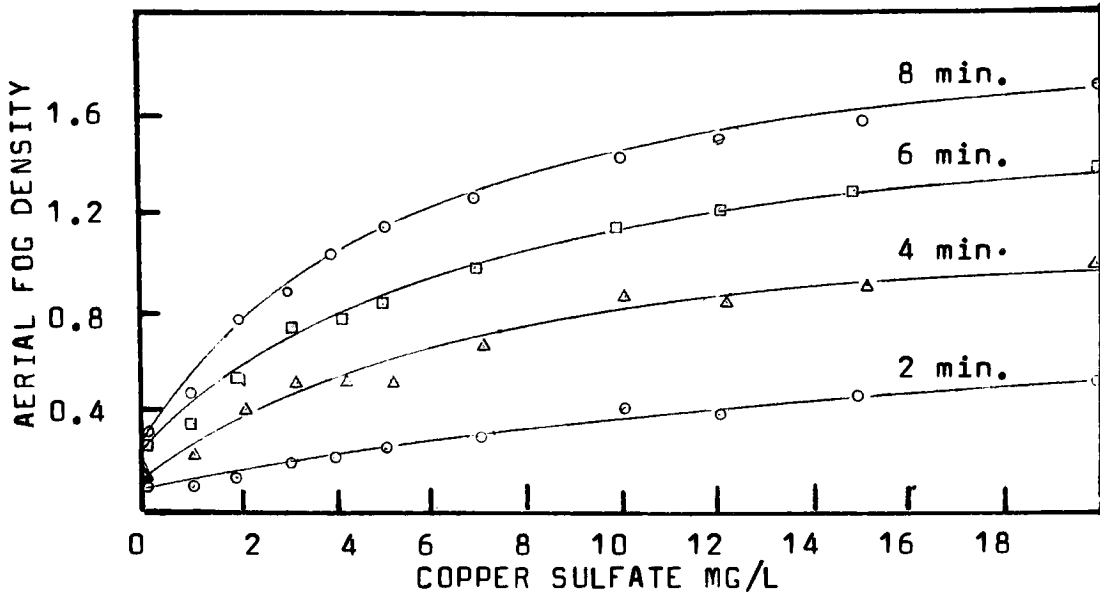


FIGURE II. EFFECT OF COPPER SULFATE ON AERIAL FOG DENSITY

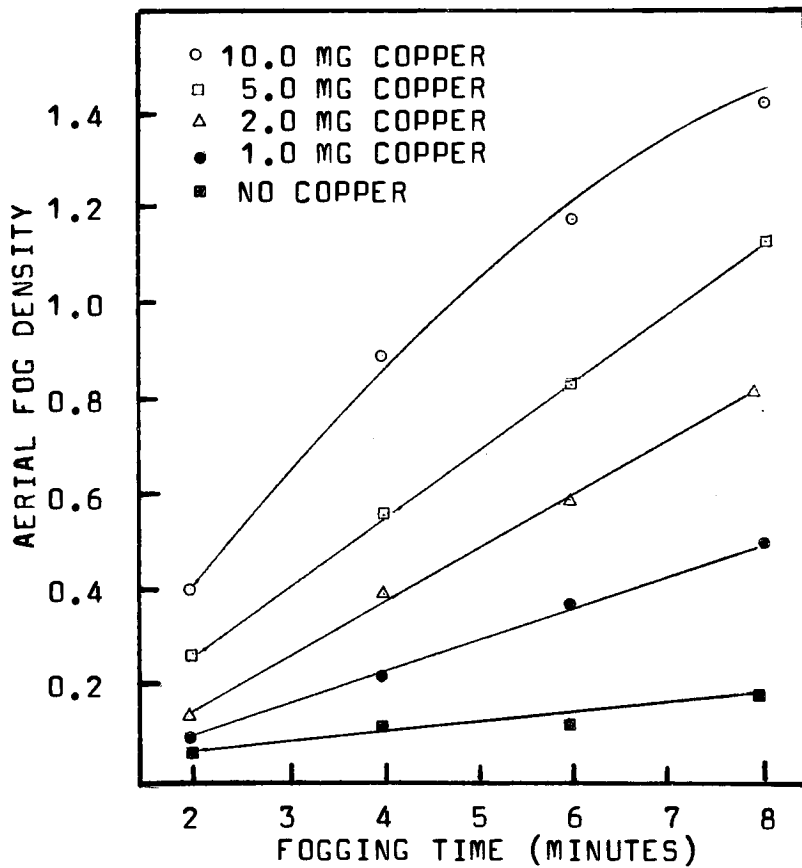


FIGURE III. EFFECT OF FOGGING TIME ON AERIAL FOG DENSITY FOR VARIOUS LEVELS OF COPPER SULFATE

concentration of copper sulfate, the curves show that the aerial fog density approaches a maximum level as the copper sulfate concentration is increased. The time of fogging is also a significant factor involved and when plotting the aerial fog density as a function of fogging time for the various levels of copper concentrations (see Figure III) a linear relationship is indicated. A statistical analysis of the data (Analysis of Variance; F test) from these tests show that both the concentration of copper sulfate added to the basic fogging developer and the time of aeration are both significant to the aerial fog density produced.

(2) Sodium Sulfite

T.H. James⁴ had reported that the basic fogging developer (see page 3) with no sulfite caused little aerial fog and that the addition of small amounts of sulfite increased the aerial fog density. He reported that the maximum aerial fog density appeared at a sodium sulfite/hydroquinone molar ratio of 1.0. For this investigation, the basic fogging developer was used in the oxidation device varying only the concentration of sodium sulfite. In order to keep the fogging times fairly short and to obtain dense aerial fogging, 5.0 milligrams of copper sulfate catalyst was added to the

⁴ T.H. James, J. Phot. Soc. Amer. IX, 8 (1943).

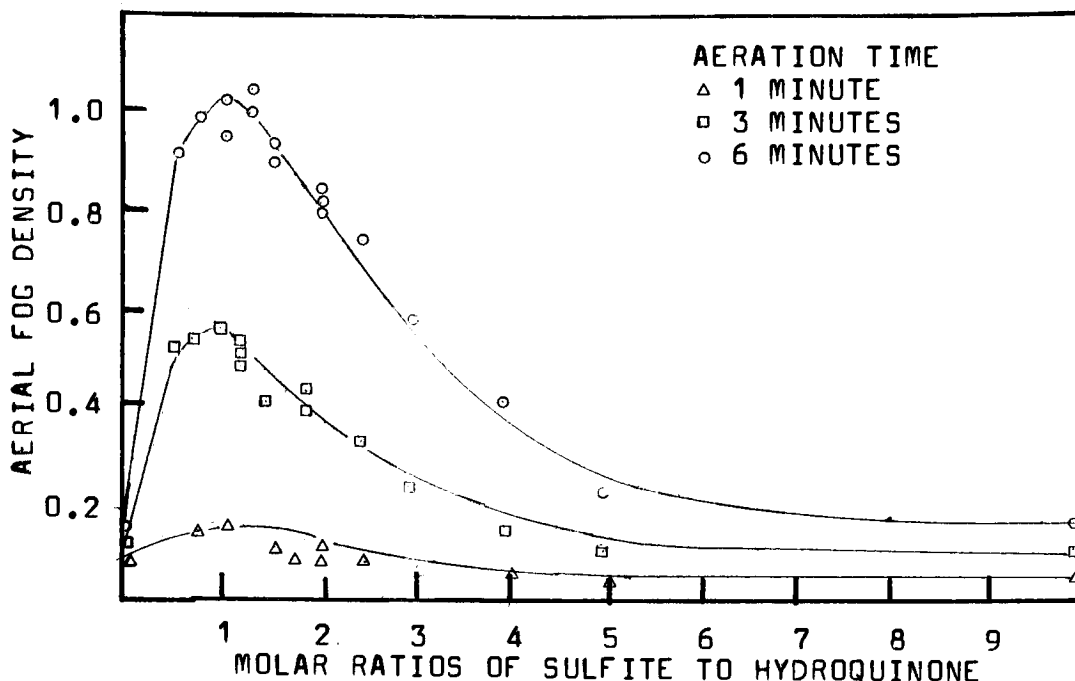


FIGURE IV. EFFECT OF SULFITE/HYDROQUINONE MOLAR RATIOS ON AERIAL FOG DENSITY

fogging developer immediately prior to pouring the solution into the fogging device in all experiments. Various amounts of sodium sulfite of from 0 grams to 63.0 grams (corresponding to sulfite/hydroquinone molar ratios of from 0 to 10.0) were added per liter of basic fogging developer. Fogging times of 1, 3, and 6 minutes were tested. The results of this experimentation as shown in Figure IV agree with those reported by James in the absence of copper. They indicate a maximum aerial fog density occurs when approximately 6.3 grams of sodium sulfite was used in the basic fogging developer. This corresponds to a sodium sulfite/hydroquinone molar ratio of about 1.0.

A statistical analysis of the data indicates that the

* Analysis of Variance; F test

aerial fog density is dependent upon the concentration of sodium sulfite in the basic fogging developer. Although it appears that this concentration is significant as the molar ratio of sulfite to hydroquinone, this statement can not be made since only the sulfite concentration was varied, the hydroquinone concentration remaining constant.

