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Comparison of Bromide, Benzotriazole, and Phenyl Mercaptotetrazole and Their Effect on Photographic Development

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COMPARISON OF BROMIDE, BENZOTRIAZOLE, AND PHENYL MERCAPTOTETRAZOLE AND THEIR EFFECT ON PHOTOGRAPHIC DEVELOPMENT

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ABSTRACT

A comparison of three commonly used antifoggants was made. Their effect on the formation of fog and image density development was studied using a rate factor of development. This rate factor is defined as the slope of the curve for density-log development time. Bromide and benzotriazole were found to have no effect on the rate of development whereas 1-phenyl-5-mercaptotetrazole was found to significantly reduce the rate of development. Bromide and benzotriazole were found to cause a suppression of image density only by increasing the time before density formation begins.

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INTRODUCTION

Antifoggants restrain the formation of developer fog during photographic development, retard the rate of development, and when added to the emulsion itself, sometimes restrict production of emulsion fog.[1] From the literature, one might get the impression that the action of antifoggants can be generalized as being simply the reduction of fog and the inhibition of the rate of development with all antifoggants creating equal effects so long as the concentrations are adjusted to take into account the differences in relative activity. It is often implied that many antifoggants could be used interchangeably so long as the concentration used reflect their differences in relative activity. The purpose of this project has been to compare the performance of three commonly used antifoggants to determine if differences in their relative effects exist.

Many compounds have been identified as antifoggants but only relatively few are commonly used. Bromide is probably the most widely used of these. Only a limited number of organic compounds have been used successfully as developer antifoggants. They include certain benzotriazoles, benzimidazoles, phenyl tetrazoles, and phenyl mercaptotetrazoles.

An antifoggant is a compound which can selectively decrease the rate of development for fog formation to a greater extent than for image density formation. Antifoggants are most generally used in developer solutions which would otherwise have poor discrimination between exposed and non-exposed silver grains. Developers which are used at elevated temperature or pH, or those which contain developing agents with high relative activity often require antifoggants to prevent excessive fog formation.

Often, compounds which act as antifoggants are added to an emulsion during manufacture, not only for the purpose of their antifoggant effect, but also because they act as emulsion stabilizers. Most antifoggants act as emulsion stabilizers but cause desensitization if excessive amounts are used.

Numerous mechanisms have been proposed for antifoggant action. Dr. James [2] has summarized these as follows:

1) The antifoggant may increase the activation energy for the formation of fog nuclei or fog development to a greater extent than for latent image development. This may cause a differential change in the rate of formation of silver during development or may cause the reaction path to change completely.
2) The antifoggant may form a silver salt layer on the grain surface that is less reactive towards development than the silver halide. The fact that lower amounts of antifoggant than is necessary to form a complete monolayer cause antifoggant activity discounts this mechanism.
3) The antifoggant may displace silver ions from the silver gelatinate complex by forming less easily reducible salts or complexes.
4) The antifoggant may be selectively adsorbed by fog centers or areas of high reactivity on the grain surface and hence reduce the reactivity towards the developer.
5) The antifoggant may eliminate fog nuclei or reduce their size by oxidation.

More than one mechanism has been proposed for numerous individual agents.

Combinations of these mechanisms rather than any singular one may be responsible for antifoggant action. Differences in mechanisms or combinations of mechanisms between different antifoggants may cause their effects to differ from each other.

A general characteristic for compounds that exhibit antifoggant action is their ability to form an insoluble silver salt. For organic compounds this is a replaceable hydrogen atom in their structure which, when replaced with a silver, forms a sparingly soluble silver salt. In the case of the azole type antifoggants (triazoles, imidazoles, etc) the hydrogen is attached to a nitrogen atom. In the mercapto type antifoggants this hydrogen is attached to a sulphur atom. The insoluble silver salts adsorb to the grain surface. The more insoluble the salt, the more strongly it is adsorbed. The antifoggants which form the most insoluble salts tend to have the highest relative activity. The mercapto salts are more insoluble and have higher relative activity than the azole type antifoggants or bromide.

