

1975

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Richard Frisicano

Jeffrey Harris

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PHOTOSOLUBILIZATION OF CUPROUS BROMIDE

Richard C. Frisicano

Jeffrey K. Harris

To: ROCHESTER INSTITUTE OF TECHNOLOGY  
Department of Photographic Science  
and Instrumentation

Thesis Advisors: Dr. B. Carroll

Dr. R. Francis

June, 1975

G923916

#### ABSTRACT

A dissolution system called photosolubilization invented in 1964 by R.K. Blake and applied to silver halide was investigated to determine the feasibility of adapting the system from silver to copper. After cuprous bromide was shown to be light sensitive and able to be insolubilized, using a mercaptan ( 2-mercapto-4-phenylthiazole ), many of the parameters affecting this process were determined.

The best photosolubilization was achieved using a 1/100 mole ratio of mercaptan to cuprous bromide. Insolubilization improved with increased mercaptan digestion time while pH appeared to have little effect on this mechanism. PH did change final print-out density. Increased sensitivity was observed when the emulsion was re-exposed while still wet. Fixing or dissolution depends on several factors including emulsion thickness.

## ACKNOWLEDGMENTS

Dr. Carroll and Dr. Francis our advisors without their help this project would not <sup>have</sup> ~~of~~ been possible.

Dr. Schumann for his kind guidance.

Central Intelligence Agency for their financial support.

## INTRODUCTION

Photosolubilization is a photographic process that was discovered and patented by R.K. Blake of DuPont in the early 1960's. This system makes use of a conventional silver halide emulsion containing an insolubilizing agent.

The photosolubilization process is best understood by comparing it to the conventional photographic process. It is similar to conventional photography but in reverse. In conventional photography, latent images are formed in the silver halide crystals upon exposure. The film is then placed in a developer which chemically reduces the crystals containing latent images to silver. When development is terminated the remaining silver halide is dissolved and washed out of the emulsion. A negative silver metal image is thus obtained.

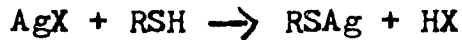
In the photosolubilization process, a photosoluble film is produced by either soaking or digesting a photosolubilizer into an emulsion. Emulsion grains coated with the photosolubilizer are relatively insoluble to silver halide solvents compared to uncoated grains. The silver halide solution rate is effectively decreased. Upon exposure, however, the solution rate returns to normal. This difference in dissolution rate between exposed and unexposed areas is kinetic, not thermodynamic.

Thus an image is obtained by exposing a photosoluble emulsion and then dissolution developing it in a suitable solvent. Exposed portions are dissolved; unexposed portions are not. A positive silver halide image results. This halide image may then be fogged and chemically reduced to obtain a final metal image.

Latent image formation in a photosolubilized emulsion is accomplished by breaking the insolubilizing layer that is absorbed to the silver halide grains. These breaks or holes in the absorbed layer are formed by the oxidation of the photosolubilizer by halogen released in the conventional photolysis of the silver halide. The oxidized photosolubilizer permits solvent to penetrate into the silver halide grain.

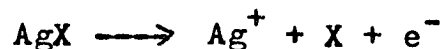
Blake, in a series of patents<sup>1</sup> and an article in Photographic Science and Engineering,<sup>2</sup> published the process in 1964. Cohen, Celeste and Fan<sup>3</sup> investigated numerous organic compounds for their use as photosolubilizers. The compounds were screened by comparing them to a known photosolubilizer as the reference compound. The most effective compounds were further evaluated in photographic coatings. Their study revealed 2-mercapto-4-phenylthiazole to be one of the most promising compounds. This compound was used throughout the project and it will be referred to as mercaptan in the remainder of this text. Haugh, Celeste, Chisholm, Cohen, Hunt, and Sincus<sup>6</sup> as a result of their studies suggest the following surface reaction

for the insolubilizing mercaptide layer.



