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The effect of emulsion stabilizers on the rate of solution of silver halide grains

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THE EFFECT OF EMULSION STABILIZERS ON THE RATE OF SOLUTION
OF SILVER HALIDE GRAINS

by

CHRISTOPHER L. DUMONT

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
College of Graphic Arts and Photography
of the Rochester Institute of Technology

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ABSTRACT

The effects of the emulsion stabilizers, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and 1-phenyl-2-tetrazoline-5-thione on the rate of solution-physical development of a monodisperse AgBr emulsion containing Carey-Lea silver sol were measured at a series of concentrations. A study of the effects of the silver halide solvent, sulfite has been studied along with a low-solvent surface developer. It was found that the tetraazaindene definitely had an effect on the rate of solution-physical development, while the 1-phenyl-2-tetrazoline-5-thione did not have a significant effect.

ACKNOWLEDGEMENTS

I would like to thank the following people and organizations for their part in my project. Mark Hinz for showing me the hand emulsion coating techniques. The Polaroid Corporation for donating the silver nitrate used in my emulsions. The Eastman Kodak Corporation for providing the emulsion stabilizers that were tested. Above all I would like to sincerely thank Dr. Burt H. Carroll for his unselfish contribution of his time and guidance, without which my project couldn't have been completed.

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INTRODUCTION

The basis of this experiment comes from the different methods in which development of the silver halide grains occurs.

The silver halide grain may be reduced by a developer which at the start does not contain any silver salt. The silver for development comes from the silver halide grain itself. This is called chemical development.

In another form of development, called physical development, the silver is present in the developer in the form of a soluble silver salt. This soluble silver salt then plates out around the latent-image centers during development.

When the silver halide dissolves in the developer, the silver ions can be reduced by physical development at the latent-image centers or on the growing silver surfaces that have already formed around the latent-image centers. This process, which involves solution of the silver halide and then physical development, is called solution-physical development. The rate of solution-physical development is mainly determined by the rate in which the silver halide is dissolved¹.

James and Vanselow² developed a method for determining

the rate of solution of silver halide in a monodisperse emulsion. Carey-Lea silver sol was added to the emulsion formula and then it was coated. The silver particles provided nuclei for the silver to plate out on during development in a low solvent action metol-d-araboascorbic acid surface developer. Fixing and washing were done normally.

If the development conditions were chosen so the rate of the reduction of silver ions at the Carey-Lea silver nuclei was rapid as compared to the rate of the plating out of the silver, then the rate of accumulation of the silver was a function of the rate at which the silver ions were present at the nuclei. The tests were done on unexposed emulsions, the Carey-Lea silver acting as latent-image sites. Density vs. time of development was used as the analysis.

In a later experiment James and Vanselow³ found that the rate of solution-physical development was determined by the rate of solution of silver halide grains in the developer.

If a silver halide solvent is present, the rate of solution of the silver halide grains increased with the increase in solubility of the silver halide respectively.

The data in the emulsion containing Carey-Lea silver sol do not give the actual rate of solution⁴, but it does give the relative effect, since the change in rate of deposition of the reduced silver halide on the colloidal silver nuclei is similar to that which occurs with an exposed emulsion sample with solution-physical development. Provided

that the rate of deposition of silver remains constant throughout the process of development and the Carey-Lea silver does not undergo a change.

An active developer is used so that the solvent action of the silver halide crystals is kept at a minimum so it won't be a contributing factor in the rate of solution of the silver halide. A hydroquinone-phenidone developer will be used rather than the metol-ascorbic acid developer used by James and Vanselow⁵ for a couple of reasons. One is that the hydroquinone-phenidone developer is believed to be of lower solvent action⁶ and that the oxidation by-products of this developer are clean and will not interfere with the analysis. Ascorbic acid will be used as the preservative since it has low solvent action. An active developer of high solvent action will also be used during these experiments.

Although emulsion stabilizers are used today in most emulsion formulas, there has not been an isolated study of the effects of these stabilizers on the rate of solution of silver halides using this technique.

HYPOTHESIS

A hypothesis is formulated that the emulsion stabilizers will have an effect on the rate of solution of silver halide grains.

Since both emulsion stabilizers, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI)⁷ and 1-phenyl-2-tetrazoline-5-thione (PMT)⁸, are adsorbed by the silver halide, it is hypothesized that they will retard solution of the silver halide.

EXPERIMENTAL

There are four major areas that have to be completed to test the hypothesis:

- 1) Make the Carey-Lea silver sol
- 2) Precipitate a AgBr emulsion
- 3) Construct a low-solvent developer
- 4) Testing the hypothesis

Attempts at making a pure colloidal silver sol by reduction with hydrazine in the presence of gelatin failed and a Carey-Lea silver sol, dextrin reduction, was used instead. The dextrin acts as the reducing agent and also as the protective colloid. The sol was coagulated twice using methanol. The coagulum was then redispersed in a 4% inert gelatin solution. The formula for the Carey-Lea silver sol can be found in appendix A.

