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2-Mercapto-4-Phenylthiazole on the Clearing Rate of a
Chlorobromide Emulsion and Evidence of the Presence of Activity
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A STUDY OF THE EFFECTS OF THE CONCENTRATION OF 2-MERCAPTO-
4-PHENYLTHIAZOLE ON THE CLEARING RATE OF A CHLOROBROMIDE
EMULSION AND EVIDENCE OF THE PRESENCE OF ACTIVITY SITES

RIT Senior Research Project

Peter D. Lloyd, May 1966

ABSTRACT:

It has been hypothesized that materials which tightly adsorb on silver halide lattices will attach themselves preferentially at certain points, usually referred to as activity sites, which have areas of only a few percent of the total crystal surface.¹ An experiment using the mechanism of Photosolubilization as revealed by R.K.Blake and others of the E.I.DuPont de Nemours Research Laboratories measuring the clearing rate of a chlorobromide emulsion doped with 2-mercapto-4-phenylthiazole indicates that the fixing rate is substantially modified by very small concentrations of this compound, and that the rate remains essentially constant over quite a wide range of concentrations with sharp breaks at what are believed to be of the order of one or two percent coverage and complete coverage of the crystal surface.²

1) H.W.Wood: J. Phot Sci 14 #2 Mar/April 1966

2) R.K.Blake, A.B.Cohen, J.R.Celeste, R.N.Fan, H.D.Hunt, R.C.Chisholm, and J.A.Sincius: Phot Sci Eng Mar/April 1965

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The purpose of this experiment has been to investigate the mechanism of adsorption of certain organic compounds on silver halide crystals in a gelatin matrix. These compounds are commonly employed to stabilize emulsions for purposes of storage and/or to inhibit development fog.¹ From the stability constants of the chelates formed, and the relatively poor solubility of these compounds in water, it is expected that they should be very tightly adsorbed on the crystal surface.² Since the desired stabilization and antifoggant properties are realized with concentrations of these compounds which would be adequate to cover but a small fraction of the grain surface, it has been surmised that there are activity sites covering but a fraction of the crystal surface at which the adsorption occurs preferentially, and, that when these sites are blocked, the adsorption of other species such as developing agents is inhibited, thereby controlling non-selective reduction of the crystals.³ Since these stabilizers also interfere with physical ripening, these centers may be areas where the silver and halide ions enter and leave the crystals during growth.⁴

1) Tamara, Hada, Noguchi, and Hayashi, J. Physical Chem 66:559

2) Cohen, Celeste, And Fan, Phot Sci Eng Vol 9 #2 page 96

3) Berendsen, Faelens, Tavenier and Klerkx, J. Phot Sci Vol 13 #4, 1965

4) ~~Personal communication, Dr. B.H. Carroll~~ *Dr. B.H. Carroll, J. Physical Chemistry*

Dr. R.K. Blake of the Photo Products DuPont de Nemours & Co, Inc., Parlin, N.J. became interested in the adsorption of sensitizing dyes and their interaction with development rates in the early 1960's after noting that cyanine and carbocyanine dyes could greatly affect the solubility of silver halide emulsions. In an effort to adsorb and otherwise inactive compound on test emulsions in addition to sensitizing dye, he found that the addition of a water/ethanol solution of Rhodamine 6GDN Extra (1-phenyl-5-mercaptotetrazole) would completely insolubilize an emulsion sol, unless the sol were exposed to light.¹

Investigations into this effect conducted by DuPont screened over 500 candidate compounds and developed a hypothetical reaction mechanism.^{2,3} Because the mechanism is selective, it allows the production of photographic images and since material is removed in the initial processing steps, the images are of a direct positive nature, in silver halide which may be adequate, without further processing for some uses, or, if fogged or developed with a fogging developing agent, used to produce silver images comparable to conventional materials.¹

1) R.K.Blake, Phot Sci Eng:vol 9 #2 1965
 2)Haugh, Celeste, Chisholm, Cohen,Hunt, and Sincius, Phot Sci Eng: vol 9 #2 1965
 3)Cohen, Celeste, and Fan, Phot Sci Eng vol 9 #2 1965

