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Color Monobath Development

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Rochester Institute Technology *May 1967*

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by

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Submitted in Partial Fulfillment
of the Requirments for the Degree
Bachelor of Seience

School of Photographic Arts and Sciences
College of Graphic Arts and Photography
Rochester Institute of Technology
Rochester, New York

1967

Rochester New York 14608
May 5, 1967

Professor Hollis N. Todd
Director of Research
Rochester Institute of Technology

Rochester, New York

Dear Professor Todd:

I respectfully submit this report on Color Monobath Development in partical fulfillment of the requirements for a Bachlor of Science Degree in Photographic Science from Rochester Institute of Technology.

Respectfully yours,

John D. Plumadore

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The formation of dye using color coupling under high silver halide solvent conditions such as those found in monobaths, varies greatly with its ratio to optical silver density under different solvent conditions, and developer activities. Generally a high activity, low solvent monobath yeilds the greatest dye formation with the lowest optical density due to silver. This combination also yeilds the best gamma and speed.

The project was conducted with a soluable color coupler[1]. using Kodak CD-3 [2] as the development agent. Development agent, Sodium Thiosulfate, and Hydrogen Ion Concentration were varied in a stastical design using Kodak Fine Grain Positive Film.

[1] 2,5,Dichloroacetoacetanilide EK No. 3495

[2] Eastman Kodak Tradename. (4, amino-N,N(diethyl)(β-toluidine sesquisulfate monohydrate)

Monobaths in the last few years have taken on considerable importance. This increase in importance has caused an increase in the amount of literature about them. The formation of an optical silver image has been the approach almost exclusively.

Clarke, Milner, and Gomez-Ibanez[1] and Murray and Spencer[2] discovered early that an increase in silver at a given optical density was greater for monobath developed images. Miller and Crabtree[3] contributed the fact that the loss in gamma and speed could be compensated for with an increase in alkalinity of the developer, which increases the activity of the development agent.

Eggenschwiller and Jaenicke[4] concluded that this increase in silver formed at a given optical density was due to physical development. Barnes[5] confirmed this

1. R.G. Clarke, C.E. Milner Jr. J.Gomez-Ibanez, Photographic Engineering 4: 431 (1953)

2. H.C. Murray and D.A. Spencer, Photographic Journal, 77: 330 (1937)

3. H.A. Miller and J.I. Crabtree, American Photography 42: 76 (1948)

4. H. Eggenschwiller and W. Jaenicke Photo Korr. 95: 165 (1956)

5. J.C. Barnes, Photographic Science and Engineering Vol 5, 4: (1965)

conclusion, and found that the presence of thiosulfate ion increased the actual amount of silver even though optical density maybe lower. He also points out that an increase in silver speed point results with the presence of thiosulfate, even though the optical density speed point may be lessened. Maragrete Ehrlich[6] also concluded the same thing with her work with Dosimeter films.

The structure of monobath developed image has been studied by many Ehrlich being among them. The conclusion of all has been that monobath development gives an increase in silver formed, with a lessening of the coverning power, especially in the low density areas. Barnes states that this is not do to high grain concentration, but to the large mass per unit grain developed

Many development agents have been studied in connection with monobath development. Little however, has been published on the color forming developers, especially with a coupler of the color forming type present. The Para-Phenylenediamine type developers

6. M. Ehrlich, Photographic Science and Engineering, Vol. 9 1: (1965)

used for color development are well known for their fine grain which is attributed to their silver halide solvent effect.

It is also well known that dye will form with physical development upon certain conditions. Since monobath development is both chemical and a high degree of physical development the dye formation characteristics will give some insight into the using this increase in silver formed.

This senior research project was designed and exceuted to gain some understanding for the amount of dye that is formed in relation to the silver optical density under monobath conditions.

The objectives where to determine the changes of silver and dye density of a black and white film developed under varing CD-3 monobath conditions with a soluble color coupler present.[7]

The orginal basic formula[8] was taken from the British Journal Annual 1962, and was intended for a substitute for Kodak C-22^tm. developer. This formulation

7. Appendix I

8. Appendix II

proved difficult to mix, and a simpler formula was adopted as the basic developer.