(3) Fogging Time

Maintaining the basic fogging developer (page 3) to which was added 5.0 milligrams of copper sulfate catalysit immediately prior to pouring the solution into the oxidation device, an investigation into the effects of fogging time was conducted. For these tests, the effects on the base-plus-aerial fog density as well as the effects on the characteristic curve were studied. The strips of film were exposed sensitometrically prior to fogging. The exposures were made in a KODAK 101 Sensitometer through an 0.86 Inconel Glass neutral density filter at 1/5 second exposure. Figure V shows a linear relationship exists between aerial fog density and fogging time for the range of times tested, i.e., 0 through 20 minutes fogging time. A plot of the characteristic curves after fogging compared to a control strip (no fogging) is shown in Figure VI. The greatest amount of fogging was generally noted in the region of least exposure, the toe of the curve. The least amount of fogging was generally noted where the light exposures were the heaviest. This indicated that the density

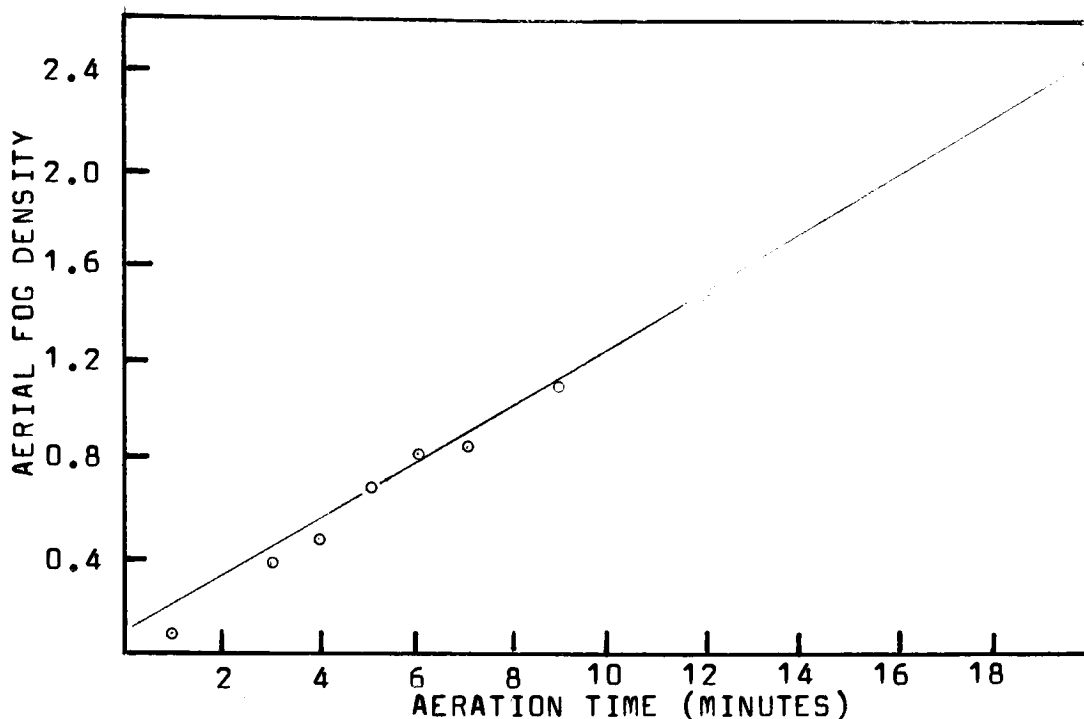


FIGURE V. THE EFFECT OF AERATION TIME ON AERIAL FOG

attributed to aerial fogging was functionally related to the amount of unexposed silver halide available for fogging along the sensitometrically exposed strip. From the data a plot was made of the density attributed to aerial fogging ΔD vs potential density. ΔD is defined here as the total density of a particular step on the sensitometric strip after aerial fogging minus the density of that same step on the control strip. The potential density is a quantitative figure relative to the amount of unexposed silver halide remaining after the sensitometric exposure based on a potential D_{\max} of 4.5 for this emulsion. A D_{\max} of $4.45 \pm .03$ was obtained by continuous fogging for 1 hour. Potential density is defined as 4.5 minus the density of

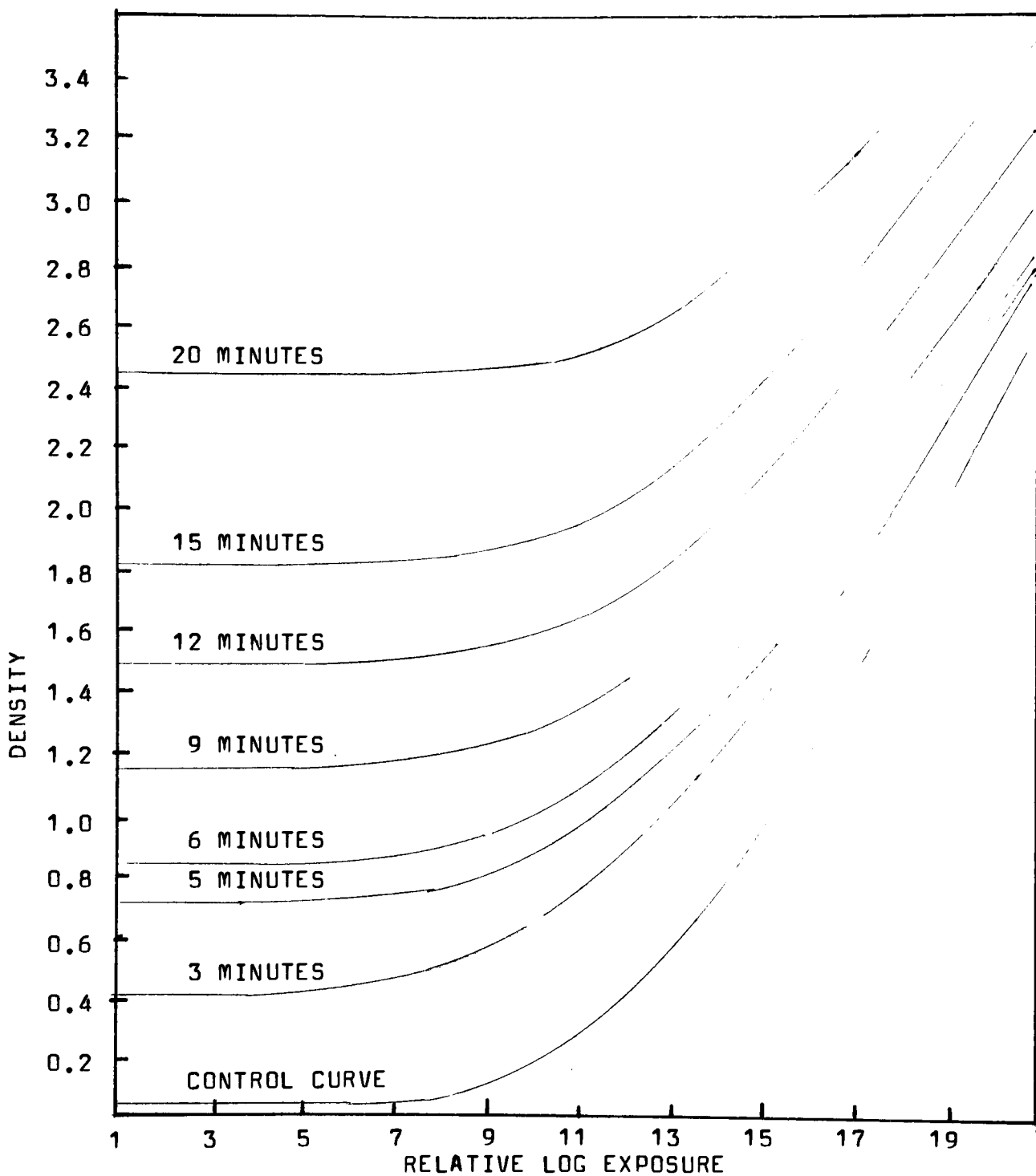


FIGURE VI. CHARACTERISTIC CURVES FOR VARIOUS FOGGING TIMES IN AERIAL OXIDATION DEVICE

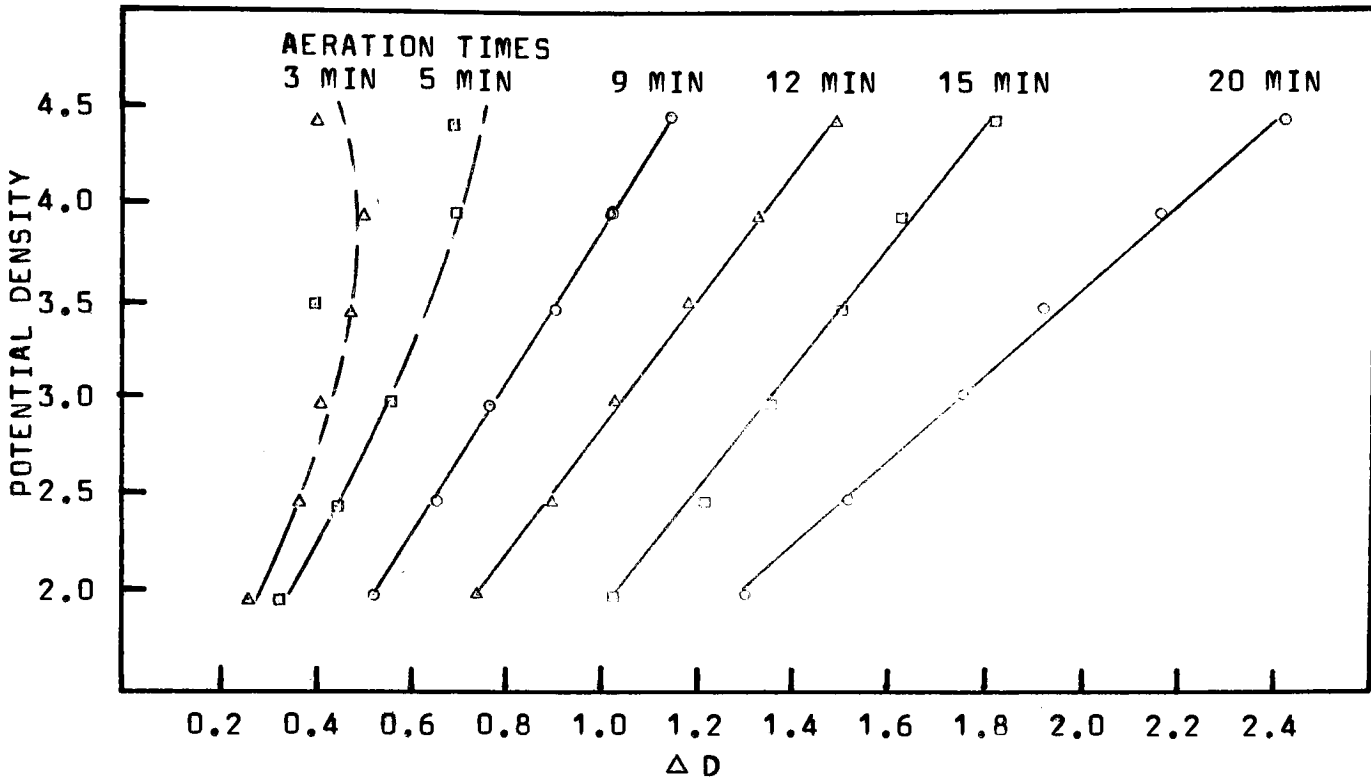


FIGURE VII. AERIAL FOG AS A FUNCTION OF UNEXPOSED SILVER HALIDE

the control strip. This plot indicates a definite linear relationship between aerial fog density and the amount of unexposed silver halide exists for fogging times greater than 5 minutes. For aeration times of less than 5 minutes, the apparent failure of the linear relationship between aerial fog and unexposed silver halide may be attributed to noise due to experimental error or to covering power noise in the density measurements. This noise can arise from many difficulties present in the study of fog formation using density measurements.⁵ Finding the fog to be linearly related

⁵ L.F.A. Mason, Photographic Processing Chemistry, Chapter IV, p. 124, Focal Press, London, 1966.

to the amount of unfogged silver halide was quite unexpected. This linear relationship indicates that the growth of fog is probably independent of grain size and sensitivity. However, no obvious reason for this linear relationship is given.