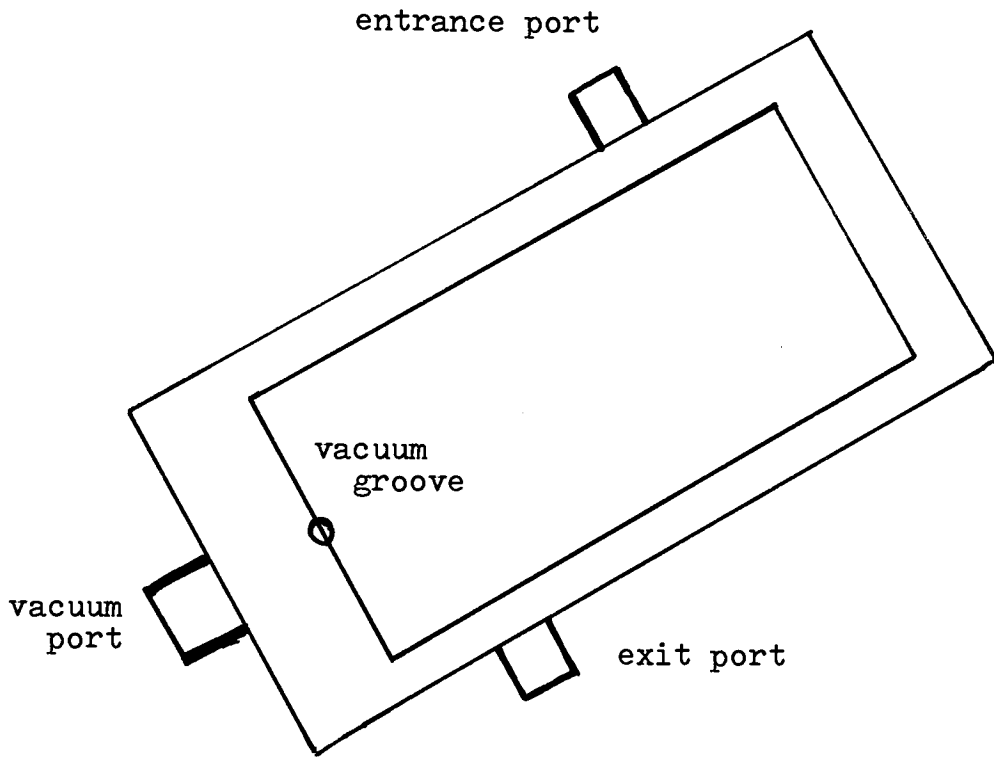
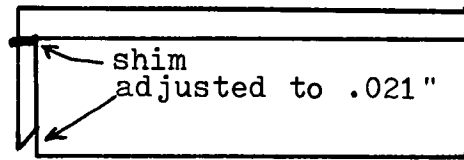
A monodisperse emulsion of .1 mole silver halide/liter was made using methods similar to Berrimans technique⁹, except that phthaloyl gelatin was used to aid coagulation. The double jet emulsion was precipitated for 4 minutes and 40 seconds at 45°C. The halide excess was kept constant at 5×10^{-4} NKBr at the start and finish. The precipitate was coagulated using 14 ml of 7NH₂SO₄. The coagulum was left overnight in a

refrigerator to settle. The liquid was then drained from the coagulum and rinsed with distilled water. The coagulum was redispersed in a 6% inert gelatin solution that contained 27 ml of .1N NaOH and 5×10^{-4} N KBr. The final volume was brought to 800 ml and NaOH was added to bring the final pH to 6.30 at 40°C. No ripening, chemical sensitization or stabilization was done on the emulsion unless stated. The emulsion was stored in a refrigerator when not in use. The formula for this emulsion can be found in appendix B.

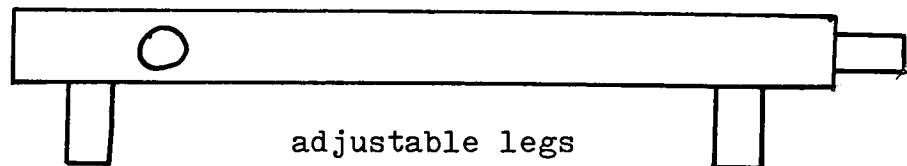
The coating of the emulsion samples were done by hand using a platen and coating knife depicted in figure 1. The platen was leveled for each sample coated. An aspiration system provided the vacuum by which the film base was held to the platen. A 7% saponin solution was added to the samples to aid in coating evenly. The platen was first heated by running hot water through it and afterwards to allow the emulsion to coat evenly. It was very important that each sample was the same thickness throughout the samples or erroneous data would result. The platen was cooled by running cold water through the platen to set the emulsion. The set emulsions were then tacked down to a flat mounting board and placed in a light tight drawer to dry. The samples contained 10 ml of emulsion plus any of the addenda being tested.

In formulating the low-solvent developer, d-(-)-araboscorbic acid was used as the preservative, hydroquinone-

coating knife



COATING PLATEN



adjustable legs

FIGURE 1

Diagram of Coating Platen and Coating Knife

phenidone was the developing agents and borax was used as the alkali. The pH was adjusted using NaOH to a pH of 9.0 at 20°C. It was found that a pH above 9 gave too high a fog level. This developer will be referred to as HP9 in the rest of this paper. The formula for HP9 can be found in appendix C.

Preceding the testing of the emulsion stabilizers were preliminary experiments to make sure the procedure in making the Carey-Lea silver sol, the emulsion, the developer formula, and the coating technique did not have an effect on the end results.

Trials of the colloidal silver alone in inert gelatin tested in HP9 and D76 both showed a B&F of 0.03. A sample of the colloidal silver with 0.5 mg of dextrin was tested also gave a B&F of 0.03. The unexposed emulsion was tested in the HP9 formula which gave a B&F of 0.05 after 5 minutes development, and a 0.08 level after a 10 minute development. An EG&G sensitometer exposure of 10^{-3} seconds without compensation generated the density vs. relative log exposure curves shown in figure 2, for 5 and 10 minute development times in HP9. A test of the Carey-Lea silver fixed for 5 minutes without development gave a B&F of 0.03.

During these tests it was found that a sufficient stop bath was extremely important to insure a complete halt of development, or solution-physical development would occur in the fixing bath. The stop bath time that was sufficient to stop development was found to be 2 minutes. The samples were

then fixed for 5 minutes, washed for 5 minutes and air dried. The formulas for the stop bath and fixer can be found in appendix C.

To test for consistency of the coatings a Dmax of each coating samples was taken with a resulting standard deviation of .04. Controls of the emulsion without the colloidal silver present was done with each processing. To make sure each sample was consistent, the Carey-Lea silver and the 7% saponin was added, in the correct proportions to 200 ml of the emulsion and thoroughly mixed to provide consistent testing. The calculation for the amount of Carey-Lea silver added to the samples was .066mg of Ag/10 ml sample of emulsion. This is the same level of colloidal silver / halide silver used by James and Vanselow in coating A of their experiment¹⁰.

Samples containing the colloidal silver in the emulsion were processed for $2\frac{1}{2}$ and 5 minutes in HP9, DK50, and D76, each with a control sample that did not contain Carey-Lea silver. These developers all had a different level of silver halide solvent.