The negative charge barrier caused by adsorbed bromide ions on the silver halide grain is displaced by the silver mercaptide formation on the grain surface. A positive charge results at the mercaptide surface from hydrogen ion produced during the reaction. These ions are free to participate in intermolecular hydrogen bonding with the adjacent mercaptide molecules thereby affecting stability and favorable orientation of the insolubilizing layer. Haugh et al. also gives evidence that the coating layer must be monomolecular, resembling that of sensitizing dye adsorption. Using the sensitizing dye analogy, the minimum amount of insolubilizing agent for maximum insolubilization was determined using a chlorobromide emulsion. Surface coverage was found to be about 85%; the remaining surface area is hypothesized to be protected by adsorbed halide ions and binder molecules.

The silver mercaptides themselves are not light sensitive. Haugh et al. has shown that silver mercaptides, like mercaptans, produce disulfide upon halogenation. Therefore, the reaction sequence as proposed is as follows:



These equations represent the classical Gurney-Mott

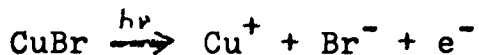
Theory with the silver mercaptide acting as the halogen acceptor. One additional reaction occurs although two alternatives are proposed:



Haugh et al. has selected the first reaction as the most probable but gives no experimental evidence permitting a justified selection of either alternative. Increased print-out is observed which agrees with the first alternative. This also agrees with the way free radical reactions generally behave.

The photosolubilization quantum efficiency was determined and it was found that only 2% of the insolubilizing layer need be destroyed by exposure for typical grains to solubilize.

Blake in U.S. Patent 3,377,169 proposed a system based on copper, lead, thallium halides, and psedohalides. Using this as our basis, we proposed the following photosoluble system for cuprous bromide;



Copper halides, those of chloride and bromide in particular, are known to darken upon exposure to light



yet very little work has been reported in the areas of copper based imaging systems. We felt that it would be interesting to supplement the present knowledge about copper halides by concentrating on the study of one particular system. We chose the photosoluble system since conventional reduction systems appeared to be disappointing. Chemical developers of sufficient redox potential for copper would rapidly be oxidized by air. Physical developers, while potentially representing a much more promising system than photosolubilization, require fixing of the final image either before or after development. ( Photosolubilization results in a print-out halide image, therefore, fixation of the final image is not required. ) Attempts at fixation of copper images has resulted in the loss of the copper image itself.

## EXPERIMENTAL

Similar to the silver halides, the sensitivity of cuprous bromide is limited primarily to the ultraviolet region of the spectrum. Due to this requirement, we chose a mercury arc lamp for exposure under experimental conditions. A commercial ultraviolet printer containing a 400 watt lamp was used. Preliminary experiments were conducted using filter paper that was soaked in a dispersion of commercial cuprous bromide and water. The filter paper while still wet was then exposed for one minute. A dark green color resulted in the exposed areas. The dark coloration, which is due to photolytic copper, is evidence that the exposing radiation is being absorbed by the cuprous bromide.

A finer, more reproducible grain size was required for further experimentation. The commercial cuprous bromide used in the preliminary tests would not be satisfactory because photosolubilization is dependent on grain size. The volume to surface increases with increasing size of the grains, therefore, the amount of halogen coming from inside the grain to attack the mercaptan on the surface will be greater for the larger grain. This effect is superimposed on the effect of increased absorption

of light by the larger grain. Thus, the size of the grain is critical when evaluating photosolubilization. Primitive emulsions with recrystallized commercial cuprous bromide were used to obtain a more constant grain size. The emulsions were coated on film base using a hand coater and a vacuum chill platen.

After considerable experimental work, the most reproducible coating for our purposes could be obtained following the procedure outlined below:

1. prepare an almost saturated solution of sodium bromide in 25 ml of distilled water at 100°C. ( 50 grams NaBr )
2. dissolve 12 grams of 7% phthalated active gelatin in 400 ml distilled water to produce a 3% solution of the gelatin. hold at a temperature of 55°C. by using a water bath.
3. saturate the sodium bromide with powdered cuprous bromide ( 3.5 grams )  
The presence of an adequate concentration of excess bromide renders the cuprous bromide halide much more soluble than it is in pure water because of the formation of complex ions.
4. add the complexed cuprous bromide - sodium bromide solution to the gelatin solution using a single jet method of addition. addition time - 15 seconds stir constantly
5. ripen this emulsion for 30 minutes by

holding it at 55° C. in a water bath.