(4) Aeration

The necessity for the film to be present in the oxidation device during the aeration in order to induce aerial fogging was next tested. Film strips were placed in the fogging developer without aeration for 10 minutes then immersed in a 1% acetic acid stop bath for 15 seconds. Care was taken when removing the film so that a minimum exposure to air prior to the stop bath would occur. After a 5 minute washing, the strips were processed in DK-50 for 4 minutes. A base-plus-fog density of 0.05 to 0.07 resulted.

A second test was conducted in which the fogging developer was aerated for 10 minutes prior to insertion of the film. After the aeration time, the solution was allowed to settle for 3 minutes. The film was then immersed in the solution without further aeration. After 10 minutes the film was removed, again being careful to allow only a minimum exposure to air before going into the stop bath. After processing as above, the resultant base-plus-fog density of 0.04 to 0.07 was noted.

When compared with the resultant density of 1.28 for the same conditions as above except that the film was present during the 10 minute aeration, it is clearly evident that the fogging agent is only present during the aeration.

(5) Bleaching

The effect of an acid-dichromate bleach on the latent fog image as compared to a latent light image was next investigated. The acid-dichromate bleach used for this test consisted of

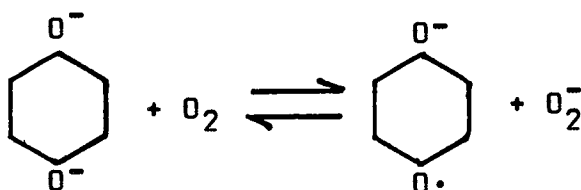
20 gm potassium dichromate
2 cc sulfuric acid (conc)
4 gm sodium sulfate
water to make 1 liter

Both unexposed and sensitometrically exposed strips of film were fogged for 6 minutes in the oxidation device. After fogging, all strips were given a 1% acetic acid stop bath for 15 seconds followed by a water wash for 5 minutes. The strips were then bleached in the acid-dichromate solution for 5 minutes. After bleaching the strips were again washed in running water for 5 minutes followed by a 5 minute bisulfite wash (15.0 gm sodium bisulfite in a liter of water). The strips were then processed in DK-50 for 4 minutes. The densities on all strips, both exposed and unexposed, varied between 0.02 and 0.05. All traces of latent fog and latent light images were removed.

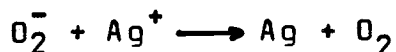
2. Discussion of Results

Since no difference was noted in the results of bleaching the aerial fog image and the image from the light exposure, the latent aerial fog is believed to be chemically reduced silver. Based on the aeration experiments, the agent responsible for this chemical reduction must be formed during the oxidation process and must be short lived. This activity suggests the formation of a short lived free radical as the reducing agent. The basic reactions probably occurring according to James⁴ are

- I. The oxidation of hydroquinone forming the peroxide radical



- II. The reduction of silver ions by the peroxide radical



The oxygen is the probable electron carrier. Since reaction I is a reversible reaction, in order to be effective in a quantitative reduction of silver ions necessary to form developable fog centers, this reaction must take place in the vicinity of the silver halide

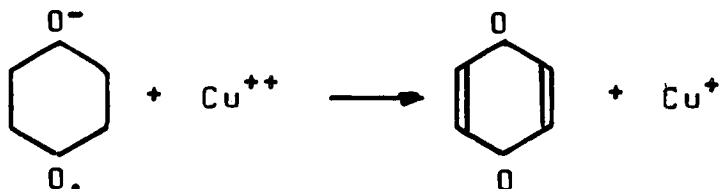
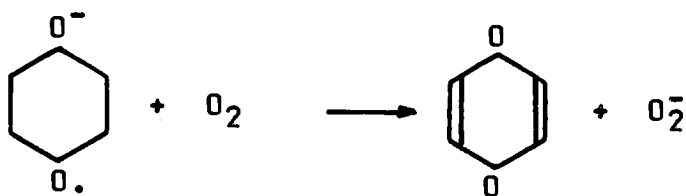
grain surface.

Copper is well known as an oxidation catalyst, and as such increases the oxidation rate of hydroquinone. When an ammoniacal solution of cuprous oxalate was tested⁴ as an aerial fogging developer with the film test strip partially immersed in the solution, aerial fogging was noted at the point of contact between air and cuprous oxalate solution. James suggests that the peroxide radical was again formed according to

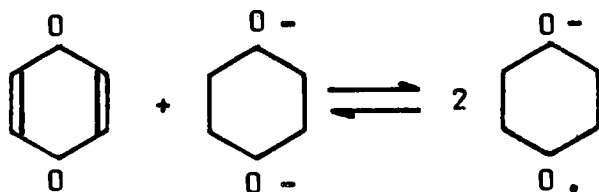


Since James also suggests that the cuprous salt is probably adsorbed to the silver halide, it acts not only as an intermediate in transferring an electron to the oxygen but also causes this transfer to take place quantitatively at the grain surface.

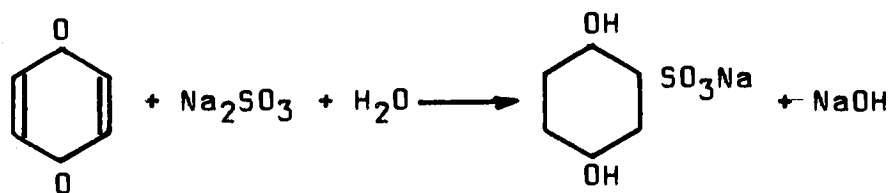
In the absence of copper, some fogging agent is formed, although much less. In addition to reaction I (page 16) the semiquinone that is formed in this reaction may also react with oxygen to form the fogging agent. When cupric ions are present however, the semiquinone may react preferentially with the cupric ions rather than with the oxygen. In either case, the semiquinone, after reacting with either the oxygen and/or the cupric ions would form quinone.



At high pH, the following equilibrium exists between the quinone, ionized hydroquinone, and the semiquinone.⁶

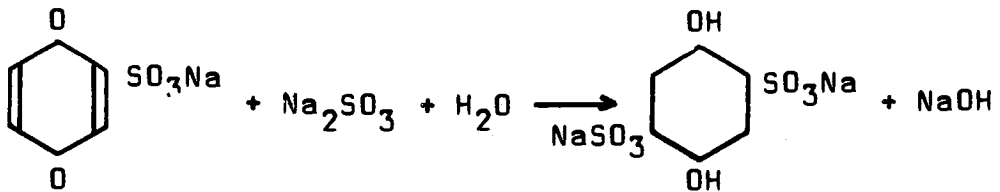


It is well known that when sulfite is present, it reacts preferentially with quinone according to the reaction

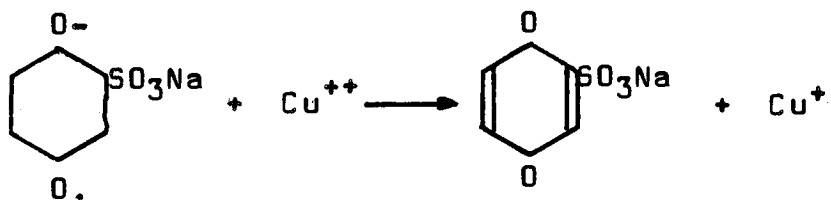


Continued addition of sulfite to quinone monosulfonate will lead to the eventual formation of hydroquinone disulfonate according to

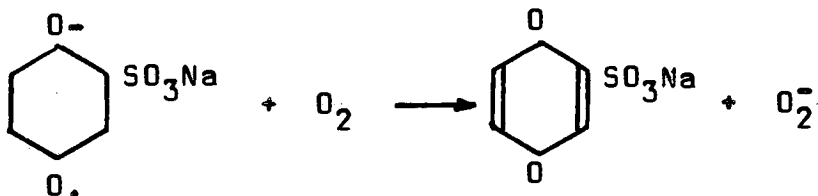
⁶ C.A. Bishop and L.K.J. Tong, J.A.C.S. 87, 501 (1965).



Bishop and Tong⁶ have shown that the ionization constants of hydroquinone and hydroquinone monosulfonate are similar, 9.85 and 9.57 respectively, so that both would be ionized at the developer pH. The equilibrium constants of the semiquinones however, differ by a factor of 10 (4.3 for the semiquinone of hydroquinone, 41.0 for that of hydroquinone monosulfonate. This indicates that the monosulfonate semiquinone is much more stable than the semiquinone of hydroquinone, therefore present in higher concentrations. Since the semiquinone of hydroquinone monosulfonate may also reduce cupric ions



and also react with oxygen to form the fogging agent



its stability and hence its presence in higher concentrations may account for the maximum aerial fog density occurring at

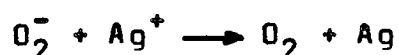
the sulfite concentration indicated in Figure IV. As was the case with the semiquinone of hydroquinone, the semiquinone of hydroquinone monosulfonate very probably reacts preferentially with the cupric ions rather than with the oxygen. Evidence for this may be found from lithographic developers which form a more active developer but not a fogging agent by the oxidation of hydroquinone by silver ions. For the case of aerial fogging, the semiquinone formed in the presence of a little sulfite may be the indirect source of the fog by reducing the cupric ions which react with oxygen to form the fogging agent.

In summary, it appears that the primary reactions leading to the formation of the aerial fog are

1. that between the cuprous ions and oxygen to form the fogging agent



2. the reduction of silver by the fogging agent



Since the concentration of copper in the fogging developer is very low (5.0 mgs/liter) regeneration of cuprous ions is necessary to cause the level of fog density obtained. The major role of the semiquinone then, would be to reduce the cupric ions back to the cuprous state. The sulfite level influences the type of semiquinone formed (either of hydroquinone or of hydroquinone monosulfonate) and hence its stability and concentration.

PART II: ATTEMPTS TO INHIBIT AERIAL FOG FORMATION

1. Experimental Procedure and Results

A. Standard Fogging Conditions

Based on experimentation and calculated experimental error from Part I, in order to obtain sufficient data to indicate statistical significance of the effects of compounds tested on the fogged control at 95% confidence with a minimum number of runs, the following conditions were chosen as standard for inducing aerial fog.