The stabilizers were tested in D76 (which contained the highest level of sulfite, 100g/l) for $2\frac{1}{2}$ and 5 minutes development times. The levels of TAI tested were 0.25g and 1.00g TAI/ mole silver halide. The levels of PMT tested were 25.0 mg, 5.0mg, 1.0mg, 0.25mg and .0063mg PMT/mole silver halide. A final control test was done on each of the above levels of stabilizers without the colloidal silver present in the

emulsion samples. These tests proved negative on any effect without the colloidal silver on the unexposed samples.

Three replicates and finding the mean was used as the plotted data points. A standard deviation was calculated and used as the measurement of error. All of the points plotted fell within the standard deviations calculated.

Beckman research pH meters were used for pH measurements, a Mettler H10 analytical balance was used for measuring chemical weights, and density values were measured on a McBeth TD 504 densitometer using the blue filter.

DATA

The data obtained in this experiment consists of graphs of density vs. relative log exposure (fig. 2), density vs. time of development with various concentrations of PMT, developed in HP9 with 1.0 g/l of KBr (fig. 3). density vs. time of development with various concentrations of PMT, developed in D76 (fig. 4), density vs. time of development with various concentrations of TAI, developed in HP9 and D76 (fig. 5), and density vs. Carey-Lea silver sample contained in an emulsion sample, and a control sample in D76, DK50 and HP9 using both the visual and the blue filter reading (fig. 6).