6. when ripening is complete, cool the emulsion in an ice bath and add 1 N  $H_2SO_4$  dropwise while stirring until the emulsion coagulates. place in a refrigerator.
7. decant the emulsion twice or until the liquid is clear (use cold water)
8. redisperse the emulsion to get the cuprous bromide to gelatin ratio desired for that experiment.

Several ratios of cuprous bromide to gelatin and several levels of pH were tested following the above emulsion preparation technique.

Since photosolubilization efficiency was the response variable, it was necessary to include mercaptan level as a variable in each experiment. Therefore, each factor was tested against various mercaptan levels using a randomized, twice replicated, block design. A 10% mole to mole ratio of mercaptan to cuprous bromide was not exceeded. This represented a reasonable amount necessary to coat only the surface of the crystal.

An emulsion redispersed to contain 1 gram cuprous bromide to 2 grams gelatin was almost clear upon drying and it was impossible to distinguish cuprous halide from film base during processing.

An emulsion containing more cuprous bromide and/or larger grain size was needed. This was accomplished

by increasing the temperature of the initial saturated solution of sodium bromide from 55° C. to 100° C.. At this higher temperature the solution will complex more of the cuprous bromide so more can be put into solution. After precipitation the solution was ripened for 30 minutes at 55° C. to obtain a larger grain size. The emulsion was redispersed with 6% active gelatin to a ratio of 1 gram cuprous bromide to 1 gram gelatin. A one factor randomized block experiment was conducted for mercaptan level.

A sample of each emulsion containing varying amounts of mercaptan were uniformly exposed for two minutes. Exposed and unexposed samples were fixed for about one minute in 4% sodium thiosulfate. All samples cleared except the unexposed sample containing  $1 \times 10^{-4}$  moles mercaptan. This sample contained an approximate ratio of 1 mole mercaptan to 100 moles of cuprous bromide. A just visually noticeable density was obtained. This emulsion was also examined under a 1000x microscope to estimate grain size and shape. It was found that the grains were generally poorly formed. To correct for this precipitation time was increased.

An emulsion was made using 3% phthalated active gelatin instead of 2% gelatin. Redispersion produced a ratio of about 2 grams cuprous bromide to 1 gram of gelatin. The emulsion was split into four aliquots

and the mercaptan ( 2-mercapto-4-phenylthiazole ) was added to produce an approximate mercaptan-cuprous bromide mole ratio of 1/50, 1/100, 1/150, 1/250 respectively. The emulsions were then digested for 20 minutes and hand coated. Samples of exposed and unexposed coatings were fixed in 4% sodium thiosulfate. Again the best apparent photosolubilization occurred with the coating containing the ratio of 1 mole of mercaptan to approximately 100 moles of cuprous bromide.

A randomized block experiment was used to determine the effect of coating pH on print-out density. A redispersed emulsion containing a 2 to 1 gram ratio of cuprous bromide to gelatin and a 1 to 100 mole ratio of mercaptan to cuprous bromide was used. PH was varied over a range of 4.5 to 7.0. The emulsions were fixed in 4% sodium thiosulfate and were re-exposed while still wet.

A sample of this emulsion was examined under a microscope. Grains were predominately octahedral in shape and approximately 2 to 3 microns in size. The emulsion appeared to be well dispersed.

The effect of pH on insolubilizing efficiency was investigated. Turbidity after a thirty second dissolution as a measure of insolubilization was the response variable for a randomized block design. Turbidity ( Percent Transmittance ) was measured with a Baush and Lomb Spectronic 20. An emulsion containing a 2 to 1 gram

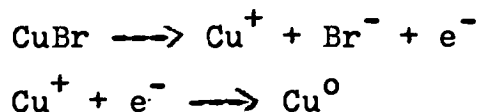
ratio of cuprous bromide to gelatin was diluted to make two liters. This allowed test tube samples to be measured using the Spectronic 20. Transmittance was measured at 600 nm; cuprous bromide and the mercaptan have minimal absorption at this wavelength.