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The proposed sensativity mechanism involves an organic compound of the form RSH which will adsorb (chelate) silver ions due to the mercapto group. R may be any one of a number of organic nuclei and the S may be sulfur, nitrogen or selenium which form homologous compounds.¹ Haugh, et al. believe that that the silver mercaptide forming an insoluble boundary is destroyed by the photolytic halogen liberated in the classical Gurney-Mott theory of sensativity and gas chromatography does indeed indicate that the expected disulfide of the mercaptan is evolved by exposure to actinic radiation.² Furthermore, photosoluble emulsions exhibit spectral sensativity analogous to conventional emulsions of the same type and may be similarly sensitized by adsorbed sensitizing dyes, indicating a silver step in the mechanism.³

The most efficient compound for the purpose of photosolubilization reported upon was 2-mercapto-4-phenylthiazole and although directions for its synthesis were included in the disclosure papers, I elected to forgo attempting its synthesis due to a very limited knowledge of organic laboratory technique and was able to procure a sample from Dr. H.D.Hunt of DuPont through the good offices of Dr. Carroll of the faculty.

- 2) Haugh, Celeste, Chisholm, Cohen, Hunt And Sincius, *ibid.*
- 1) Cohen, Celeste and Fan, Phot Sci Eng.: vol9 #2 1965
- 3 Haugh, et al. *ibid*

In order to perform this experiment an emulsion had to be formulated and a method of repeatably determining clearing rates had to be devised.

The emulsion for this experiment had to be designed around a somewhat contradictory set of criteria. First of all, the DuPont team states that trace amounts of iodide which is commonly included in camera emulsions totally destroys the photosoluble character.¹ Since the reports in Photographic Science and Engineering speak of a 70% chloride/30% bromide emulsion, I chose this as a basis for the experimental emulsion.² Since a nearly uniform grain size would tend to give a more uniform fixing rate than an extended distribution would, a double jet emulsion with high mixing rates was chosen and the formulation based on the assumption that constant pAg during precipitation would give the desired properties. High mixing rates should discourage physical ripening and a moderately high concentration of gelatin was chosen for the same reason. A neutral emulsion was chosen since I have had some experience in preparations of this type. There should be sufficient gel in the completed emulsion to allow coating, if desired, yet not enough to interfere with dye adsorption measurements which require the silver halide to be centrifuged out of a water gelatin solution.

1)Cohen, Celeste, and Fan; *ibid.*

2) Sincius and Chisholm, Phot Sci Eng: vol 9#2 1965

Furthermore, the gelatin concentration should be small enough that Rayleigh-Tyndall scattering due to the gel should not seriously mask the clearing endpoint. The formulation should allow for a simple change of grain size without modifying the character of the distribution. Although the latter option was not employed, a change in precipitation temperature would be sufficient, judging from a microscopic examination of a sample of the same formula which was precipitated at high temperature, but not subsequently used due to time limits. Finally since it was reported necessary to ripen the insolubilizer on at quite high temperatures for a protracted time, the pAg of the final emulsion should be such that physical ripening would be discouraged even at elevated temperatures in the absence of stabilizers, for the purpose of preparing comparison samples.¹

I encountered considerable difficulty producing a satisfactory test emulsion. My original formulation was taken from an instruction manual used in the third year chemistry course at RIT for the production of a positive type bromo-iodide emulsion with the substitution of appropriate amounts of the proper halides.² The resulting emulsion was a mess, consisting of an extremely fine dispersion and a coarse sediment which would fall out of the gelatin liquor on standing. I was however able to produce a satisfactory all

1) Hunt and Chisholm, Phot Sci Eng: vol9 #2 1965
 2) Dr. B.H. Carroll, RIT 1963 (Mimeographed)

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bromide emulsion, but preferred to continue with the preparation of a satisfactory chlorobromide one.

At this time I was employing a small laboratory stirring motor driving a triangular glass rod. Dr. Carroll suggested that the stirring rate might be too low to provide the necessary degree of homogeneity in the reaction phase and an unreasonable local variation in pAg. A portable electric eggbeater was procured and proved entirely satisfactory in a test precipitation carried out by Dr. Carroll on an emulsion formulation which approximated what I needed. Since this formulation appeared to be satisfactory in all respects, I adopted it for all further preparations. The only difficulty encountered was frothing in the gel at the maximum stirring rate. In order to prevent froth from overflowing the reaction vessel, I was forced to reduce the stirring speed part through the runs, but this was compensated for by having a greater percentage of the beater blades submerged during the later portions of the run.