A fogging developer containing

5.5 grams hydroquinone
12.6 grams sodium sulfite
10.6 grams sodium carbonate
0.6 grams potassium bromide
1.0 liter distilled water

was mixed from the raw laboratory grade chemicals for every run made. 5.0 milligrams of copper sulfate in the form of 25.0 ml. copper sulfate solution was added to the fogging developer just prior to pouring the fogging developer into the aerial oxidation device. The temperature of the fogging developer with copper sulfate added was held to $70^{\circ} \pm 0.5^{\circ} \text{F}$ when used in the oxidation device. At this temperature the pH of the fogging developer was 10.18.

Where sensitometric exposures were required prior to inducing the aerial fog, the strips of film (Type 5302) were exposed in a KODAK 101 Sensitometer. A 0.86 neutral density Inconel glass filter was inserted

into the illuminance path and a 1/5 second exposure was used.

The oxidation device as described in Part I of this report was used for all fogging. A 6 minute fogging time was used for the fogged control strip. After fogging, the strips were removed from the oxidation device and immersed in a 1% acetic acid stop bath for 15 seconds, followed by washing in $70^{\circ}\pm 2^{\circ}\text{F}$ running water for 5 minutes. The strips were then taped in place in a standard 8x10 processing tray and tray processed for 4 minutes using the standard ASA agitation technique. The developer used was full strength DK-50 at $70^{\circ}\pm 0.5^{\circ}\text{F}$. Any deviation from this procedure has been noted and described where necessary.

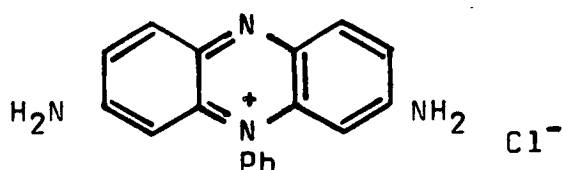
The 15 control strips (fogged) processed by this procedure produced an average base-plus-fog level of 0.828 with a standard deviation of 0.0289 between runs.

B. Attempts to Inhibit Aerial Fog

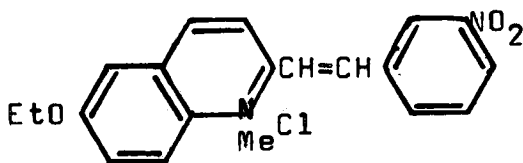
Four structurally dissimilar organic chemical compounds were chosen to study their effectiveness on the reduction or inhibition of aerial fog. Although structurally dissimilar, they are representative of what may be classified as desensitizing agents and organic antifoggants; phenosafranine and pinakryptol yellow as desensitizing dyes and benzotriazole and

5-mercapto-4-phenyltetrazole as organic antifoggants.

Three necessary characteristics of practical desensitizing dyes are⁷ 1) they must reduce sensitivity to light to a very low value under the conditions of development, 2) they must not destroy the latent image previously formed and 3) they must not retard development. As practical desensitizers, phenosafranine



and pinakryptol yellow



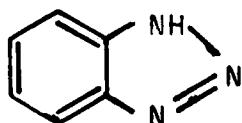
possess the above characteristics. Many hypotheses on the mechanism of desensitization by dyes have been proposed, however, the electron trapping mechanism⁸ has been reported to be the main mechanism. This mechanism will be used to explain the results of the effects of phenosafranine and pinakryptol yellow on aerial fog.

Benzotriazole and 5-mercapto-4-phenyltetrazole represent antifoggants differing widely in activity.

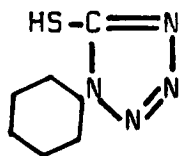
⁷ M. Tamura and N. Hada, Phot. Sci. Eng. 11, 82 (1967)

⁸ W. West and B.H. Carroll, J. Chem. Phys. 15, 529 (1947)

These agents must be capable of enhancing developer differentiation between exposed and unexposed silver halide grains, allowing development of the unexposed grains and inhibiting or retarding development of the unexposed grains. Benzotriazole



is a much less active antifogant than 5-mercapto-4-phenyltetrazole.



Possible mechanisms by which these agents operate will be discussed later.

(1) Phenosafranine

Since work had been reported in 1924 by Dundon and Crabtree² showing phenosafranine to be very effective in inhibiting aerial fog, it was chosen as the first compound for investigation. Its effectiveness against aerial fog when used 1) prior to fogging, 2) during the fogging, and 3) after the fogging was experimentally investigated.

Phenosafranine Pre-bath:

Strips of unexposed film were bathed for various lengths of time in a very dilute (1 part in 500,000)

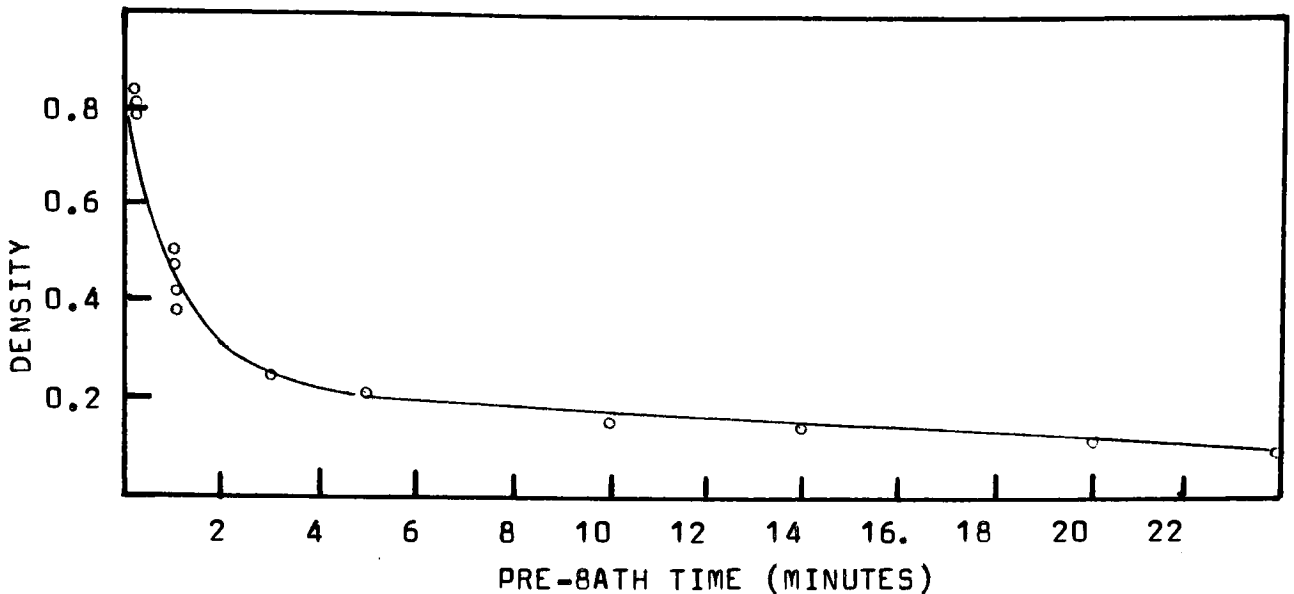


FIGURE VIII. EFFECT OF PHENOSAFRANINE PRE-BATH ON AERIAL FOG FORMATION

solution of phenosafranine, then dried. After drying, some strips were given a sensitometric exposure before fogging for 6 minutes in the oxidation device. Some of the sensitometrically exposed strips were not fogged but were checked to see what influence the pre-bath had on the speed and sensitivity of the film. As can be seen in Figure VIII, the pre-bath did have an inhibiting effect on the formation of aerial fog, the effect being dependent on the length of time in the pre-bath. A plot of the characteristic curves (Figures IX and X) show a decrease in speed along with the decrease in base plus aerial fog level. The pre-bath also had the effect of reducing the sensitivity of the film to the sensitometric exposure before fogging (Figure X). These results also indicate that the inhibiting effect on fog level is real since the fog level depression is of a greater magnitude