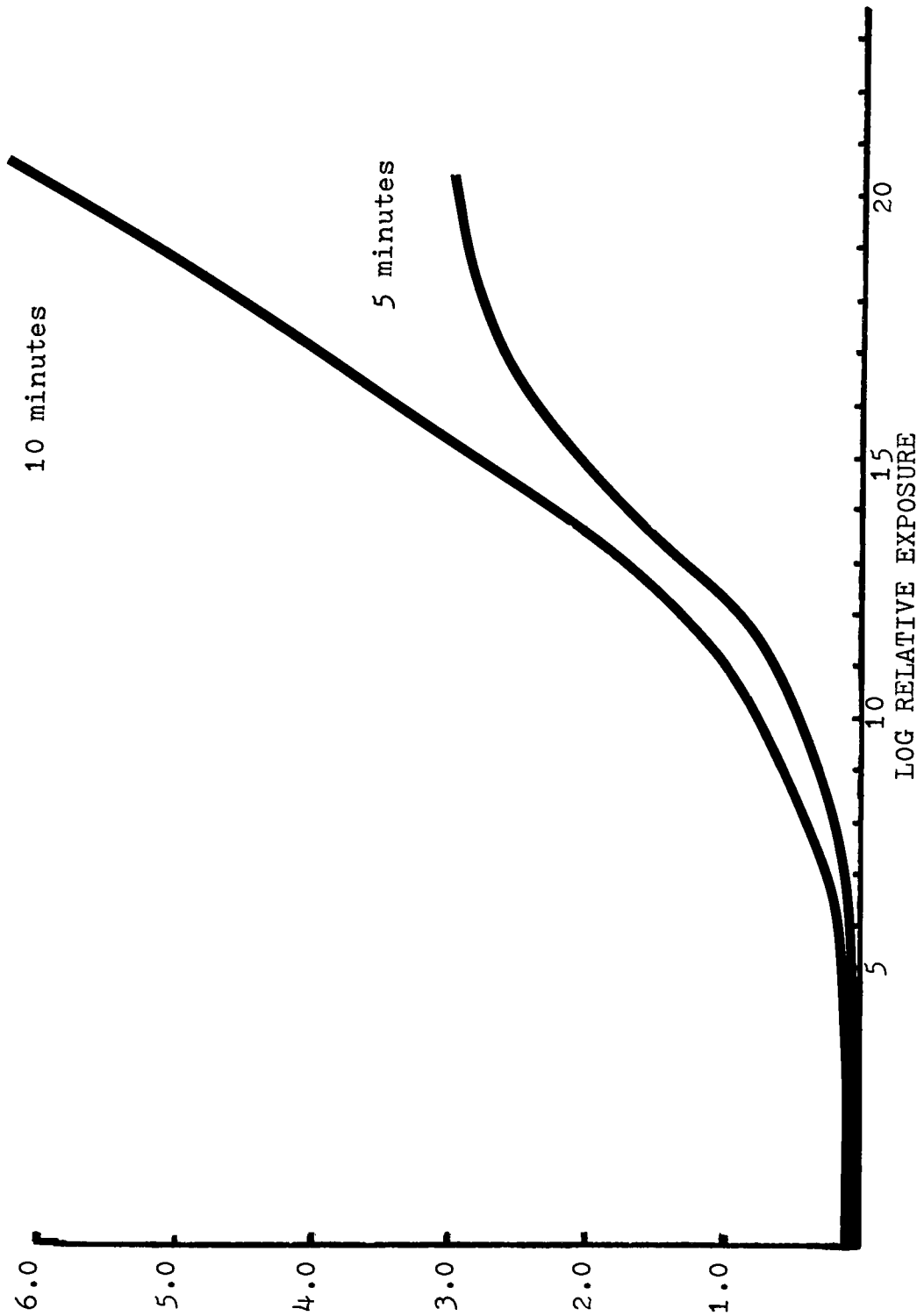


FIGURE 2

Density vs. Relative Log Exposure in HP9

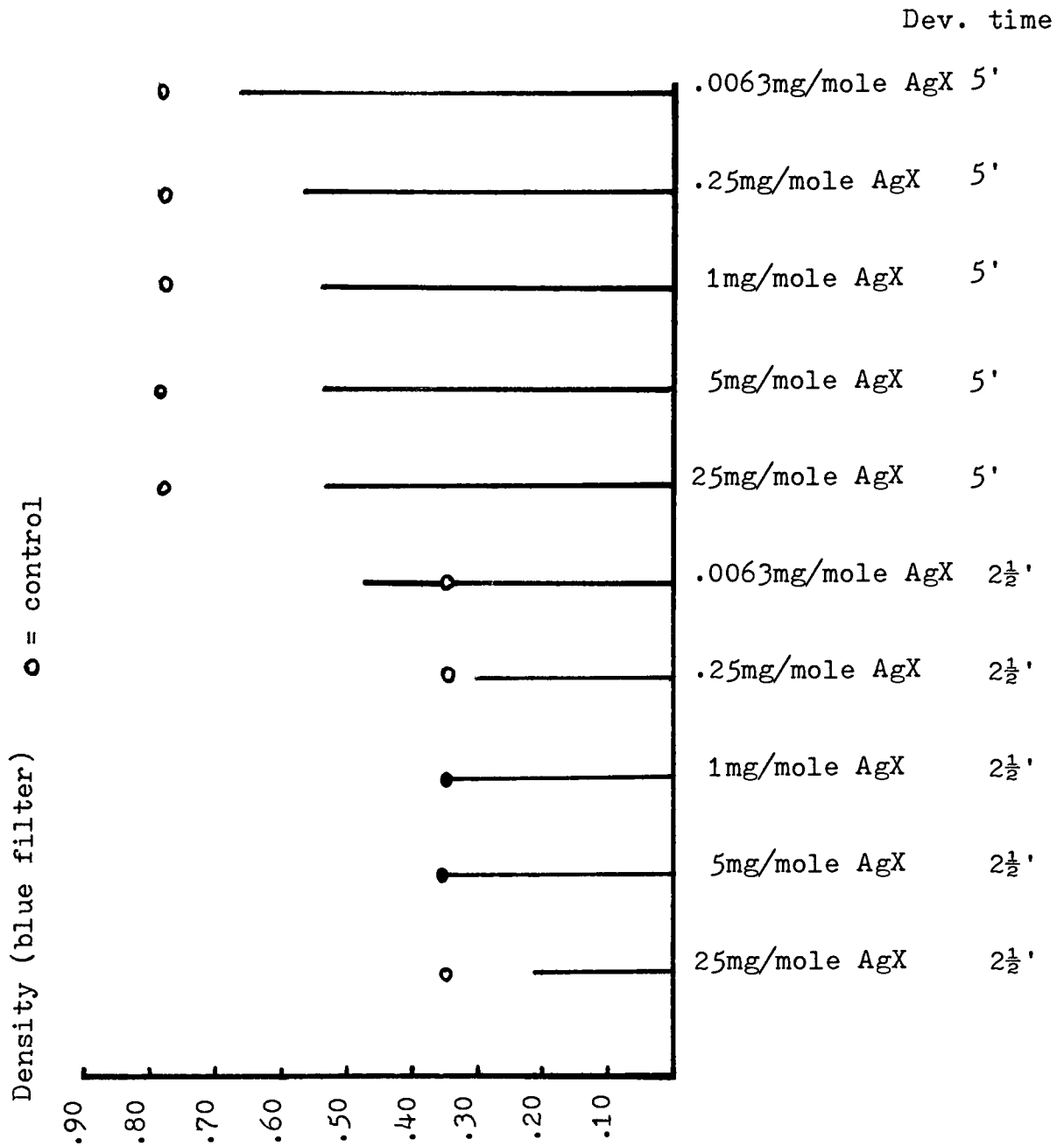


FIGURE 3

DENSITY vs. TIME OF DEVELOPMENT WITH VARIOUS CONCENTRATIONS OF PMT, DEVELOPED IN HP9 WITH 1.0g/l OF KBr

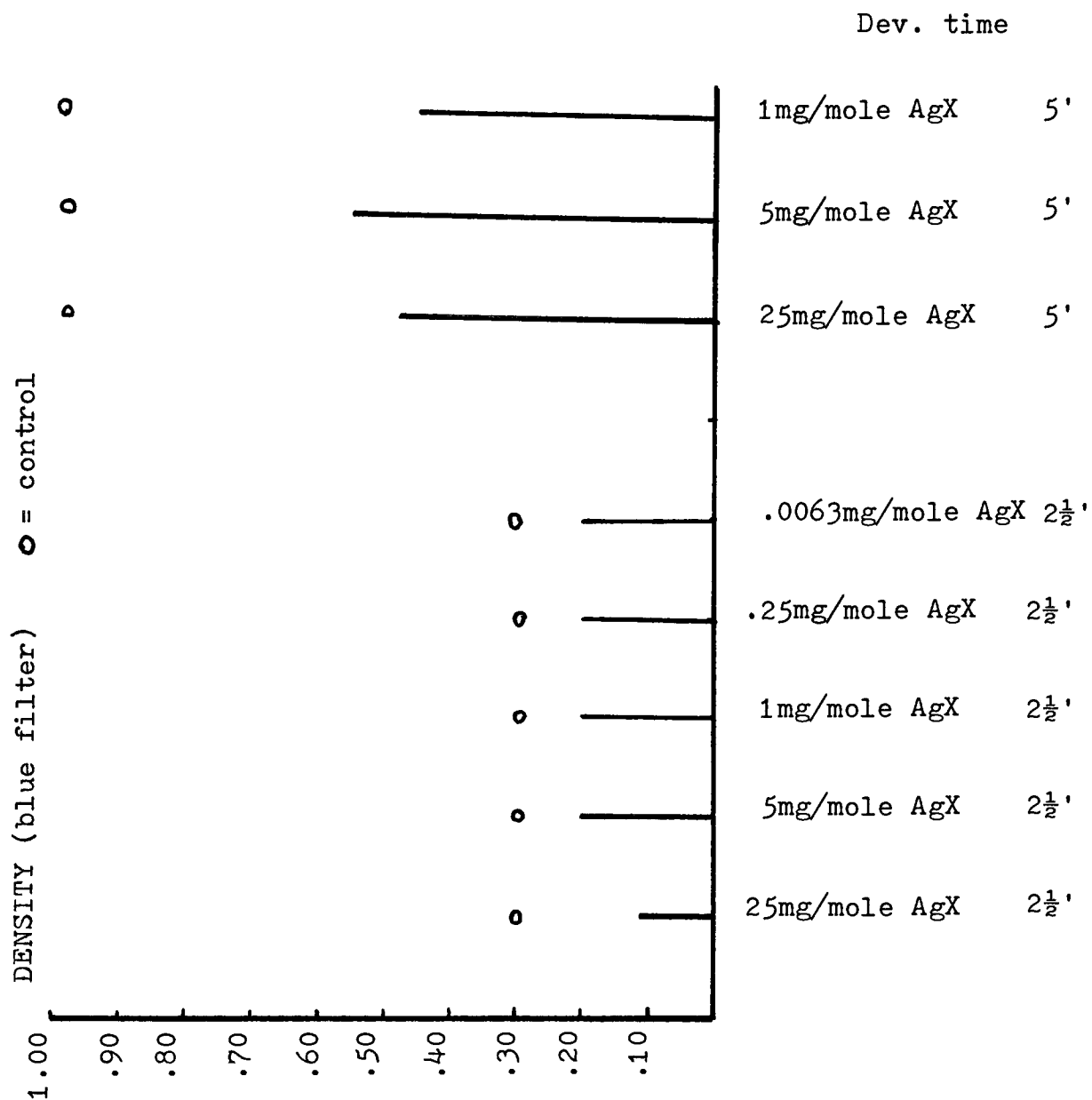