The precipitated emulsion was knocked out of solution by adjusting the pH to the gelatin isoelectric point and adding sodium sulfate to coagulate the gel. The emulsion was then refrigerated over night in a stainless steel beaker under distilled water to wash out soluble salts. Redispersion was done in rather less gelation than would have been commonly used for coating purposes. This redispersion was then melted down and parceled out in samples as the need arose.

An attempt to estimate the grain surface area by the method of Carroll, West and Whitcomb was made, but without success.

The adsorption behavior of sensitizing dyes has been extensively studied and it has been found that a number conform rather well to the Langmuir equation for isothermal adsorption, $m/M = kc/(1+kc)$, where c represents the micromolarity of free dye in solution, M the saturated amount of dye adsorbed, m the micromoles of dye actually adsorbed and k an empirically determined constant. This isotherm has a very pronounced break at the saturation point which is not particularly temperature dependent. If known amounts of dye are digested to equilibrium on known samples of dilute emulsion and the silver halide thrown down in a centrifuge, the free dye remaining in the liquor may be measured by its absorption in a spectrophotometer.¹ I was unable to achieve satisfactory separation with the centrifuge at my disposal and the residual silver halide with its adsorbed dye completely masked out the free dye peaks, so no measurement was possible. If I had been able to obtain the saturation point, I could have estimated the crystals' surface area from published data on the area occupied by the individual dye molecules.

1) West, Carroll, and Whitcomb. J. Phys Chem, 56, 1054 (1952)

To estimate clearing rates, I chose to measure the time required to have the silver salt in in an emulsion sol come to equilibrium with added sodium thiosulfate solution.

Since the halide crystals are of very small size, with dimensions approaching the wavelength of light, a dispersion of them will scatter light quite strongly. I therefore constructed a device which would shine a beam of light, filtered to reduce photolysis in the spectrally unsensitized emulsion, through the bottom of a glass beaker and allow me to measure the luminance of a small spot on the side of the beaker with a photoelectric exposure meter. The brightness of this spot is a measure of the scattering due to the silver halide crystals present and is, therefore, an indirect measure of the quantity remaining in solution. By using a syringe, I was able to add a controlled amount of thiosulfate solution rapidly enough to insure complete, turbulent, mixing and have a repeatable point from which to begin timing. An emulsion was considered to be cleared when the time rate of change of the scattered luminosity became negligible.

Ten ml samples of the emulsion previously described were placed in test tubes and the desired amount of 2-mercapto-4-phenylthiazole solution added to each. The samples were then placed in a water bath and ripened for twenty minutes at about 70 C, diluted with 240 ml water and parcelled out for individual runs. The dilution and quantities of emulsion and thiosulfate solution were empirically determined for convenient operating times.

If there are indeed two rates of fixation as there appear to be, then the presence of activity sites is strongly suggested. At very low or negligible concentrations, the primary attack on a silver halide crystal begins at these activity sites and occurs somewhat faster than if these sites are effectively blocked by competing adsorbed molecules. If the sites are blocked, the rate is cut by better than a factor of two, then if the entire crystal is protected, the fixation is cut so drastically as to be almost zero. With increasing concentration, I found that the cleared end points became progressively more turbid, indicating that the silver mercaptide simply did not want to give up and had a stability constant somewhat greater than the argento-thiosulfate complex ions normally found in solution.

Sincius and Chisholm noted a similar effect in photomicrograms of a photosoluble emulsion taken during processing.¹ The micrograms indicate that once the solvent has penetrated the barrier about a given crystal, it dissolves away the interior, but leaves a silvermercaptide skeleton. Since this skeleton is the same size as the original grain, it should be a rather efficient light scatterer and be noticeable with my apparatus.