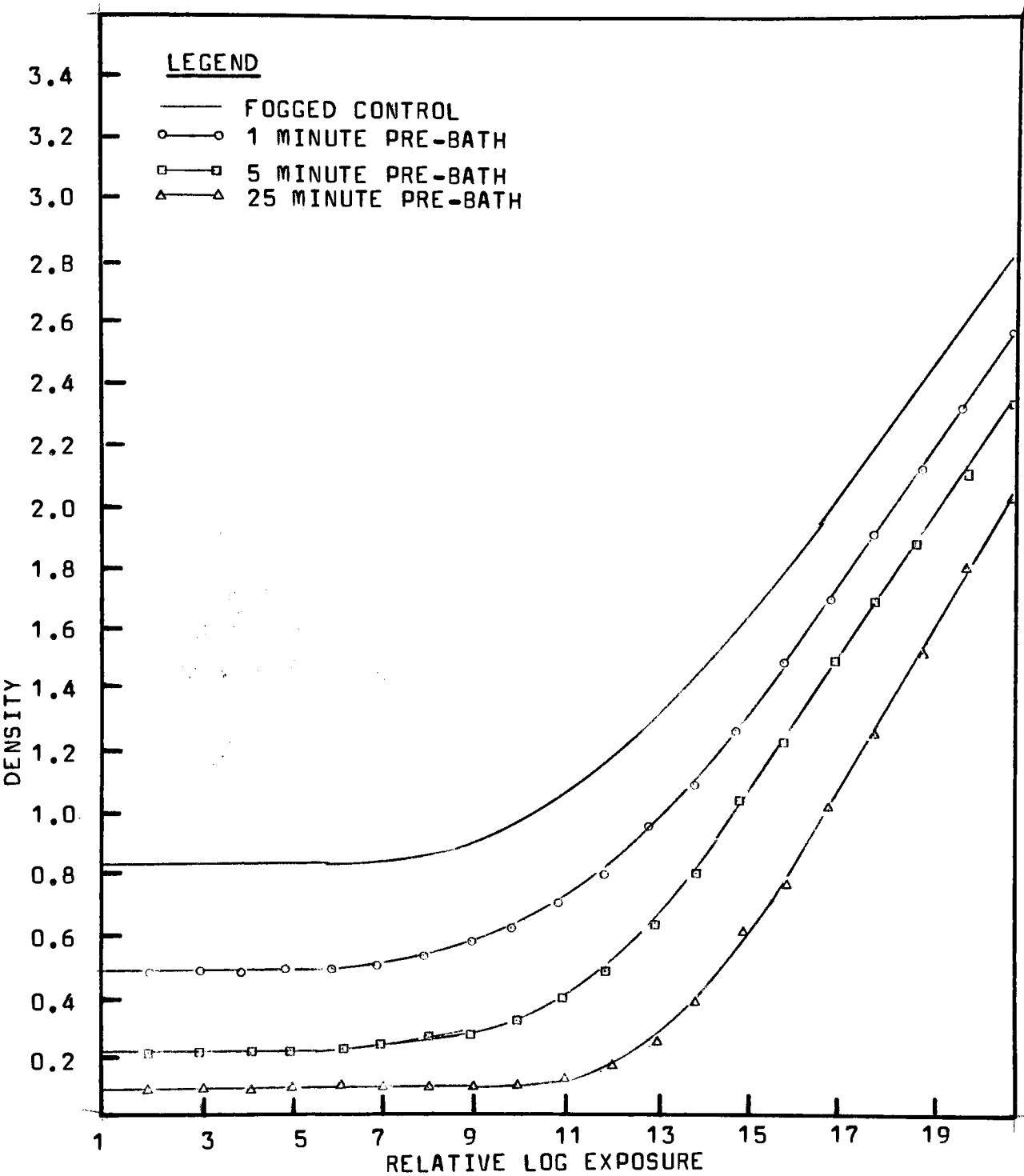


FIGURE IX. EFFECT OF PHENOSAFRANINE PRE-BATH BEFORE FOGGING: CHARACTERISTIC CURVES

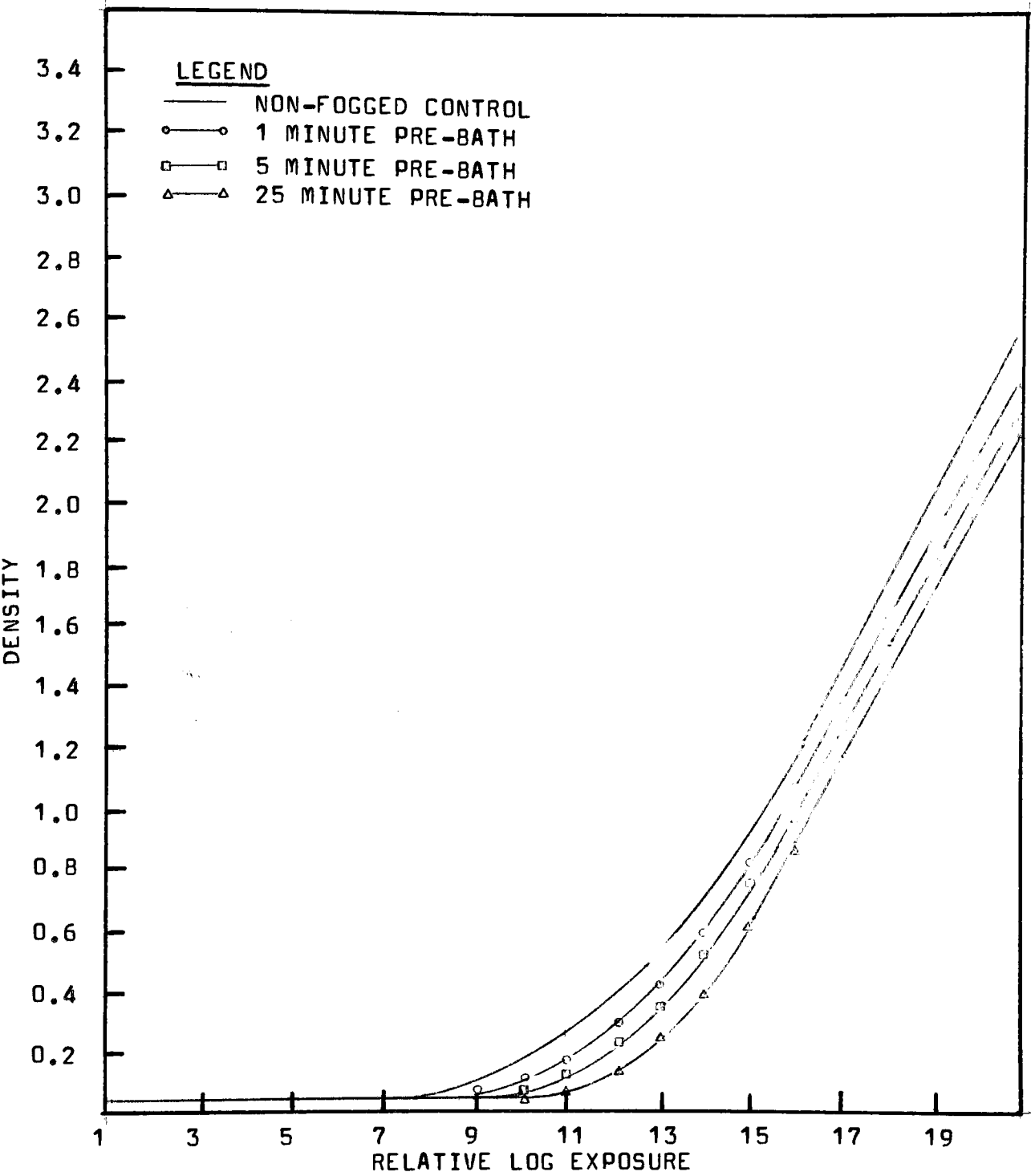


FIGURE X. EFFECT OF PHENOSAFRANINE PRE-BATH ON NON-FOGGED CONTROL: CHARACTERISTIC CURVES

than would be expected if the difference in levels was attributed to merely a depression in sensitivity.

Phenosafranine Added to Fogging Developer:

2.0 milligrams of phenosafranine added to a liter of the standard fogging developer had a very significant effect on the inhibition of aerial fog (see Figure XI).

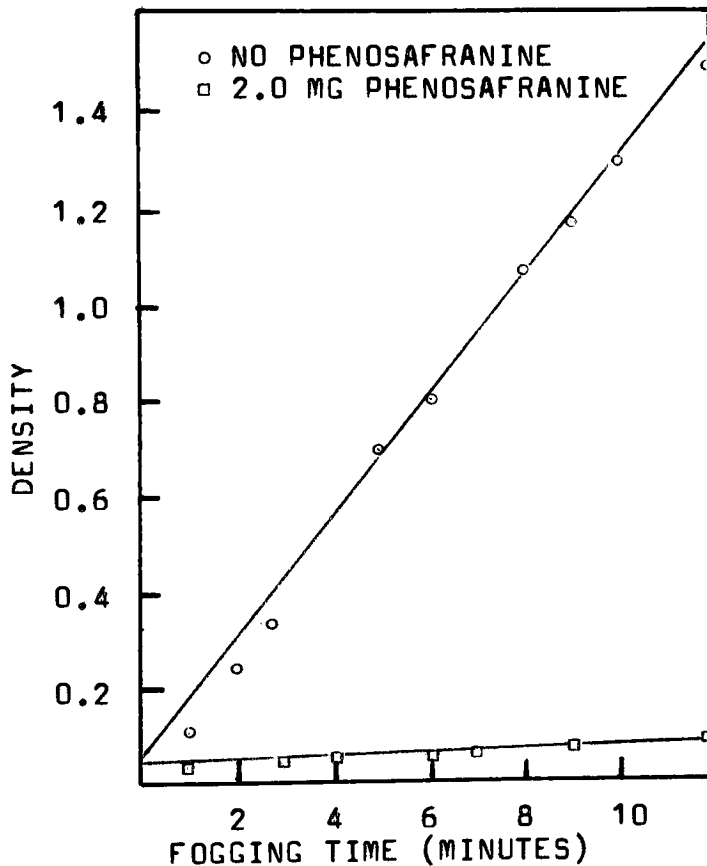


FIGURE XI. EFFECT OF PHENOSAFRANINE ON INHIBITING AERIAL FOG FORMATION

The aerial fog level of the film strips in the fogging developer for as long as 12 minutes showed no appreciable fog. When the characteristic curves of film strips

fogged in the standard fogging developer both with and without phenosafranine added are compared (see Figure XII) it should be noted that the curve for fogging with phenosafranine added is approaching that of the control curve (non-fogged). Note too that there is very little difference in speed and sensitivity of the two curves.