Sodium carbonate	40.0	gm.
CD-3	*	gm.
Sodium sulfite	1.0	gm.
Water to make 1 liter		

*Variable 5.0 or 7.5 gms.

Because of the simplicity of the formulation the variables of hydrogen ion concentration (pH), CD-3 and Sodium Thiosulfate where decided upon. Kodak Plus X^{tm} film was tried in the beginning, however, because of many problems[9] it was disregarded and Kodak Fine Grain Positive $^{tm.}$ substituted.

The Fine Grain Positive was exposed in an EG&G Mark VI sensitometer at 10^{-3} seconds with no compensator. A specially designed extended range scale[10] was used to allow for a wide range of speed variations without having to change the basic incident exposure. This allowed for ease in evaluation, and assurance that the speed point would always be present, along with a large portion of the stright portion of the characteristic curve.

[9] Appendix III

[10] Appendix IV

The exposed strips where processed in their respective solutions using a tumble type processor[11] which proved to be much more repeatable than the Jiggler type processor[12] which the beginning experiments where conducted on.

A basic developer was mixed up with the concentration of CD-3 set. Hydrogen ion concentration was adjusted with six molar sodium hydroxide. Sodium Thiosulfate (solid) was added to each hundred milliliters of developer solution, to which ten milliliters of coupler solution[13] was added. The strips where processed for ten minuets at twenty one degrees centigrade, which was room temperature. The lights where then turned on,(only on the ones run at monobath conditions) strips removed, washed for ten minuets, and placed in the stablizer [14] for one minute.

Tri-Color densities where taken on the unbleached strips. The strips where then bleached in C-22 bleach and fixer (10 min. each), washed for ten minutes,

11. Appendix V

12 Appendix VI

13. 25 g. 2,5-Dichoroacetoacetanilide in 1 liter Methanol

14. Appendix VII

and dried. The resultant strips were read blue density only.

CALCULATED SILVER DENSITY AT 0.5 (unbleached blue filter)
0.5/calculated silver density ← inverted

CD-3		5.0			7.5		g/l
$Na_2S_2O_3$	15	20	25	15	20	25	g/l
pH 10.5	0.42	0.28	0.25	0.23	0.14	0.25	
pH 11.0	0.50	0.25	0.24	0.50	0.33	0.33	
pH 11.5	0.63	0.28	0.33	0.63	0.63	0.50	
pH 12.0	1.00	0.50	0.42	1.00	0.50	----	

CALCULATED SILVER DENSITY AT 1.0 (unbleached, blue filter)
1.0/ calculated silver density ← inverted

CD-3		5.0			7.5		gm/l
$Na_2S_2O_3$	15	20	25	15	20	25	gm/l
pH 10.5	0.50	0.45	----	0.29	0.25	----	
pH 11.0	0.33	0.29	0.20	0.40	0.25	0.20	
pH 11.5	0.50	0.33	0.20	0.50	0.40	0.22	
pH 12.0	0.67	0.40	0.33	0.67	0.50	----	

NOTE: The above data was calculated from the density at the indicated silver and dye density, and was divided in to that density. Thus, the higher the number, the greater the dye formation at a given optical density of silver.

RED DENSITY AT 0.5 (unbleached blue filter)
0.5/red density unbleached. ← inverted

CD-3		5.0			7.5		g/l
$Na_2S_2O_3$	15	20	25	15	20	25	
pH 10.5	0.20	0.42	0.36	0.17	0.28	0.42	
pH 11.0	0.25	0.33	0.50	0.25	0.25	0.42	
pH 11.5	0.25	0.33	0.42	0.20	0.25	0.33	
pH 12.0	0.25	0.33	0.42	0.25	0.25	----	

RED DENSITY AT 1.0 (unbleached blue filter)
1.0/red density unbleached ← inverted