1) Sincius and Chisholm, *ibid.*

APPENDIX OF CALCULATIONS,
PROCEDURES AND
USEFUL INFORMATION

Emulsion recipe:

| | | |
|-------------|-------------------|--------|
| solution 1) | KCl | 2gm |
| | Gelatin | 12gm |
| | Distilled water | 200ml |
| solution 2) | AgNO ₃ | 15.3gm |
| | Distilled water | 250ml |
| solution 3) | KBr | 3gm |
| | KCl | 7gm |
| | Distilled water | 250ml |

Add ingredients for solution 1) and swell gelatin for about an hour at room temperature in a liter stainless steel beaker.

Mix solutions 2 and three placing them in separatory funnels with matched capillary tips which deliver 250ml in 35-40 seconds at room temperature.

Place solution 1) and container in water bath at 45 C, mount a Sunbeam Portable Mixmaster so that the beaters reach into the cup and stir at low speed. Mount the two separatory funnels so that the nozzels will feed opposite sides of the beaters. Turn to high speed and open funnels. After about 20 seconds reduce to medium speed. As soon as the reactants have mixed, Remove beaker and add 200ml of saturated Na₂SO₄ solution with 14.5 ml .05N H₂SO₄. If a froth persists, break it up with 5-10ml isopropanol and add about 35gm solid Na₂SO₄ while stirring, making the additions slowly until the gelatin coagulates. Pour off the liquor and fill beaker with distilled water, refrigerate contents overnight.

To redisperse this emulsion mix 47 ml .054N NaOH, 100ml distilled water, 50ml .02N KCl and 6gm gel, swelling the gel as before. Drain the wash water from the coagulum and add the gelatin solution above. Place in water bath at 45 C and stir for about 10 min. Refrigerate and remove samples as needed.

Calculated pAg: start = 6.9, finish = 5.2 ; actual measurements would be needed after ripening.

The 2-mercapto-4-phenylthiazole molecule is essentially planar with the exception of the mercapto group. As such it is not too difficult to estimate the projected area of the molecule from standard tables of bond angles and distances.¹ In the case of this molecule, I calculate its area to be $8.8 \times 10^{-19} \text{ m}^2$. From this, the molecular weight of the molecule and Avogadro's number it is possible to calculate the area covered by the molecules when adsorbed in a flat orientation.

Since the dye measurements were useless, I cannot give a reasonable answer for the surface area of the crystals in my emulsion, but from literature sources, it should be on the order of $1 \text{ m}^2/\text{gm halide}$.^{2,3} As a result, my results must be presented in the form of a graph of the ratio of the mercaptan treated emulsion's clearing time to the clearing time of an untreated, but similarly ripened sample versus the logarithm of the concentration of the mercaptan added. This graph shows two break points in the rate, one in the vicinity of $1/25 \text{ ml}$ of 1.4% solution and one in the vicinity of 3 ml of the additive. Over a region of $40-50 : 1$ the fixing time remains essentially constant. Indication that within this region the fixing mechanism is disrupted by the presence of the mercaptan and equally important, this disruption is of an essentially constant nature, indicating that there are two modes of fixation involved which are competitive in rate.

1) R.T Morrison and R.N.Boyd. Organic Chemistry. New York: Allen and Bacon, inc 1959
 2) West. et al. ibid
 Berendsen, Faclens, Tavenier and Klerkx, ibid

The clearing rate apparatus consisted of an Accura 150 watt slide projector mounted vertically with a Kodak Wratten K2 (#11) filter placed over the lens. This was placed inside a cardboard box to shield against extraneous actinic light with a sheet of glass over a 1" square hole directly above the lens. A cardboard V was used to repeatably position the emulsion vessel, a 50ml beaker directly over the light source.

By trial and error, I found that 10ml of emulsion (plus whatever additions were called for) diluted with 240ml water produced a usable turbidity and that one test tubeful (approximately 30ml) provided a reasonable amount. I chose to use a single test tube throughout the experiment as I found it to be easier to fill completely than to read a graduated cylinder under safelite conditions. The clearing rate measurements were carried out under a Wratten OC safe-light which would not fog the unsensitized emulsion.

Similarly, I found that 5ml of 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution gave me clearing times on the lower limit of the electrical response of my meter, a Honeywell 1/21st spot instrument, with unmodified emulsion (about 15 seconds) so this amount was used throughout the experiment.