It may be possible that two different types of antifoggants, when used in combination, may cause interactions which in turn cause significantly different antifoggant effects. Competitive adsorbtion on the grain surface could cause a decrease in activity of one agent in the presence of another. DeCastro and Eisenberg [3] studied the interactions of bromide and benzotriazole and found there were significant interactions when the two were used together in viscous developers. These effects were confined to the low exposure areas and short development times.

Some individual antifoggants have been found to cause changes in the microstructure of the developed image. Sheberstov and Borovhova [4] have shown losses in image quality caused by developers containing antifoggants and Kurz [5] has disclosed that the addition of 1-phenyl-5-mercaptotetrazole to a metol-hydroquinone solvent developer increases image sharpness by causing edge effects. If there are differences in the changes in image quality by different individual agents or their interactions with each other, it would be further evidence that the agents act in different manners. Due to time restrictions no investigation of these changes in image quality were made and no further discussion of them will be made in this project.

EXPERIMENTAL

Three antifoggants were chosen to be studied in the project, potassium bromide and two organic compounds, benzotriazole (BZT) and 1-phenyl-5-mercaptotetrazole (PMT). These three agents represent three types of antifoggant compounds as well as a correspondingly wide range of relative activities. Potassium bromide, an inorganic antifoggant, is commonly used at concentrations of 1-15 grams per liter of developer. Benzotriazole, an azole type organic antifoggant, is commonly used at concentrations of 0.1 grams/liter. The salts formed by bromide and benzotriazole are similar in relative activity. The order of relative activity between the two depends on the pH at which benzotriazole is used. At higher pH, as in most developer solutions, the salt of benzotriazole is less soluble than silver bromide and hence has higher relative activity. At lower pH the salt is more soluble and hence the order of activity is reversed. PMT is a mercapto type organic antifoggant which has a considerably higher relative activity than bromide or benzotriazole regardless of pH.

Concentrations of PMT normally used range from 10 to 100 milligrams/ liter.

A factorially designed experiment was planned to compare the effects if varying levels and combinations of the three agents. This method was desirable not only for being a systematic and statistical approach to the comparison, but also would lead to a study of the interactions between agents. In order to make valid comparisons the relative activities of the levels of the antifoggants used had to be equal. But because the relative effects of the various agents were found to differ in preliminary results, a method of defining equal relative activity had to be determined. Equal activity was defined for the factorial design as the concentrations of antifoggants which gave equal fog level after eight minutes of development.

The film used for the project was Kodak Commercial Film 6127. This film has a moderately slow, blue sensitive emulsion with no development accelerators and hence is less likely to have complicating effects on the results. With the blue sensitive emulsion a number #1 (deep red) safelite was used during handling of the film. Film handled in the safelite showed no distinguishable difference in fog level from film handled under total darkness when given equal development.

The developer was also chosen for its simplicity.

It contains:

Table 1		
	Metol	2 grams
	Sodium Sulfite	25 grams
	Potassium Carbonate	25 grams
	Antifoggant	________
		H_2O to make 1 liter

The sulfite level was chosen so as to have sufficient capacity to act as an acceptor for oxidized developer but yet not so high so as to cause excessive silver halide solubility. The carbonate was chosen to give the developer a pH near 10.5. The level was chosen so that the solution would be well buffered. The organic antifoggants are also weak acids. With a well buffered solution no significant pH changes were encountered when the antifoggants were added. Stock solutions of the three antifoggants were used for addition to the developer. One stock solution for each agent was used during the final factorial experiment. The bromide solution contained 100 grams/liter potassium bromide in water. The benzotriazole stock solution contained 25 grams/liter benzotriazole in 20% methanol in water. The PMT solution contained 2.0 grams/liter in 50% methanol in water. The concentration of the bromide and benzotriazole solutions were checked by potentiometric titration with silver nitrate and found to be within 4% of the given concentration. Photo grade chemicals, with the exception of potassium bromide which was ACS reagent grade, were used for all developer solutions.