FIGURE 4

DENSITY vs. TIME OF DEVELOPMENT WITH VARIOUS CONCENTRATIONS OF PMT, DEVELOPED IN D76

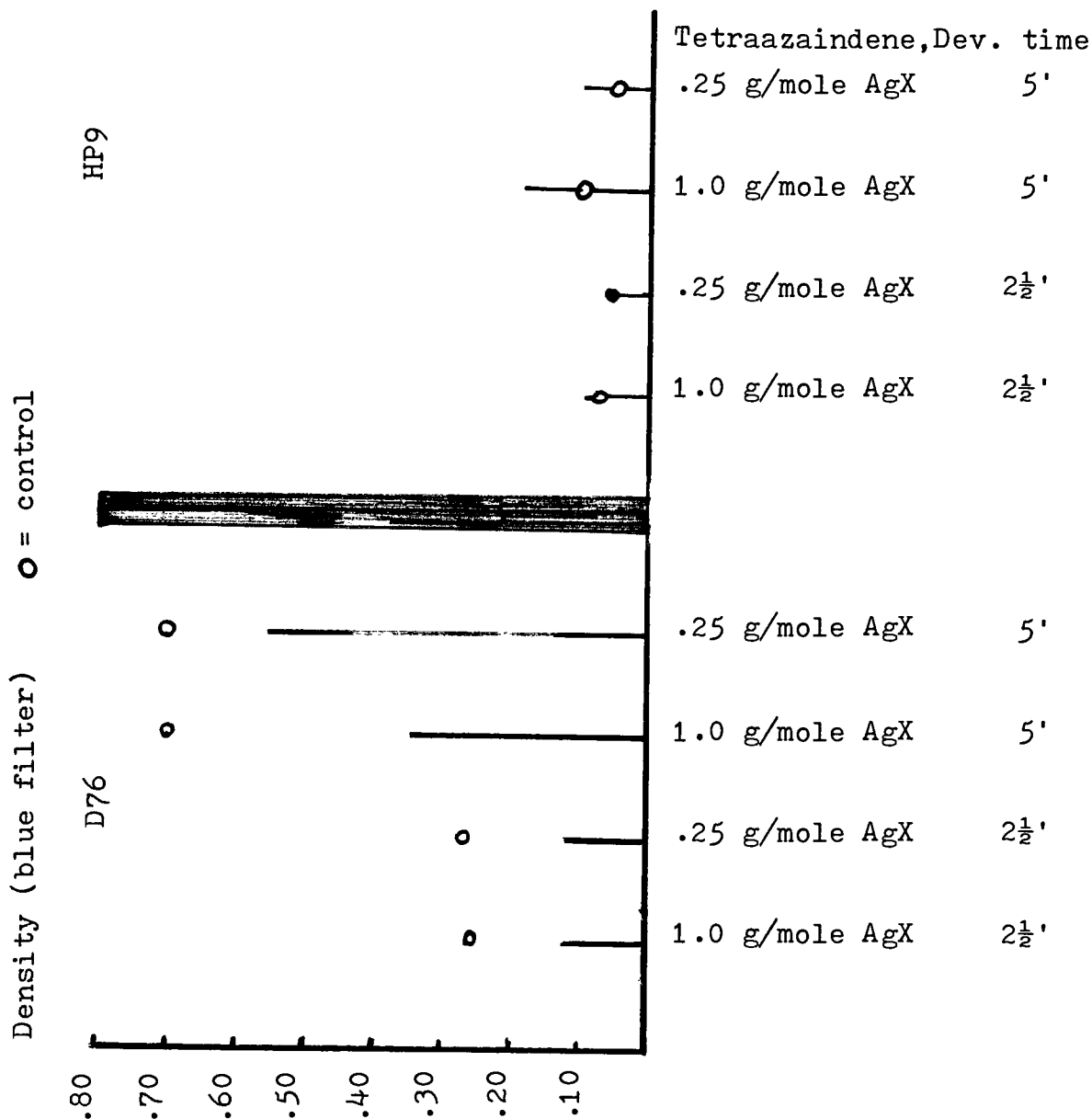


FIGURE 5

DENSITY vs. TIME OF DEVELOPMENT WITH VARIOUS CONCENTRATIONS OF TAI, DEVELOPED IN HP9 (top), and D76 (bottom)