The spot meter was mounted on a tripod about a foot from the beaker and measured a spot about $\frac{1}{4}$ " in diameter about $\frac{1}{2}$ " above the base of the beaker. The apparatus was left assembled throughout the experiment to reduce alignment problems from reassembly procedures,

The operational procedure in making a clearing rate measurement was to first prepare the turbid solution by dispersing a 10ml (+additions) sample of emulsion in 240 ml water and bringing it to 75 F (24 C) which was approximately the ambient temperature of the experimental area. This was then broken down into 8 samples of about 30 ml each (with a little excess) and placed in 50 ml beakers which had been matched via turbidity checks.

I would then load a calibrated syringe with 5ml of my fixing solution which was Kodak's F-24 solution diluted 1 : 1.4 to give me 100 gm/lit sodium thiosulfate plus a sulfite/bisulfite buffer to keep the pH under control and give a solution whose pH was in the vicinity of the gelatin isoelectric point without decomposing the thiosulfate ion. I would then inject this solution into the emulsion sol and begin to time the reaction with a stopwatch as soon as the fluids were mixed completely.

I found that I could repeat myself to within about 3.5% of the measured time interval (one sigma limits) or to within about 10% with almost absolute certainty of finding the correct time, based on a sample size of 8.

DATA SUMMARY:

no mpt

- 1) avg = 18.5 sec s=1.2 sec sm=.45 (only 6 runs)
- 2) avg = 14.75 sec s=1.72 sm=.65
- 3) avg = 14.73 sec s=1.3 sm=.5

no mpt, not chemically ripened

avg = 14.75 sec s=1.1 sec sm=.4sec

1/125 ml mpt (1.35 mg/ml)

avg = 18.4 sec s=2 sec sm=.8

1/25 ml mpt

avg = 23.6 sec s=1.4sec sm=.53

3/25 ml mpt

avg = 35.6 sec s=3.7 sec sm=1.4

1/5ml mpt

- 1) avg = 31.6 sec s=2.9sec sm=1.1
- 2) avg = 35.1 sec s=4.2 sm=1.6

3/5 ml mpt

- 1) avg = 38.1sec s=5.3 sm=2
- 2) avg = 41.5sec s=3.9 sm=1.5

1 ml mpt

- 1) avg= 34 sec s=3.3sec sm=1.25
- 2) avg = 42.9 sec s=2.7 sm=1

2 ml mpt (suspected mislabeled of 1 ml #2 and 2 ml samples)