Exposures were made using a Kodak Model 101 Sensitometer. Exposure time was 0.2 seconds. A Kodak #2 Step Wedge and a Kodak Wratten 0.7 Neutral Density filter were used for attenuation of intensity.

Development was carried out in a vertical developing tank using nitrogen bursts for agitation. The burst rate used was 1 second bursts at 10 second intervals. Gas burst agitation was used with the intent of minimizing the variability of the process during development. A study of the process was made using repeated control runs. A developer containing no antifoggants was used for these runs. From the control runs the following standard deviations density levels were found; 0.08 to 0.10 density units in high exposure regions (2.0 density areas), 0.04 to 0.06 in the middle regions (1.0 density areas), and 0.01 to 0.04 in the toe and fog regions. The range of standard deviations given correspond to the range in developing times (up to 8 minutes of development). In all cases the variability increased with increasing development time.

For each of the antifoggants to be tested, a series of preliminary tests were made which varied the concentrations of the individual agents over their useful range, measuring the restraint of fog and their effect on the rate of development. From these preliminary results, three levels of the antifoggants to be used for the factorial experiment were chosen on the basis of the ability to restrain fog formation. The first level chosen was 0 grams/liter to isolate the individual agents. The highest level chosen was the lowest level which would maintain a constant level of fog during the first eight minutes of development. The low or middle level of antifoggant was chosen as a level which had nearly equal fog restraint during the first eight minutes of development for each of the agents. The levels chosen were:

Table 2

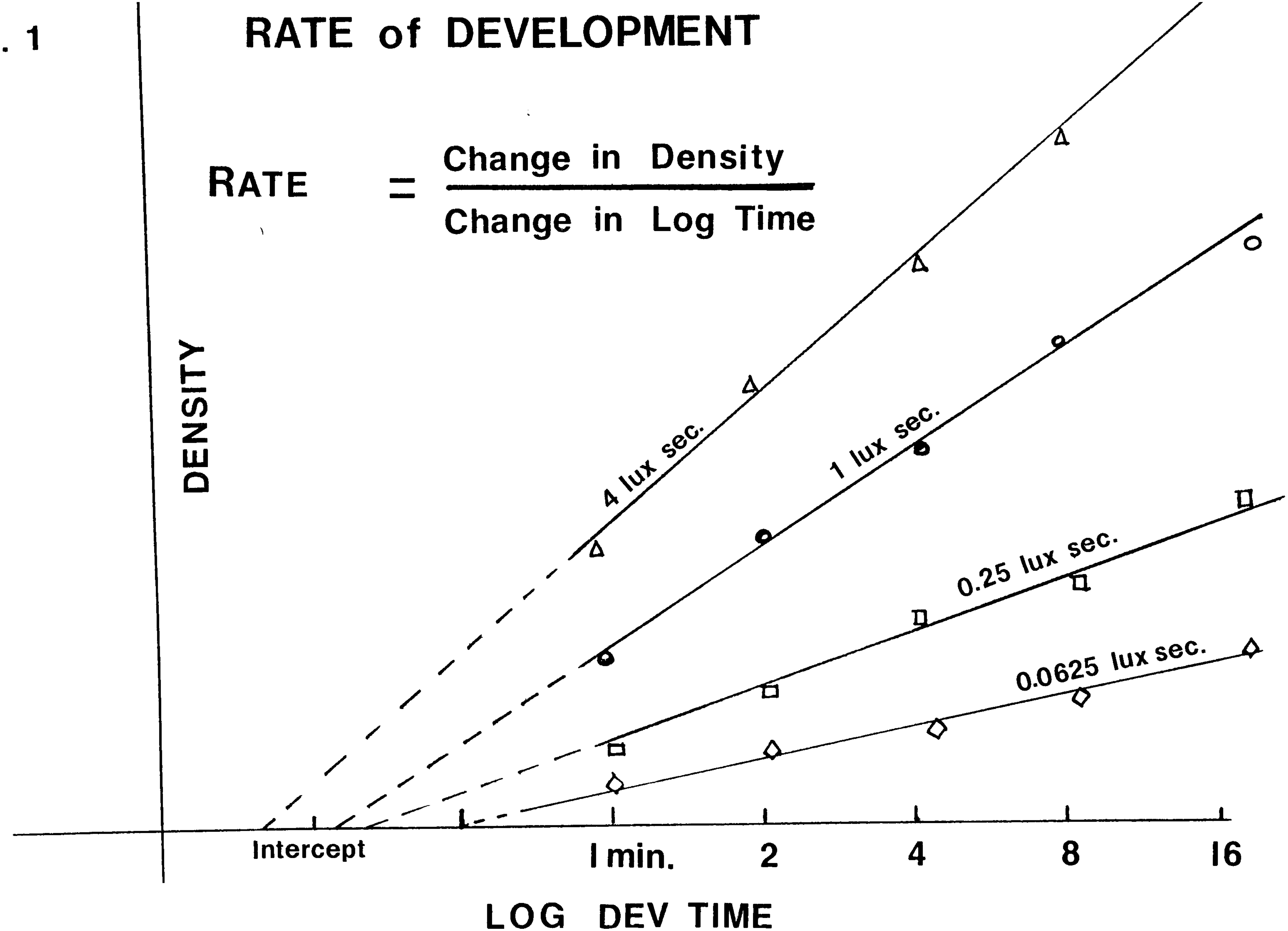
Potassium Bromide	Low	1.0g/l	0.0084 M
	High	5.0g/l	0.0420 M
Benzotriazole	Low	0.025g/l	0.0002 M
	High	0.5 g/l	0.0042 M
1-Phenyl-5-Mercaptotetrazole	Low	0.025g/l	0.00014 M
	High	0.1 g/l	0.00056 M