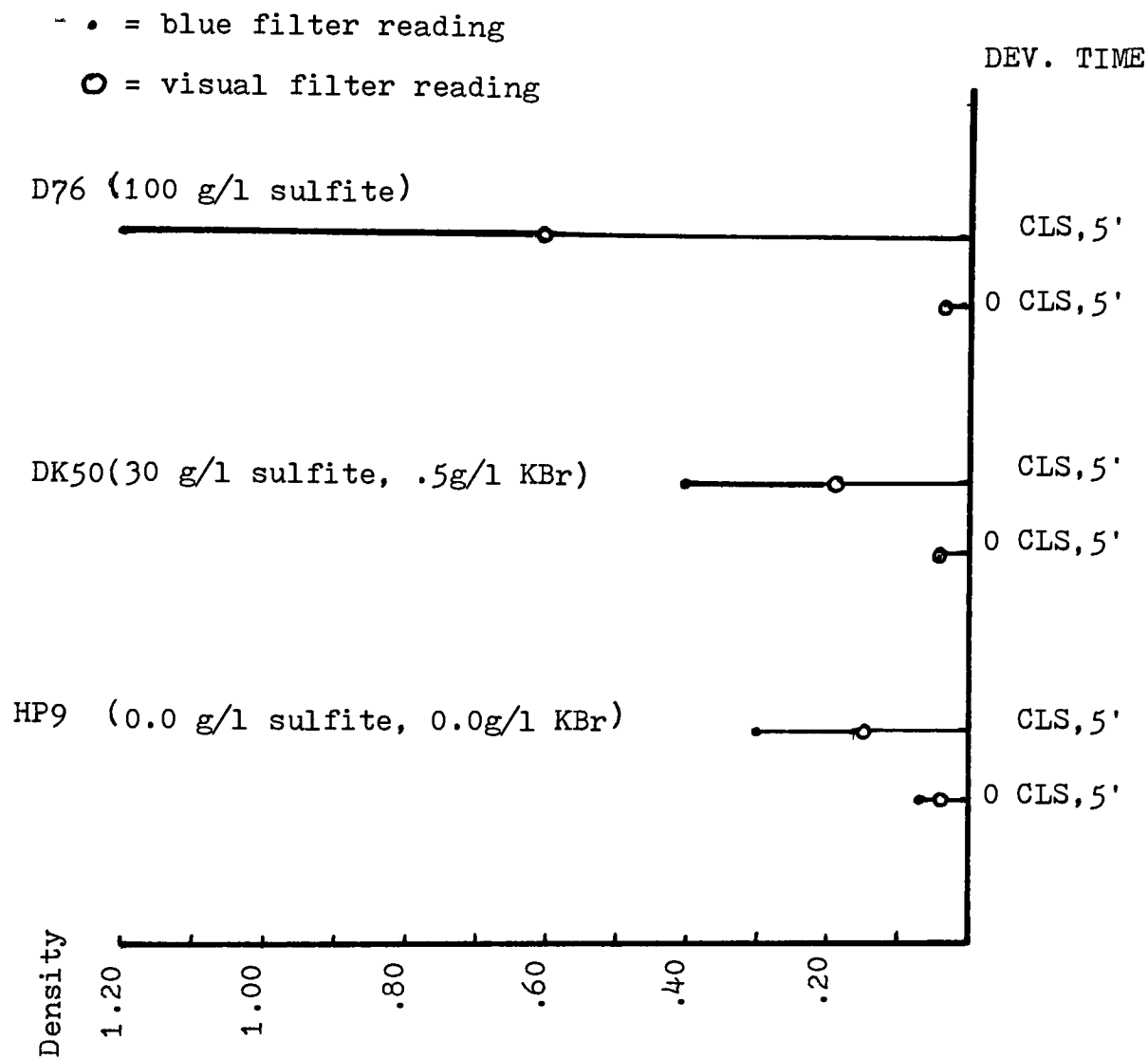


FIGURE 6

DENSITY vs. CLS SAMPLE, AND CONTROL SAMPLE IN D76, DK50, & HP9

ANALYSIS OF DATA

For the experimental procedure used to determine the effects of the emulsion stabilizers, a check of James and Vanselow's results from using Carey-Lea silver sol as nuclei sites for solution-physical development¹¹, and their results that increasing the rate of solution-physical development is the result of the increased solubility of the silver halide in the presence of a silver halide solvent¹² such as sulfite.

In looking at figure 6 it is shown that increasing the solubility of a silver halide by using sulfite or potassium bromide, increased the rate of solution-physical development by deposition of silver on the Carey-Lea silver nuclei. The higher the level of silver halide solvent in a development time long enough to overcome the induction period (5 minutes), showed a higher density level than a developer that did not contain any silver halide solvent. The largest change in density occurred in D76, which contained the highest level of sulfite (100 g/l). As the level of silver halide solvent decreased, the less of a difference in density was observed between the control emulsion sample and one that contained Carey-Lea silver nuclei.

In the testing of the TAI on the rate of solution-physical development (figure 5), it shows that the TAI definitely

slows down the rate of solution-physical development. The effect was more pronounced at the 1.0g/mole AgX than at the .25g/mole AgX level when developed in D76. In the low-solvent action developer, HP9, it seems to accelerate the rate of solution-physical development slightly.

The results of PMT developed in D76 showed an increase in solution-physical development (figure 4), but in this case the sulfite present in D76 could be the cause of the effect obtained. When the PMT was tested in the low-solvent action, surface developer, HP9 (figure 3), the effect is less pronounced. In comparing the results in figure 3 and the results in figure 4, the effect of the PMT on the rate of solution-physical development is very small, if at all within the standard deviation limits of .04.

An interesting effect of the lowest level of PMT (.0063 mg/mole of AgX) was observed. The PMT seemed to increase the rate of solution-physical development at the $2\frac{1}{2}$ minute development time in HP9. The error limits of $\pm .05$ fall within the data, although it remains very close. A closer check of this result using more replicates would provide a better answer.

DISCUSSION AND CONCLUSIONS

The result of testing 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene on the rate of solution of the silver halide proved that it definitely slows down the rate of solution-physical development using the Carey-Lea silver as nuclei sites. This is consistent with the fact that TAI is an anti-ripening agent and is adsorbed on the silver halide¹³. This adsorption to the silver halide slows down the rate of solution of the silver halide. TAI also interferes with Ostwald ripening, or the smaller crystals dissolving and reprecipitating on the coarser crystals¹⁴. TAI stops the ripening of the crystals even though it is weakly adsorbed. There is much more activity present from the TAI than is expected¹⁵. The hypothesis has been found correct in the case of 4-hydroxy-6-1,3,3a,7-tetraazaindene.

The result of testing the effects of PMT on the rate of solution of silver halide proved negative. If there was any effect, there might be only a slight increase in the rate of solution-physical development using this experimental technique. There are many possibilities in this experiment that could effect the results of adding PMT to an emulsion. The PMT, which is causing an increase in the fog level

produced by the colloidal silver may be a result of a change in the colloidal silver that has occurred during development.