A similar technique was used to test the effect of digestion time at 55°C. on insolubilizing efficiency. This temperature was chosen due to emulsion instability above 60°C.. Turbidity again was the response variable for a 6<sup>2</sup> factorial design.

## DISCUSSION

The best photosolubilization occurred with a coating containing the ratio of one mole of 2-mercapto-4-phenylthiazole to approximately one hundred moles of cuprous bromide. Insolubilization of cuprous bromide grains improved with increased mercaptan digestion time with an optimum occurring at 55° C. for twenty minutes. It appears that digestion probably promotes an ordered arrangement of mercaptan on the surface of each grain.

The insolubilization was found to be pH independent, over the range of pH 4.7 to pH 6.6, however, pH did affect print-out density. Density increased as pH decreased for a pH range of pH 5.0 to pH 7.0.



Two alternatives exist to account for the increased density observed. The higher concentrations of hydrogen ion apparently act as a halogen acceptor. However, this does not explain the optimum occurring at pH 5.0. The more probable mechanism is the result of density being evaluated after photosolubilization. PH may be affecting photosolubilization, not the print-out mechanism. The optimum pH occurs near the gelatin isoelectric point.



This suggests that the gelatin, at its isoelectric point, has less tendency to compete with the protective mercaptide layer for adsorption to the grain surface. Better grain protection is obtained and less of the halide image is dissolved, more is converted to metal upon re-exposure.

A difference in sensitivity was also found between the wet and dry states. Print-out density was enhanced by the presence of water.

Fixing rate was found to be dependent on emulsion thickness as well as on the degree of insolubilization of the grain. Variation in fixing times occurred from coating to coating dependent on the thickness of the coating. Sodium thiosulfate and sodium bromide were both found to be adequate fixing agents. Thiosulfate concentrations while not directly investigated appear to affect photosolubilization in several ways. The penetration of thiosulfate into the emulsion is inhibited by a charge barrier caused by excess halide whose negative charge repels the anion approach and the gelatin adsorbed on each grain. The insolubilizer further inhibits solvent penetration. High thiosulfate concentrations attack unexposed as well as exposed grains and the print-out density is lower. Also, cuprous bromide complexes probably diffuse out of the emulsion slower at high thiosulfate concentration.