Having three antifoggants at three levels each gives a 3^3 factorial experiment and hence has 27 developer combinations. From the results of the 27 developer runs significant changes in the effects on fog formation and the rate of development were identified using a statistical analysis of variance.[6] The results of the three factor interactions were pooled together and used as a residual estimate of error. F-Tests of significance were made using $\alpha = 0.10$.

The fog level used in the project is defined as the net density above the base level (0.03) of the film measured in an area receiving no exposure adjacent to the sensitometric exposure. Density was measured using a McBeth TD 504 transmission densitometer.

A rate factor and an intercept point were defined and used as a quantitative means of studying the rate of development and initiation time of development. (See Fig. 1) The rate of development as considered in this project is defined as the change in density over the change in the time of development. For moderate development conditions, it was found that if the density for a given exposure is plotted against the logarithm of the developing time, a linear relation would be found usually through at least the first 8 minutes of development.

A rate factor of development can then be defined as the slope of this straight line portion of the curve. The development times 1,2,4, 8,16 were chosen to have equal log time intervals. This rate factor was studied for density defined by two different methods, gross density, the actual density as measured on film sample and net density, the actual density minus the base and fog densities of the sample. Only small differences were found in the shoulder of the density-log development time curve for the two methods. These differences caused only a small difference in the rate factor and shifted the curve only slightly. No change in the conclusions on the effect of rate or intercept resulted from the two methods. The intercept point is defined as the point where, if the straight line portion of the density-log development time curve is ig. 1


RATE of DEVELOPMENT
RATE = Change in Density / Change in Log Time
DENSITY
4 lux sec.
1 lux sec.
0.25 lux sec.
0.0625 lux sec.
Intercept
I min.
2
4
8
16
LOG DEV TIME

extended, the curve intercepts the development time axis. These points correspond to the displacement of the curves along the development time axis. They may also be a relative indication of the change in the initiation time or even the induction period between the various developers. The point at which the curve crosses the axis should ocrrespond to the time at which density formation begins. It is highly unlikely though that the relation is a straight line during the initial stages of development. As a result, this point must only be interpreted as a relative indication of the time before density begins to form and not the actual time.