In using PMT as an emulsion stabilizer, much less is added since it is more strongly adsorbed than TAI, but PMT's activity is less than the amount of stabilizer adsorbed/surface area of the crystal as compared to the TAI.

Both TAI and PMT are competing adsorbers on the silver halide crystal and can be important factors in the photographic action¹⁷. They can replace certain sensitizing dyes on the surface of the silver halide grains, and thus reduce the spectral sensitivity of the emulsion¹⁸.

One of the reasons that have been proposed for the reduction of sensitivity by the emulsion stabilizers is the destruction of the sensitivity centers by these anti-ripening agents¹⁹. Either the centers are filled by the stabilizers or the sensitivity centers may be destroyed by the stabilizers. "Thomas R. Thompson²⁰ has proposed that restraining compounds may prevent the growth of active or partially formed sensitivity specks."

Another possible cause of the results obtained may be a cause of interactions with the stabilizers with the thiosulfate in the fixing bath. The thiosulfate is also strongly adsorbed by the silver halide, and could be poisoning the rate of reaction of the silver halide²¹.

There are many factors beside the emulsion stabilizers that could be effecting the rate of solution-physical

development. Gelatin concentrations, development effects on the colloidal silver, and development times are just a few suggestions of other possible interactions. There are still many areas that must be better understood to find out more about the effects of the stabilizers in all phases of the processing steps.

LIST OF REFERENCES

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1. T.H. James and W. Vanselow, "The Rate of Solution of Silver Halide Grains In a Developer," Photographic Science and Technology, 2, (2) 135 (1955)
2. Ibid 1
3. T.H. James and W. Vanselow, "The Role of Silver Halide Solvents in Practical Development," Photographic Engineering, 7, 90 (1956)
4. Ibid 2
5. Ibid 1
6. Conversation with Dr. B. H. Carroll
7. C. E. K. Mees and T. H. James, "The Theory of the Photographic Process," Macmillan Publishing Co., Inc. 3rd Edition, 1966, p 11.
8. Ibid 7, p 330.
9. R. W. Berriman, "Crystal Growth During the Formation of a Silver-Bromide Dispersion in Gelatin," Journal of Photographic Science, 12, 121 (1961)
10. Ibid 1
11. Ibid 1
12. Ibid 2
13. G. F. Duffin, "Photographic Emulsion Chemistry," Focal Press, 1966, p138.
14. Grant Haist, "Modern Photographic Processing," John Wiley and Sons, vol 2, 1979, p 63.
15. Conversation with Dr. B. H. Carroll
16. Ibid 13, p 139.

17. Ibid 7, p 11.
18. E. J. Birr, "Stabilization of Photographic Silver Halide Emulsions," The Focal Press, p 150.
19. Ibid 18
20. Thomas R. Thompson, "Action of Organic Stabilizers on a Photographic Emulsion," Photographic Science and Engineering, 3, 272 (1959)
21. Ibid 7, p 330.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. T.H. James and G.C. Higgins, "Fundamentals of Photographic Theory," John Wiley and Sons, Inc., New York, N.Y. 1954
2. C. E. K. Mees and T.H. James, "The Theory of the Photographic Process," Macmillan Publishing Co., Inc. 1977
3. T. H. James, "The Reduction of Silver Ions by Hydroquinone," Journal of Physical Chemistry Society, 61, 648 (1939)
4. T.H. James, "Development by Hydroquinone," Journal of Physical Chemistry, 43, 701 (1939)
5. E. Klein, "The Influence of Silver Halide Solvents in the Developer on the Characteristic Curve in Negative and Reversal Development," The Journal of Photographic Science, 8, 178 (1960)
6. Shiao, Fortmiller and Hertz, "Dissolution Rates of Aqueous Silver Halide Dispersions," Journal of Physical Chemistry, 79, 816 (1975)
7. Grant Haist, "Modern Photographic Processing," John Wiley and Sons, Inc., volume 1, 1979
8. W. H. Simpson, and J. J. Hourigan, Jr., "Relative Dissolution Rates of Silver Halide Crystals by Kinetic Calorimetry," Photographic Science and Engineering, 24,1 (1980)
9. Zolio C. H. Tan, "Investigation of the Formation of Simple and Mixed Complexes in the Silver-Phenylmercaptotetrazolate-Halide System," Photographic Science and Engineering, 19, 1 (1975)
10. R.M. Cole and R. B. Pontius, "Characteristics of Physical Development with Developer Solutions Containing Thiosulfate-Silver Complex Ions", Photographic Science and Engineering, 5, 3 (1961)
11. G. F. Duffin, Photographic Emulsion Chemistry, Focal Press Limited, 1966