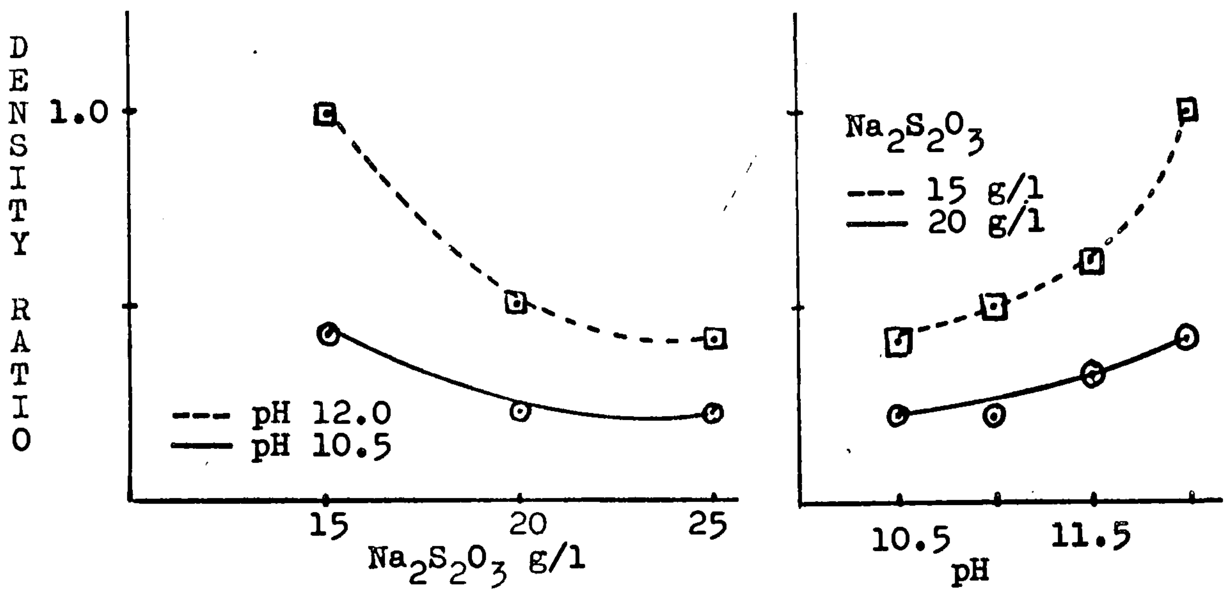
CD-3		5.0			7.5		g/l
$Na_2S_2O_3$	15	20	25	15	20	25	
pH 10.5	0.33	0.33	----	0.25	0.29	----	
pH 11.0	0.23	0.29	0.40	0.25	0.29	0.33	
pH 11.5	0.25	0.33	0.33	0.25	0.25	0.40	
pH 12.0	0.25	0.33	0.33	0.23	0.25	----	

NOTE: The above data was calculated from the density at the indicated silver and dye density, and was divided in to that density. Thus the higher the number, the greater the dye formation at a given optical density of silver.

STASTICAL EVALUATION using the above data see Appendix VIII

After the strips were read, the hard part came in analyzing the data. The method which yeilded the most meaningful results was the density ratios between the calculated optical silver density, and the silver and dye density. The calculation of optical silver density consisted of substracting dye density (bleached film) to blue light, from dye and silver density to blue light. This method showed the most change over the variables.

It was supposed that red density of the unbleached image would also give a good indication of optical silver density. The results however, vary signifigantly from the calculated optical silver density.



Calculated silver density
ratio at 0.5 silver and
dye density. 5.0 g/l CD-3

At both density levels 0.5 and 1.0 of silver and dye density the calculated silver density indicated that the addition of sodium thiosulfate (15-25 g/l). produced less dye formation in comparrison with the optical density of the silver. Increasing pH

increased formation of dye over the range 10.5-12.0 pH units. CD-3 was not stastically singificant, with calculated optical silver density, it did prove significant however for the red silver density.
At the low density level,(0.5) there was a significant interaction between CD-3 and pH.

The red density of the unbleached image in comparison to the blue density give very different results. The addition of sodium thiosulfate increased formation of dye at a given silver density. This result is opposite from what happened to the calculated optical silver density. This effect was much more pronounced at the lower density levels. From the evaluation of the curves in their raw state it is concluded that this effect can be contributed to the formation of yellow colloidal silver which reacted like a dye, but was removed by bleaching.

It should be noted that while this effect was stastically significant, it is much less than a comparable effect of the calculated silver density.