RESULTS

No evidence was found to indicate that antagonistic interactions exist between the agents tested. In all cases the combinations of agents gave a greater effect than the agents individually. It appears that adding these antifoggants causes, in general, an addition in effects. With the levels of antifoggants which were used no maximum in this additive effect was found.

Differences were found in the effect on fog formation between developers containing bromide or benzotriazole and those containing PMT Fig. 2 is a comparison of the effects of the individual agents on fog formation. All agents at the levels tested caused a significant decrease in fog formation when compared to a developer with no antifoggant. During the first eight minutes of development bromide and benzotriazole have nearly equal effect. Developers with PMT, during the same time period of development had a lower effect as evidenced by the higher fog level. Beyond eight minutes development with bromide and benzotriazole at the levels tested, caused a rapid increase in fog level. With the developer containing PMT though no significant increase in fog density has occurred after eight minutes of development.

It appears then, that bromide and benzotriazole have a stronger or more rapid effect on fog suppression during the initial stages of development. PMT, on the other hand, has slower action but appearantly greater capacity for fog suppression.

Fig. 3 compares the effect the antifoggants have had on the rate of development. The rate was studied at four levels of exposure; 4,1, 0.25 and 0.0625 lux seconds. No significant change in the rate of development was found to be caused by bromide or benzotriazole. Bromide shows a small but inconsistant effect on rate - a decrease for low levels of bromide and an increase for the higher level. PMT causes a significant and consistant decrease at all exposure levels when compared to a developer containing no antifoggant. The suppression of the rate of development appears to increase in magnitude as the concentration is increased.

PMT appears to have a greater effect on the formation of image density than bromide or benzotriazole. Bromide and benzotriazole on the other hand initially had a greater effect on fog density formation. One possible explanation may be that PMT, which is known to adsorb to the silver halide grain more strongly than bromide or benzotriazole, may absorb initially only in the uppermost layers of the emulsion, the layers where the greatest amount of exposure-formed latent image exists. There would be a smaller effect of PMT on the lower layers of the emulsion where the more uniformaly distributed fog centers exist. Further evidence of this may be that when PMT is used as an emulsion incorporated antifoggant and is uniformly deposited throughout the emulsion, it has an overall greater relative activity.

Finally, in considering the effect of the antifoggants on the intercept (Fig 4) PMT has again caused a different effect than bromide or benzotriazole. Bromide and benzotriazole have shifted the rate curve, and as a result the intercept, in a direction which corresponds to a later time of development initiation than for development containing no antifoggants. Shift of the intercept to a more positive log development time corresponds to a longer time. In contrast, PMT causes a shift in the intercept which corresponds to an earlier initiation of development. Again it must be remembered that our measure of the initiation doesn't necessarily correspond to the actual time when density first begins to form.

CONCLUSION

Evidence has been found that the relative effects of bromide and benzotriazole differ from the effects of 1-phenyl-5-mercaptotetrazole. The actual effects, the restraint of fog formation and the suppression of image density formation occur for each of the agents, but they differ in magnitude and occur at different rates. It appears that PMT suppresses image density by a decrease in the rate of development. Bromide and benzotriazole do not cause this decrease in the rate of development but appear to suppress image density formation at any development time by increasing the time before the formation of density begins.