- 1) avg = 35 sec s=1.8 sm=.7
- 2) avg = 44.5 sec s=2.4 sm=.9

4 ml mpt

takes approximately 15 min to clear

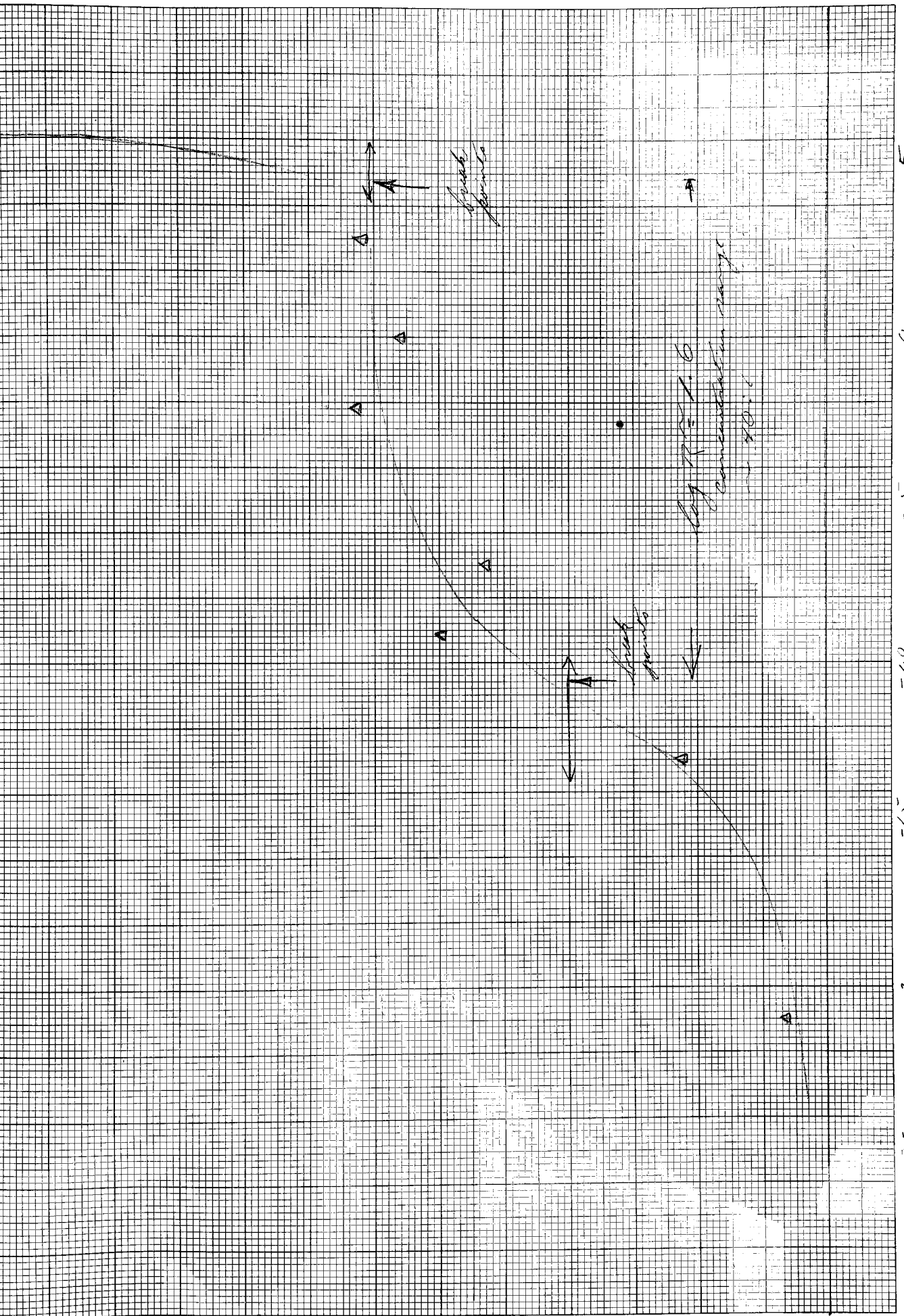
Fluid quantities refer to 1.35% 2-mercapto-4-phenylthiazole in methanol or methanol/water solutions capable of covering .378 square meter of silver halide/ml of solution. 10 ml of emulsion contains .38 gm silver halide with surface area of about 1 sq meter/gram halide.

All data on the previous page refers to samples of size 8.

Since the standard deviations appear to increase with increasing clearing time, I believe that I am justified in pooling the relative deviations (standard deviations divided by the average about which the deviations occur) and in doing so (using the standard deviation in the means' estimators, s_m), I find that the pooled relative standard deviation in the mean is 3.5% which I consider to be relatively precise considering the equipment in use.

Using the Student T distribution, 90% confidence limits would be $\pm 6.6\%$, 99% confidence, $\pm 12.2\%$ and the probable error (50%), $\pm 2.5\%$ ($v = 8-1$ degrees of freedom).

If the 3.5% relative deviation figure may be accepted as a good estimator of the variance, we can use the Student T distribution to test the consistency of the the points plotted such as between the 1/125 ml sample and the 3/25 ml samples gives an outlandishly high probability of the populations being different (14.5 s)



no of living forms to count
 10 ml microplasm / 10 ml sample

ACKNOWLEDGEMENTS:

This report owes a very great deal to Dr. B.H.Carröll who went out of his way to locate chemicals and apparatus employed in the research conducted and for the invaluable assistance rendered in solving the sedimentation problem encountered in the early emulsions. I wish to thank Dr. John Dietrich of the biology department for the use of that department's centrifuge and centrifuge accessories, and Mr. Irving Pobboravsky of the Graphic Arts Research Department for the use of Beckmann model DU spectrophotometer in the abortive attempt to measure the crystal surface area by dye adsorption techniques.

I am particularly thankful to Dr.H.D.Hunt of DuPont's Parlin, N.J. facility who provided the school with sufficient 2-mercapto-4-phenylthiazole to perform this experiment.

*Respectfully
Submitted
12 May 1966*