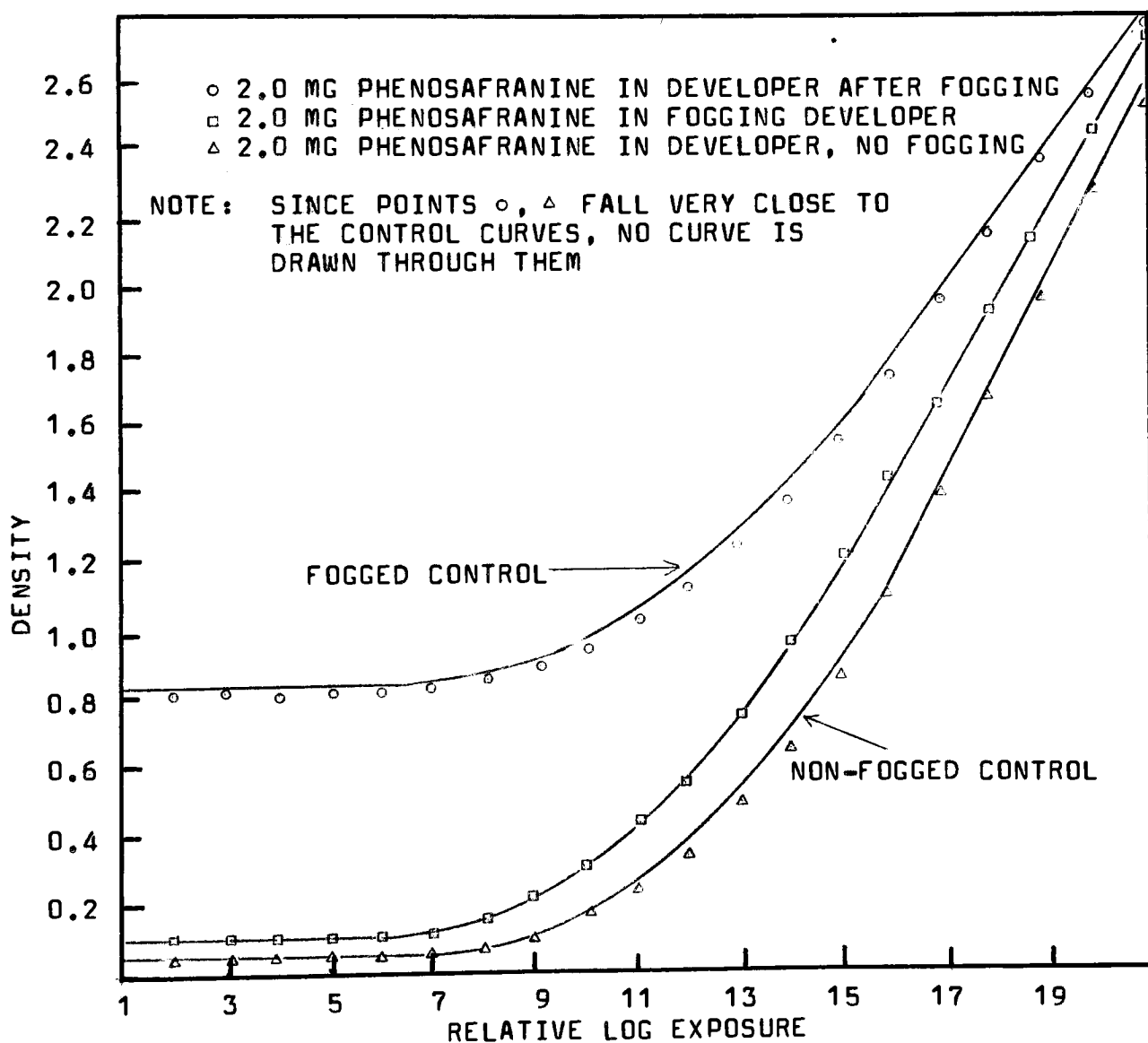


FIGURE XII. EFFECT OF PHENOSAFRANINE ON INHIBITING AERIAL FOG: CHARACTERISTIC CURVES

Phenosafranine Added to Developer

For this study, sensitometrically exposed strips were fogged for 6 minutes in the oxidation device using the standard fogging developer. After the usual fogging, stop bath, and wash, this time the strips were developed in a DK-50 developer to which was added 2.0 milligrams of phenosafranine per liter of developer. As an additional test, the effect on non-fogged film strips compared to the non-fogged control was also tried. In both cases, when compared to their respective control strips, the addition of phenosafranine to the DK-50 developer resulted in no detectable density differences between the curves (see Figure XII). These results are in keeping with the characteristic properties of phenosafranine when used after the formation of a latent image.

(2) Pinakryptol Yellow

Pinakryptol yellow, a styryl derivative, was the second of the desensitizing dyes tested. It is another practical desensitizing dye and its effects on the inhibition of aerial fog were very similar to those of phenosafranine, the main difference being the effective concentrations.

Pinakryptol Yellow Added to Fogging Developer

10.0 milligrams of pinakryptol yellow was added to a liter of the standard fogging developer. Sensitometric-

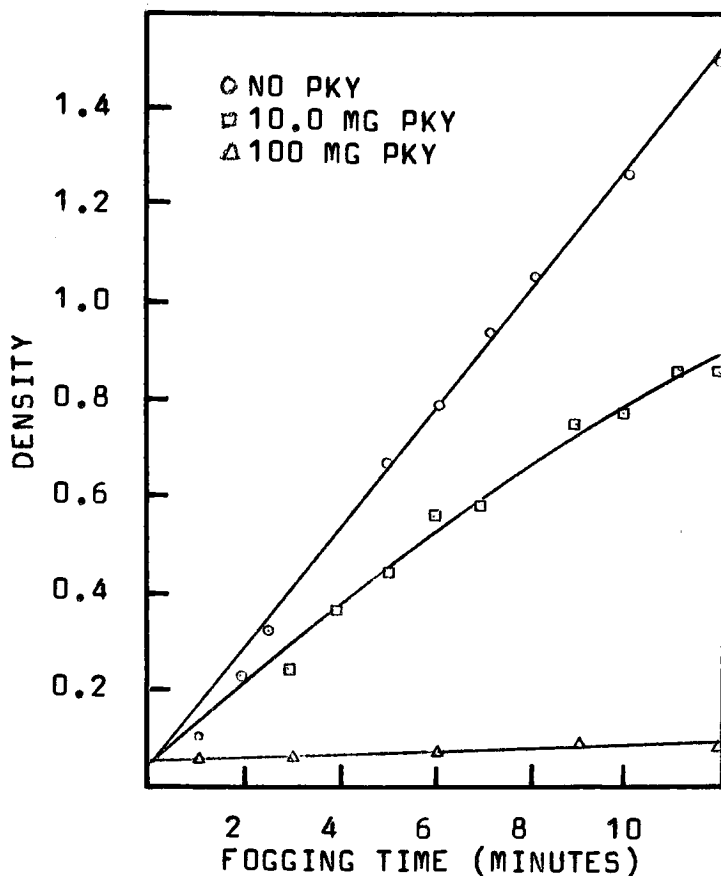


FIGURE XIII. EFFECT OF PINAKRYPTOL YELLOW ON INHIBITING AERIAL FOG

ally exposed strips were then fogged in this solution for fogging times up to 12 minutes. The addition of the pinakryptol yellow did inhibit the aerial fog formation. The concentration of the pinakryptol yellow was then increased to 100 milligrams per liter of fogging developer. The resulting base plus fog density at this concentration was approximately the same as that resulting from 2.0 mgs phenosafranine per liter of fogging developer. When the characteristic curves of the film strips were plotted (see Figure XIV) it was noted that the inhibition of the aerial fog when 100 mgs pinakryptol yellow was added to the fogging developer closely matched the non-fogged

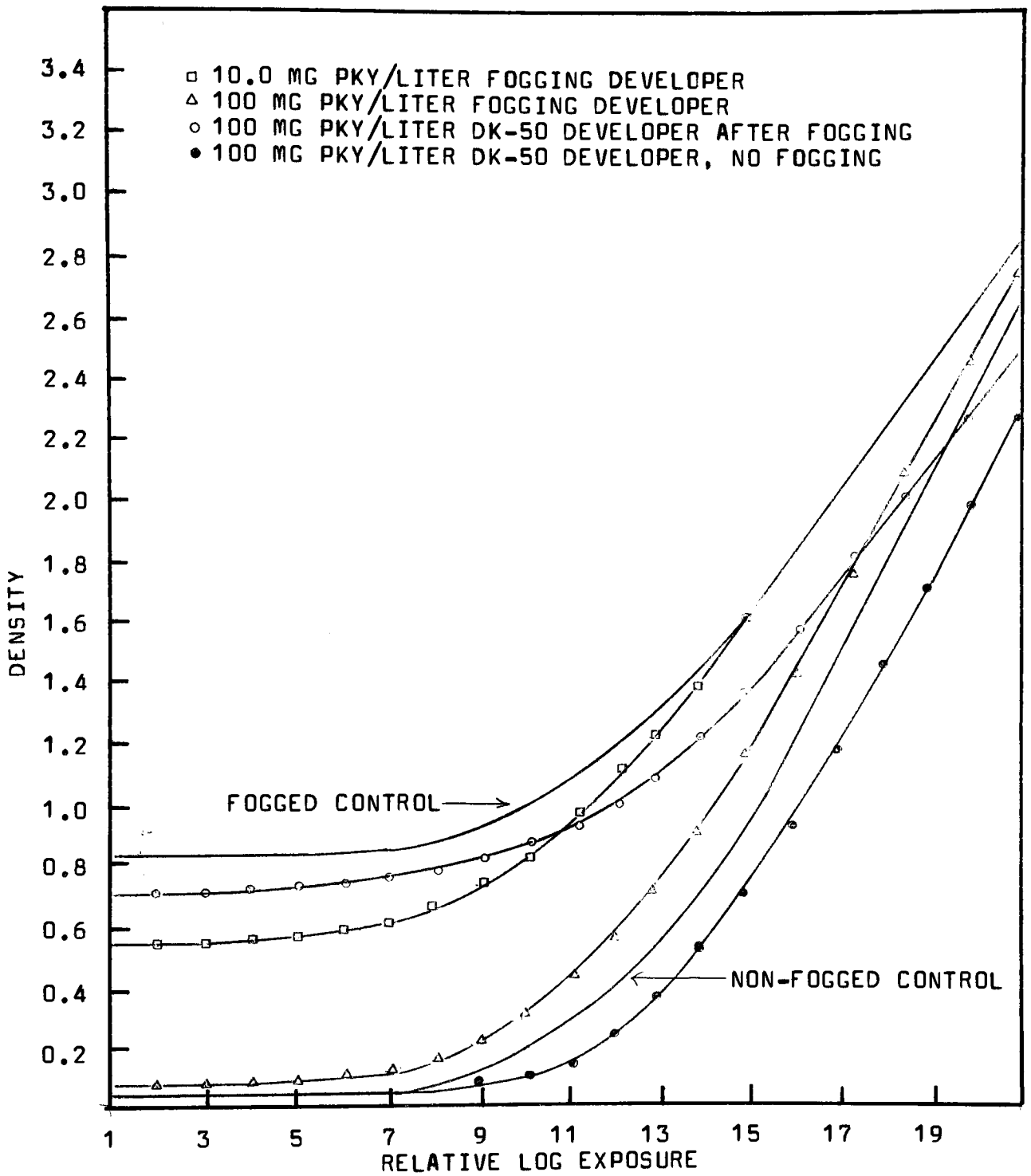


FIGURE XIV. EFFECT ON PINAKRYPTOL YELLOW DURING AND AFTER AERIAL FOGGING: CHARACTERISTIC CURVES

control curve. It appears that a slightly higher concentration of pinakryptol yellow could be found which would essentially inhibit completely the formation of aerial fog without changing the speed or sensitivity of the film.

Pinakryptol Yellow Added to DK-50 Developer

Again, sensitometrically exposed strips of film were fogged for 6 minutes in the oxidation device using the standard fogging developer. After fogging, stop bath, and wash, the film strips were developed in DK-50 to which was added 100 mgs of pinakryptol yellow per liter of developer. Although there appeared to be some difference in this curve when plotted compared to the fogged control, based on the sample size and the sensitivity of the experiment, no statistical significance could be attributed to this difference.

When non-fogged sensitometrically exposed film strips were processed in the DK-50 with 100 mgs pinakryptol yellow added per liter of developer, again no statistical significance could be attributed to the difference from the control curve.