Fig. 2

Effect on Fog Level

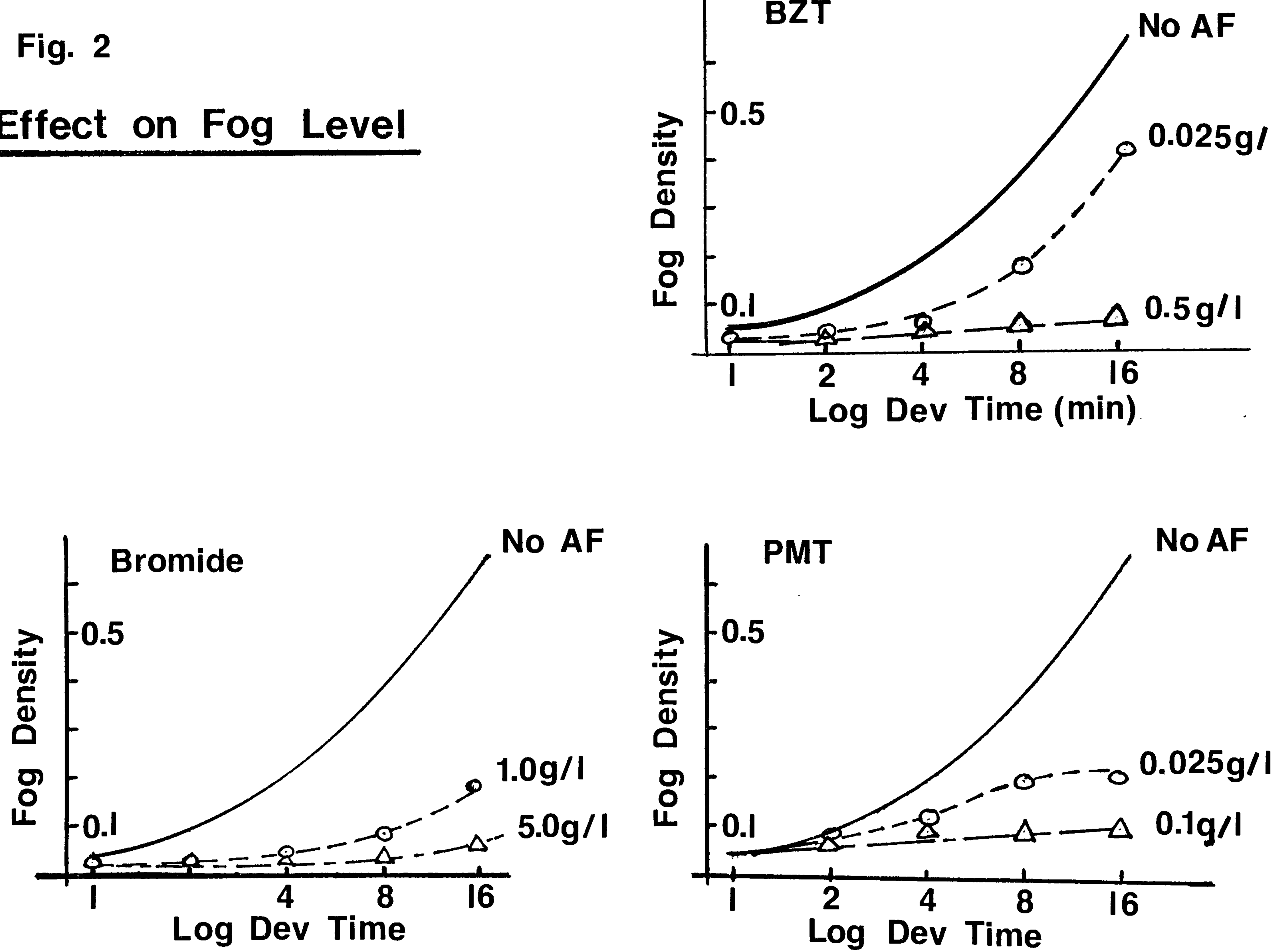


Fig. 3

Effect on Rate