APPENDIX A

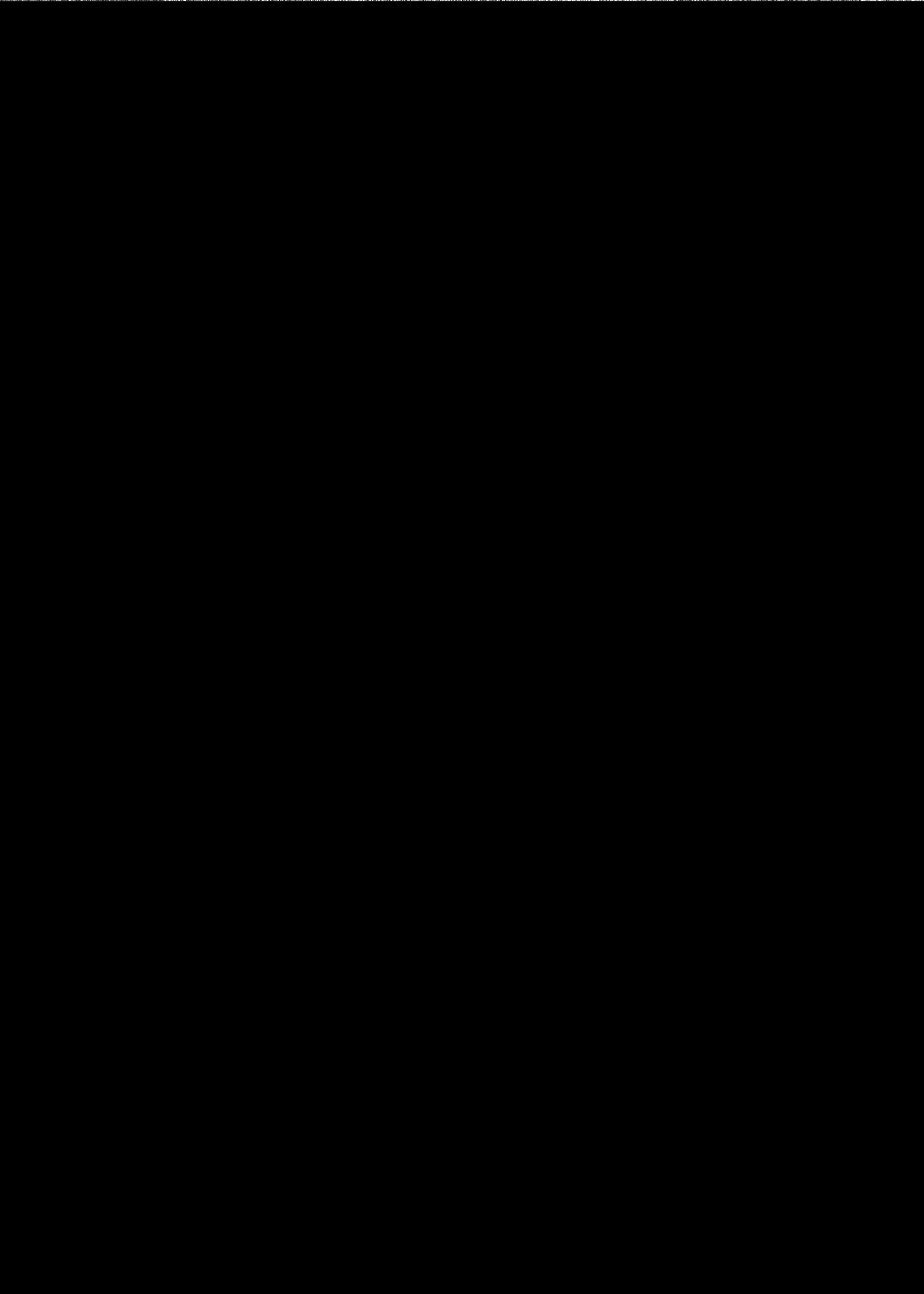
CAREY-LEA SILVER FORMULA

- A) 5.0 g Dextrin in 50 ml distilled water
1 ml of 0.5N Sodium Hydroxide
- B) 0.1000 g Silver Nitrate in 10 ml distilled water

Mix solution A and solution B with constant stirring for approximately 5 minutes, let solution stir until color remains constant (brownish-yellow color).

Coagulate solution with methanol. Let solution settle, drain off liquid and save it. Add 50 ml of distilled water to coagulum and stir. Coagulate a second time using methanol. Let solution settle and drain liquid saving the liquid and adding it to the previously drained material. Add additional methanol to the drained off liquid to insure that all of the reduced silver has been coagulated. Add any additional material that has been coagulated to the rest of the coagulum.

Redisperse the coagulum in a 4% inert gelatin solution. The 4% gelatin solution consists of 20 g inert gelatin and enough water to bring final volume to 500 ml.



APPENDIX B

SILVER BROMIDE EMULSION FORMULA

A 0.1 mole silver bromide / liter emulsion (monodisperse) is precipitated as follows:

- A) Pthaloyl gelatin 6.0 g
Potassium bromide 0.24g
Distilled water to make 800 ml
- B) Silver nitrate 34.0 g
Distilled water to make 100 ml
- C) Potassium bromide 24.14 g
Distilled water to make 100ml

Run solution B and solution C into solution A at 45°C following double jet emulsion techniques under constant turbine stirring. Run time of 4 minutes and 40 seconds. Add 14 ml of 7N H_2SO_4 to coagulate the emulsion. Let the solution settle overnight in refrigerator. Drain liquid from coagulum and rinse with cold distilled water. Redisperse the coagulum in a solution that contained 27 ml of 0.1N NaOH and 5×10^{-4} N KBr in an inert 6% gelatin solution. Add sufficient NaOH to bring pH to 6.30 at 40°C. Bring final volume to 800ml. Store emulsion in stainless steel beaker covered with aluminum foil in a refrigerator.

APPENDIX C

HP9, FIXER and STOP BATH FORMULAS

HP9 FORMULA:

750 ml of distilled water at 125°F
20 g D-(-)-araboascorbic acid
12 g Hydroquinone
40 g Borax
.5 g Phenidone
Distilled water to make 1.0 liter, adjust pH to 9.0 @ 20°C

FIXER FORMULA:

750 ml of distilled water at 125°F
200 g Sodium thiosulfate (pentahydrated)
20 g Sulfite
Distilled water to make 1.0 liter @ 20°C

STOP BATH FORMULA

125 ml 28% acetic acid
1 liter of distilled water

APPENDIX D

APPENDIX D

CALCULATIONS FOR AMOUNT OF CAREY-LEA SILVER SOL
FOR 10 ml EMULSION SAMPLE

$$\frac{.10 \text{ mole silver halide}}{800 \text{ ml}} = \frac{\text{moles silver halide}}{10 \text{ ml}}$$

$$= 1.25 \times 10^{-3} \text{ moles silver halide}$$

(MW AgBr 187.77) (1.25 x 10⁻³ moles silver halide)

$$= 2.347 \times 10^{-3} \text{ g silver halide in 10 ml Carey-Lea Silver sol}$$

$$\text{Carey-Lea silver sol to add to 10 ml emulsion} = \frac{2.813 \times 10^{-3} \text{ g silver/silver halide}}{2.347 \times 10^{-3} \text{ g}}$$

$$= 6.602 \times 10^{-1} \text{ mg Carey-Lea silver}$$

$$\text{ml Carey-Lea silver sol to add to 10 ml emulsion sample} = \frac{100 \text{ mg silver}}{500 \text{ ml Carey-Lea silver sol}}$$

$$= 2.64 \text{ ml of Carey-Lea silver sol to add to 10 ml of emulsion}$$