(3) Benzotriazole

Benzotriazole Added to Fogging Developer

10.0 milligrams of benzotriazole was added per liter of the standard fogging developer. Sensitometrically

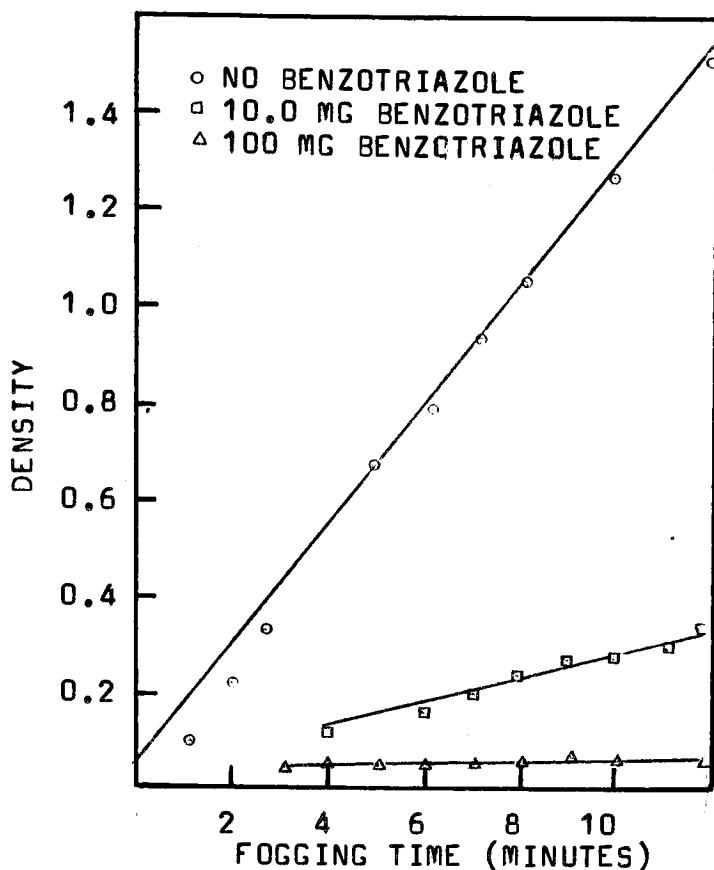


FIGURE XV. EFFECT OF BENZOTRIAZOLE ON INHIBITING AERIAL FOG

exposed strips of film were fogged in this solution for 6 minutes followed by the standard processing. This addition of benzotriazole to the fogging developer resulted in a significant inhibition of the base plus aerial fogging level (see Figure XV). When the concentration was increased to 100 milligrams per liter of fogging developer, essentially all traces of the aerial fog were gone. When the characteristic curves were plotted when 100 milligrams of benzotriazole was added to the fogging developer this curve and the non-fogged control curve were almost identical. No difference in speed

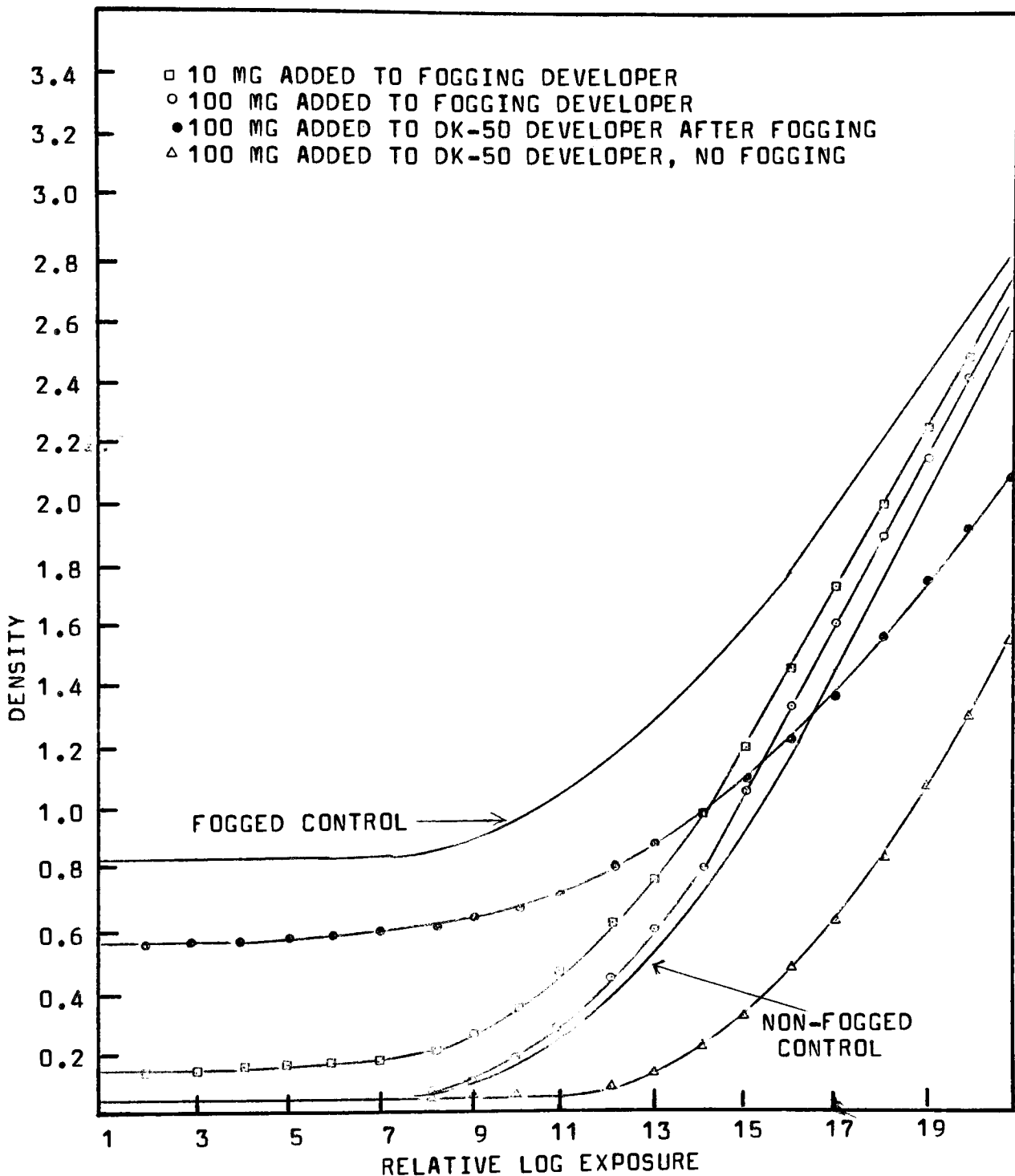


FIGURE XVI. EFFECT OF BENZOTRIAZOLE DURING AND AFTER AERIAL FOGGING: CHARACTERISTIC CURVES

or sensitivity are apparent. When the fogging was continued for 12 minutes, no detectable differences in the base plus aerial fog level were noted when compared to the non-fogged control base density.

Benzotriazole Added to DK-50 Developer

When 100 milligrams of benzotriazole was added per liter of DK-50 developer and film strips fogged for 6 minutes were processed in this solution, a significant decrease in the base plus aerial fog level was noted when compared to the fogged control (see Figure XVI). Also noted however, was a significant decrease in all density levels along the characteristic curve. When a non-fogged sensitometrically exposed film strip was processed in this same solution again a very noticeable decrease in density along the entire characteristic curve resulted. It was readily apparent that the addition of that concentration of benzotriazole added to the developer could not inhibit a high level of aerial fog without retarding the development at all exposure levels.

(4) 5-Mercapto-4-phenyltetrazole (5-M-4-PT)

5-M-4-PT Added to the Fogging Developer

2.0 milligrams of 5-M-4-PT was added to the fogging solution and the sensitometrically exposed

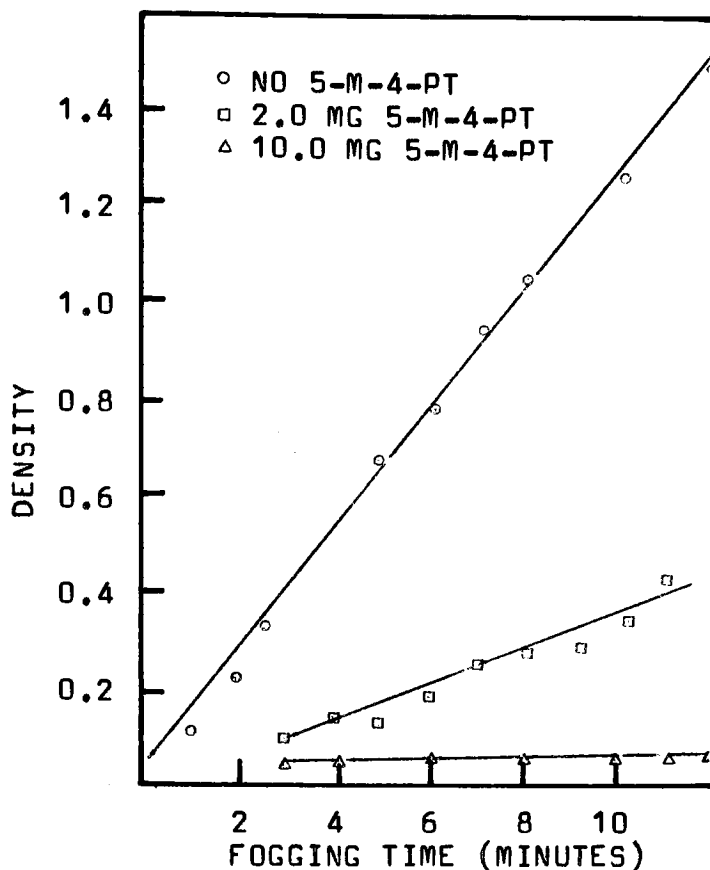


FIGURE XVII. EFFECT OF 5-MERCAPTO-4-PHENYLTETRAZOLE ON INHIBITING AERIAL FOG

strips were fogged in this solution in the oxidation device for various fogging times. Again a significant inhibiting effect on the formation of aerial fog was noted. When the concentration was increased to 10.0 milligrams per liter of fogging developer, the inhibition was complete over the range of times tested. When the characteristic curve for the 6 minute fogged strip is compared to the control at the 2 milligram per liter concentration the fogged curve is approaching the non-fogged control curve (see Figure XVIII). The 10.0 milligram per liter concentration not only inhibited