$$\text{Rate} = \frac{\Delta\,\text{Density}}{\Delta\,\text{log time}}$$

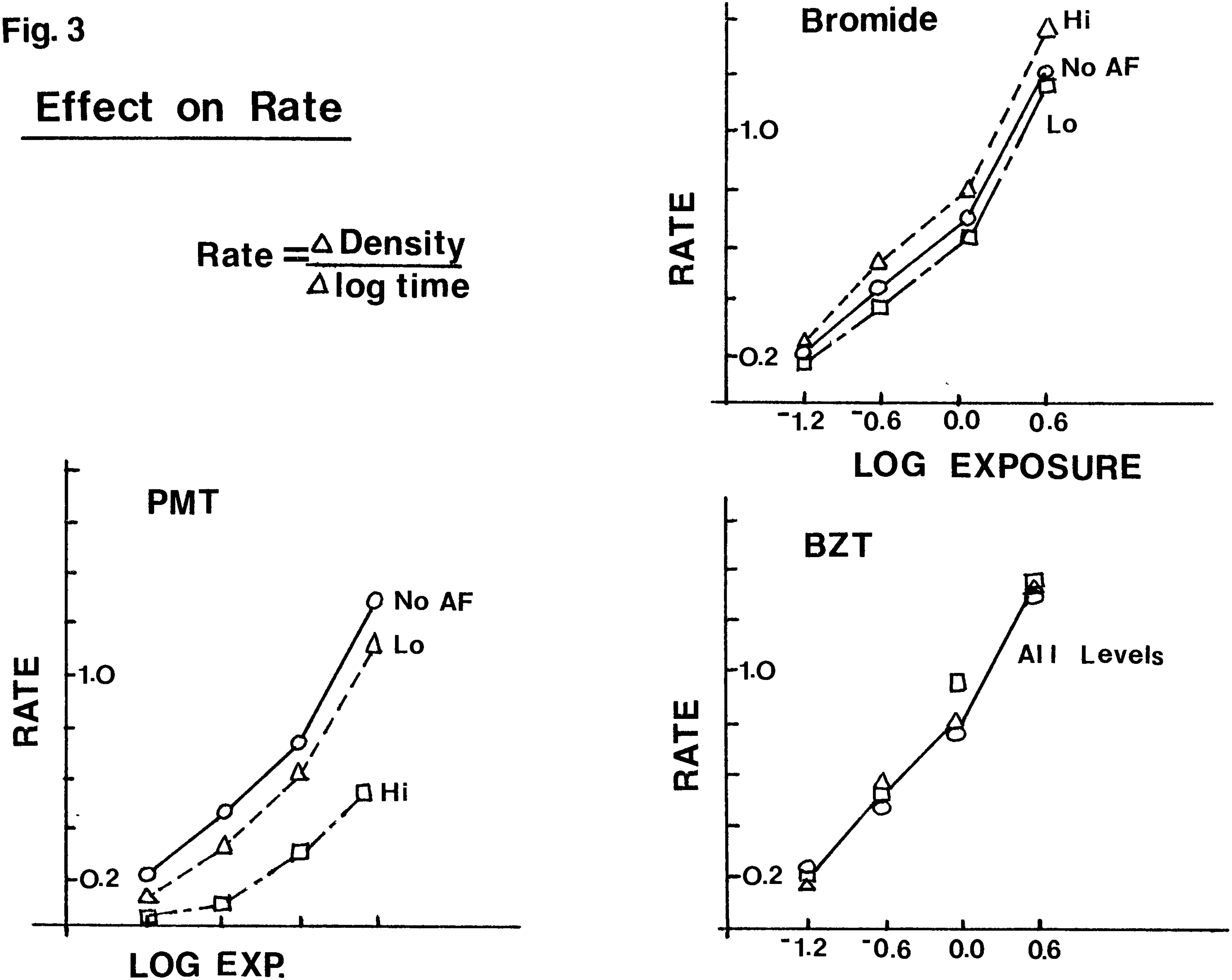