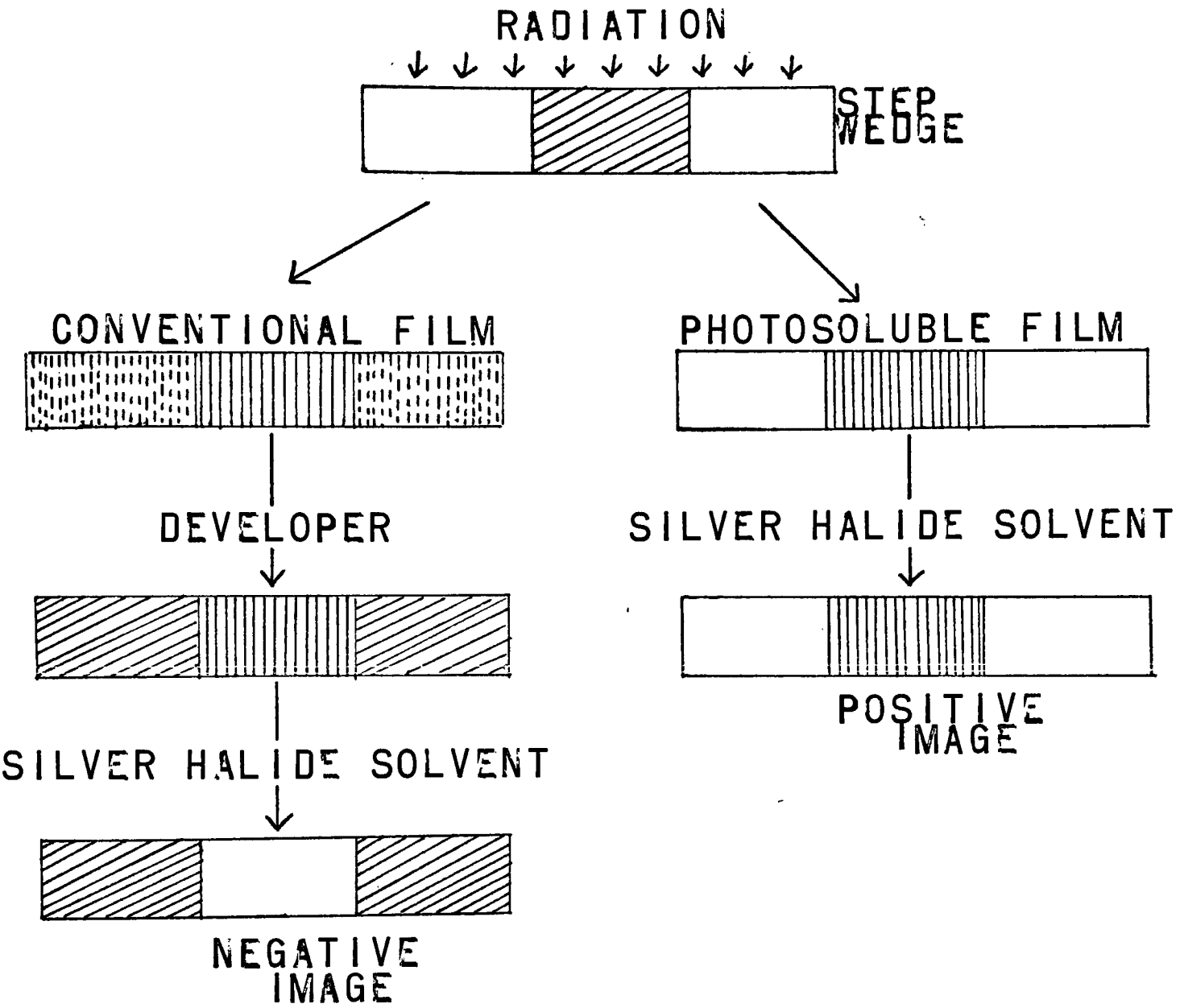
The largest variable in the experimentation proved to be the preparation of the emulsion. As previously mentioned, grain size plays an important part in photosolubilization. To obtain better control of grain size, the concentration of cuprous ion should be monitored throughout the precipitation. Potentiometric techniques are not possible because a cuprous ion electrode is not made.

Stability of the emulsions are very poor. The cuprous ion is readily oxidized to cupric ion. Shelf life of coated emulsions are very short requiring them to be used as soon as possible after coating and drying.

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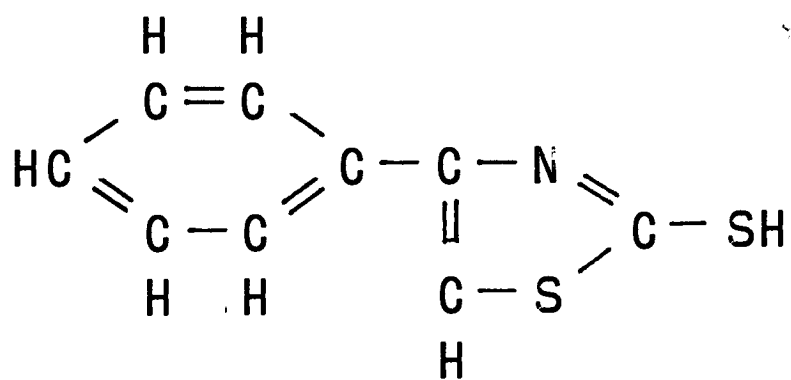
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SILVER