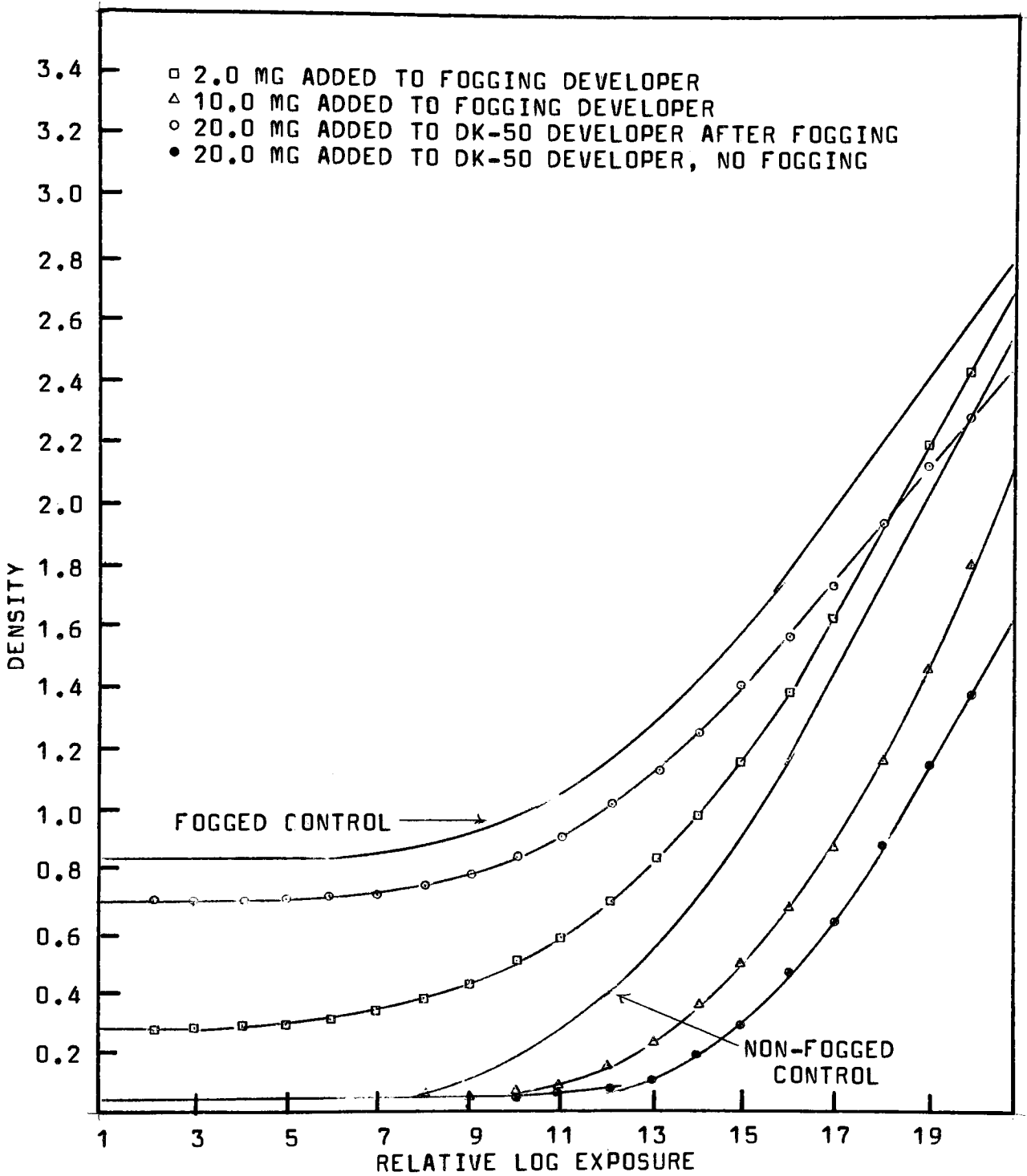


FIGURE XVIII. EFFECT OF 5-MERCAPTO-4-PHENYLTETRAZOLE DURING AND AFTER AERIAL FOGGING: CHARACTERISTIC CURVES

the aerial fog formation completely but also significantly retarded development over the entire strip. It appears that some intermediate concentration could be found that would inhibit the formation of the aerial fog without affecting the development of the sensitometric image.

5-M-4-PT Added to the DK-50 Developer

20 milligrams of 5-M-4-PT was added per liter of DK-50 developer. After sensitometric strips were fogged in the standard fogging developer for 6 minutes, they were processed in the DK-50 with 5-M-4-PT for 4 minutes. The addition of this concentration resulted in no significant inhibition of the aerial fog formation. When a sensitometric strip with no fogging was processed as above and compared to the non-fogged control, a very substantial retardation of development was evident. These results are very similar to those obtained for the benzotriazole.

2. Discussion of Results

The experimentation described in Part I indicated that the latent aerial fog centers are chemically reduced silver. This is further supported by the fact that neither the desensitizing dyes nor the organic antifoggants could distinguish between latent light centers and latent fog centers once formed. The retardation of development noted in the case of 5-M-4-PT

and the benzotriazole added to the developer after exposure and fogging was not selective for either the light or fog latent images. The desensitizing dyes tested exhibited no noticeable effects on either the latent light or fog images after the images were formed.

On the assumption that the general overall reaction mechanism as proposed in Part I is correct, the prevention or inhibition of the latent aerial fog formation should be possible in the following ways.

- 1) Removal of free electrons. Without the free electrons the reduction of silver ions to latent aerial fog centers could not take place. Additionally, the cupric/cuprous redox reactions could not take place thereby inhibiting the catalytic action by the copper.
- 2) Removal of mobile silver ions. Without sufficient mobile silver ions, any possible latent fog centers could not grow to a developable size.
- 3) Formation of a physical protective barrier around the silver halide grains. The formation of such a layer could physically prevent other agents from coming in contact with the silver halide grains.

All the compounds tested either prevented or inhibited the formation of the latent aerial fog centers. None of the agents are effective in either removing the fog once formed or selectively inhibiting the development

of the latent fog over the latent light centers. Based on known chemistry of the desensitizing dyes and the organic antifoggants, these two types of agents probably inhibit the formation of aerial fog through different means. Because of similarities obtained in the results of the experimentation, the discussion will not be based on the individual compounds but rather on the type, i.e., desensitizers and antifoggants.

Desensitizers

Phenosafranine and pinakryptol yellow both prevent the formation of the latent fog centers when present in sufficient quantity during the fog formation reaction. Since they both are effective electron traps and since the redox reactions necessary for the silver reduction involve electron transfer, this mechanism is the probable reason for their effectiveness in inhibiting the aerial fog formation. In the normal course of aerial fog formation as discussed in Part I, an electron is transferred from the hydroquinone to the cupric ion, forming the cuprous ion. The cuprous ion in turn transfers an electron to the oxygen forming the peroxide radical. This peroxide radical in turn transfers an electron to a silver ion forming latent aerial fog.



It is reported in the literature⁹ that desensitizing

⁹C.E.K. Mees and T.H. James, The Theory of the Photographic Process, Macmillan, New York, 1966.

effects are a function of the presence of electron-accepting groups in the dye structure. It is also known that the desensitizing effect may not be directly related to the dye adsorption although adsorption would enhance the desensitizing effect. In the case of desensitization to light, it is generally agreed that the desensitizing dye traps the photoelectrons preventing their reduction of silver ions. For the case of aerial fog formation, no photoelectrons are produced. However, electrons are produced as discussed above. Since the dyes are adsorbed to the silver halide, they probably hinder the electron transfer to the silver ion.

Antifoggants

Benzotriazole and 5-mercapto-4-phenyltetrazole when present in sufficient quantities also inhibit the formation of aerial fog. It is interesting to note however that benzotriazole has been used to intensify aerial fog in producing direct positive photographs.¹⁰ For this case however, the author uses special "internal latent image" emulsions. He also reports that from observations, the benzotriazole appears to increase the rate of oxidation of the hydroquinone accounting for the aerial fog enhancement while still maintaining

¹⁰ R.E. Stauffer, U.S. 2, 497,917 to Eastman Kodak Co., (1950).

its antifoggant properties. For this investigation where benzotriazole was found to inhibit the formation of aerial fog, copper was present with hydroquinone and the resultant fogging effect may mask out any due to the benzotriazole. In addition, the emulsion used is primarily a surface rather than an internal image emulsion.

Both the benzotriazole and the 5-M-4-PT are known to be adsorbed to silver halide and as the case with the desensitizing dyes, adsorption may inhibit the aerial fog formation. Since benzotriazole in the fogging developer had about the same effect on both the light and the fog images, this indicates that it was probably not present during development after the fogging treatment. The 5-M-4-PT, on the other hand, when added to the fogging developer was probably strongly adsorbed since it retarded the final development. Although adsorption may result in inhibiting aerial fog, it is probably not the main mechanism involved. The antifoggants readily form silver complexes but are not easily reduced and should not behave as electron traps.

The main mechanism involved is probably explained on the basis of work done by Hamilton and Brady¹¹ in a study of the role of mobile silver ions in latent image formation. They explain that phenylmercaptotetrazole forms a complex with some of the surface silver ions. This complexing action removes the silver ions from a reversible

¹¹ J.F. Hamilton and L.E. Brady, J. Phys. Chem. 66, 2384, (1962).

exchange with the interstitial ions upsetting the equilibrium and reducing the concentration of interstitial ions. Without sufficient mobile interstitial silver ions, developable latent centers, either light or in this case, fog, cannot form. It can be assumed that the same type of silver complexing is probably occurring with the benzotriazole. These agents then, in contrast to the desensitizing dyes, inhibit the formation of aerial fog by affecting the mobile silver ions rather than the electrons responsible for their reduction. The antifoggants inhibited the formation of aerial fog almost completely as did the desensitizers, however, at concentrations necessary for this equivalent effect, the antifoggants retarded development of the film much more than the desensitizing dyes.

In summary, aerial fog is chemically reduced silver. Necessary for this reduction is the combination of electrons and mobile silver ions. The desensitizing dyes effect the balance of electrons and the antifoggants effect the balance of mobile silver ions. Either of these effects would result in an inhibiting effect on the formation of aerial fog.

Conclusions

Based on the experimental work conducted in the course of this investigation, the following conclusions were reached:

1. Aerial fog is chemically reduced silver.
2. Phenosafranine, pinakryptol yellow, benzotriazole, and 5-mercapto-4-phenyltetrazole inhibit the formation of aerial fog only when present during the fogging treatment.
3. Phenosafranine, pinakryptol yellow, benzotriazole, and 5-mercapto-4-phenyltetrazole showed no selective distinction between fog and light image during development.

Acknowledgment

The author is indebted to Professor B.H. Carroll for his valuable suggestions and discussions during this investigation.