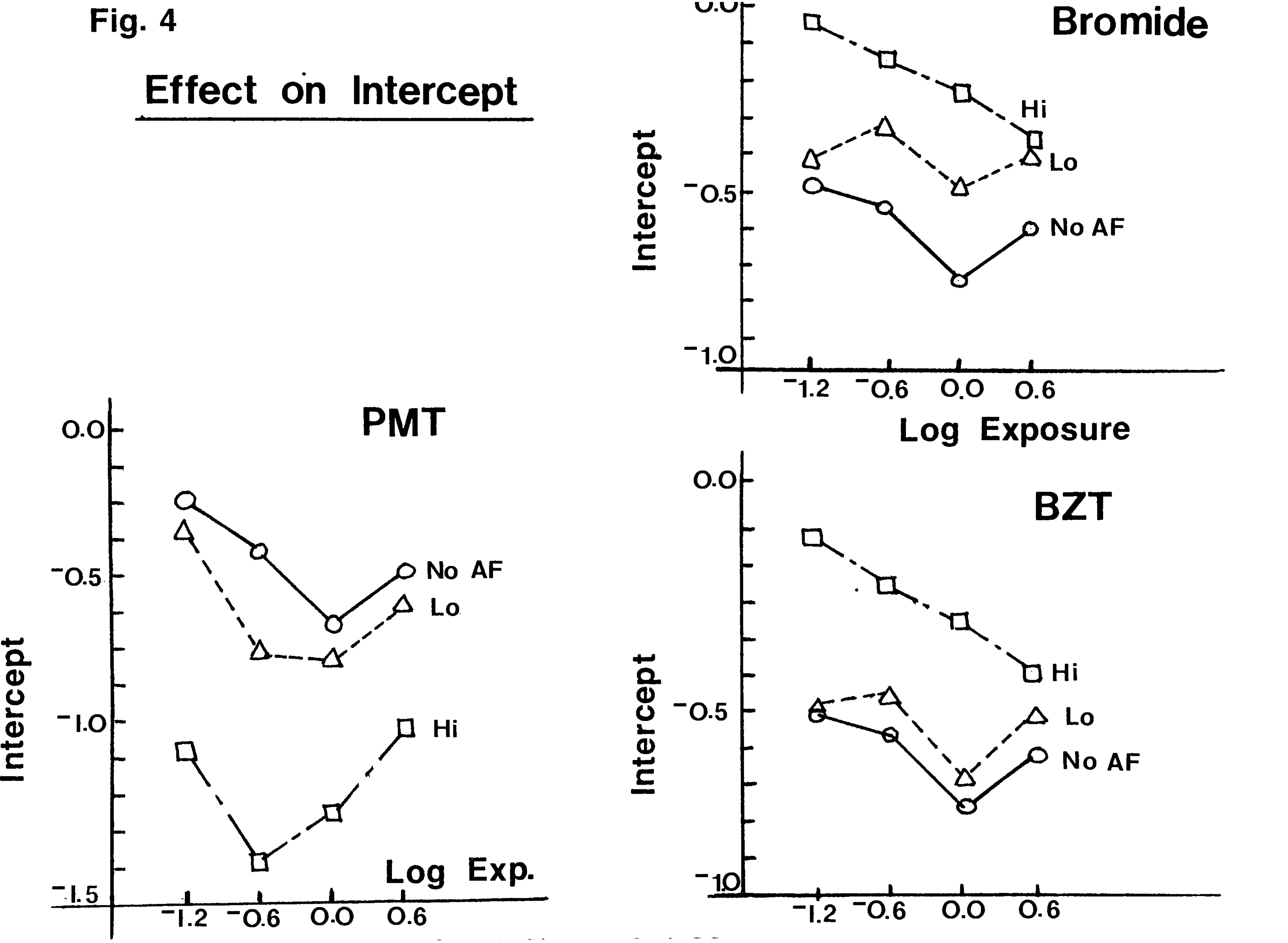


Fig. 4

Effect on Intercept



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