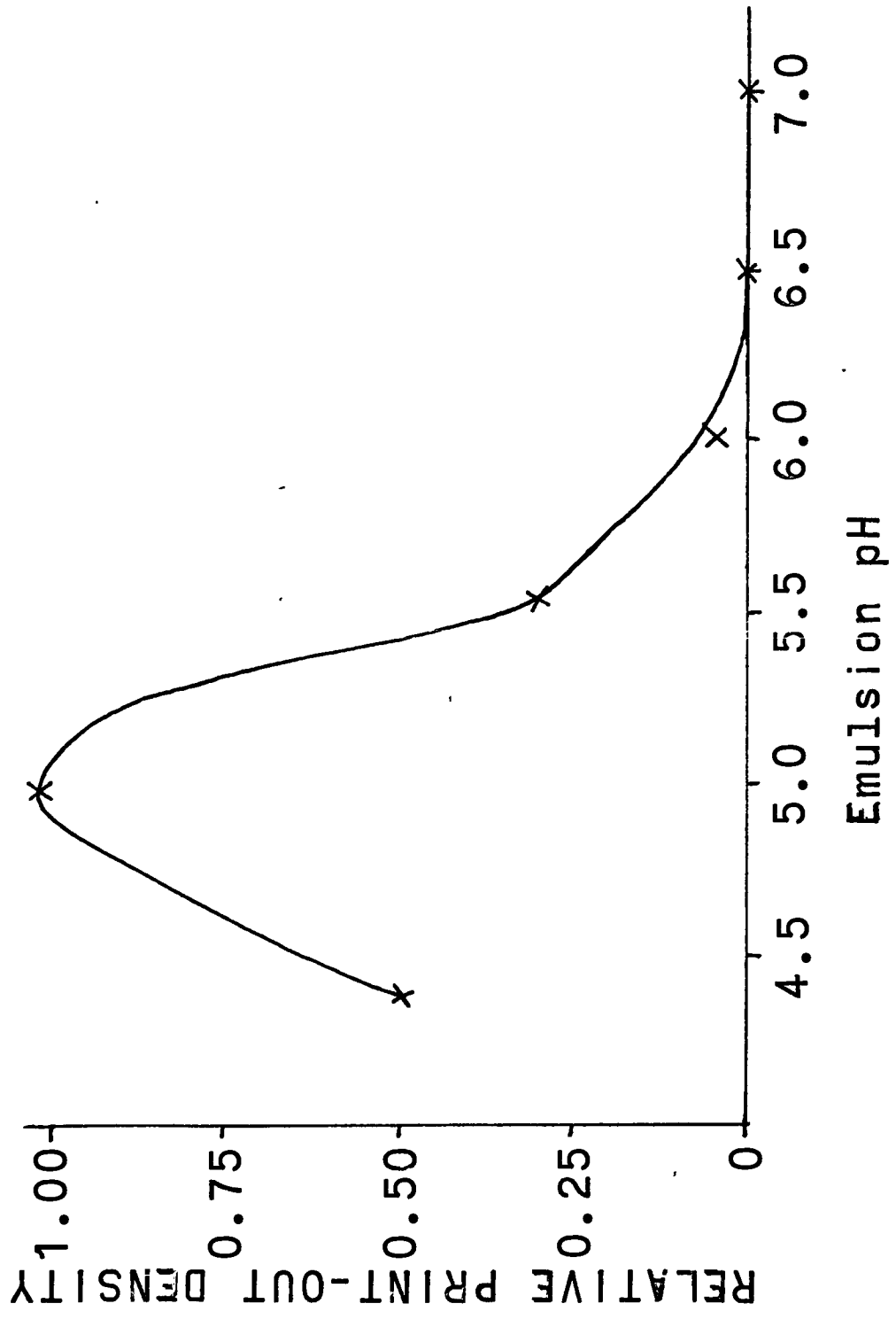
  
SILVER HALIDE

  
SILVER HALIDE WITH LATENT IMAGES



2-mercapto-4-phenylthiazole

RELATIVE PRINT-OUT DENSITY VS. EMULSION pH



EFFECT OF DIGESTION TIME  
INSOLUBLIZATION VS. AMOUNT OF MERCAPTAN