It was assumed that the dye density would be higher than the calculated silver density oweing to the fact that the dye image itself asbsorbes some red light. There is no correlation however, between the calculated optical silver density and the red density of the unbleached image.

CD-3 proved to have a significant effect on the red density readings at both levels of density (silver and dye to blue light at 0.5 and 1.0). It tended to decrease dye efficiency lightly at the higher level which 7.5 g/l. This can probably be attributed to a change in the optical quality of the silver formed at the higher CD-3 level. [15]

The calculated silver density gives a truer understanding as to what is happening to the image, and the effects due to the different pH and sodium thiosulfate combinations are much more pronounced. The red density is most useful in determining the quality of the image in its unbleached state. It is likely however, that different dyes would greatly alter the results.

What happened to the gross curves generally follows close to the calculated silver density indications. Sodium thiosulfate gave a marked loss in speed and gamma. At the higher pH levels this loss was some what compensated for. Increasing pH greatly increased gamma and speed in areas where gamma infinity was not approached, such as the higher thiosulfate concentrations.

15. Appendix IX

At the lower sodium thiosulfate concentrations silver optical density formation is depressed in the toe areas, which is accompanied by higher dye densities. this can be attributed to dye formation from physical development.[16] At higher exposures however the gamma increases, becoming equal or even surpassing the gamma of the dye alone, ie.more silver optical density than dye density. The length and degree of depression of the silver density varies considerably depending on the conditions. Generally the lower sodium thiosulfate and the higher the pH the greater the depression, The gamma after a strong and long depression such as those at higher pH's however is higher.[17]

In conclusion, the lower the sodium thiosulfate concentration, and the higher the pH the better the dye formation in relation to the optical silver density. This combination may not yeild the dye purity however, when viewed with the dye and silver together.

16. Appendix X

DISCUSSION

This project was tackled with the possibility of a negative color monobath in mind. I feel that it has proved that the idea is atleast worth investigating, in the fact that silver optical density can be surpressed while dye density increases.

More work however must be done in ways of producing more dye formed by physical development. There is all probility will be great changes in an incorporated color coupler system.

Study into the mechanism which controls the physical development is also needed. This might include the study of such things as foggents, latensification, temperature, and so on.

I feel that this project has barely marred the surface to dye formation under high silver halide solvent conditions.

John D. Plumadore

APPENDIX I

The orginal objectives where stated as follows:

To determine the speed, gamma, and fog changes in both silver and dye images resulting in a black and white emulsion when developed in Kodak Color Development Agent CD-3 under varing monobath conditions with a color coupler present.

The changes where made because speed, gamma, and fog changes did not show the true relationships between the silver and dye images. Two density levels where chosen (0.5 and 1.0 of the silver and dye images to blue light) and the optical silver compared to this. The red light density of the unbleached image was also compared at this point.

APPENDIX II

The orginal formulation was as followes:

benzyl alcohol	8.5	cc
sodium metaborate	40.0	gm
tri-sodium phosphate	2.5	gm
sodium sulfite anh.	2.5	gm
AF-71	.02	gm

Water to make 1 liter.

APPENDIX III

Plus X film was orginally chosen for this project because it was thought that it would closely resemble a high speed negative color emulsion.

Plus X however caused many problems. Silver retension by the film made the bleach results highly suspect. Because it is a double coated film the curves often did not match, making evaluation most difficult.

I was also believed that thiosulfate, at low concentrations would increase dye formation, this did not happen. The simpler Kodak Fine Grain Positive however, did give a dye yeild which followed more closely to theory. This film was used thoughout the rest of the project.

It was suggested by Dr. B.H. Carroll that accelerators, and the high iodine concentration which make Plus X the remarkable film it is may have hindered the formation of dye. This seems feasiable since I was able to get relatively complete development with out any coupler, and very low sulfite concentration.

It was discovered that potassium bromide was not necessary when using thiosulfate. A fact which also held for the Fine Grain Positive.

APPENDIX IV

The extended range scale was made by sandwiching two Kodak N° 2 step wedges, emulsions the same direction with Dupont Duco[tm] cement. The sandwich was rolled with a hand holler and left to dry. The density increments are 0.3 ± 0.03 over the range which the densitometer could read. (up to a density 4.0)

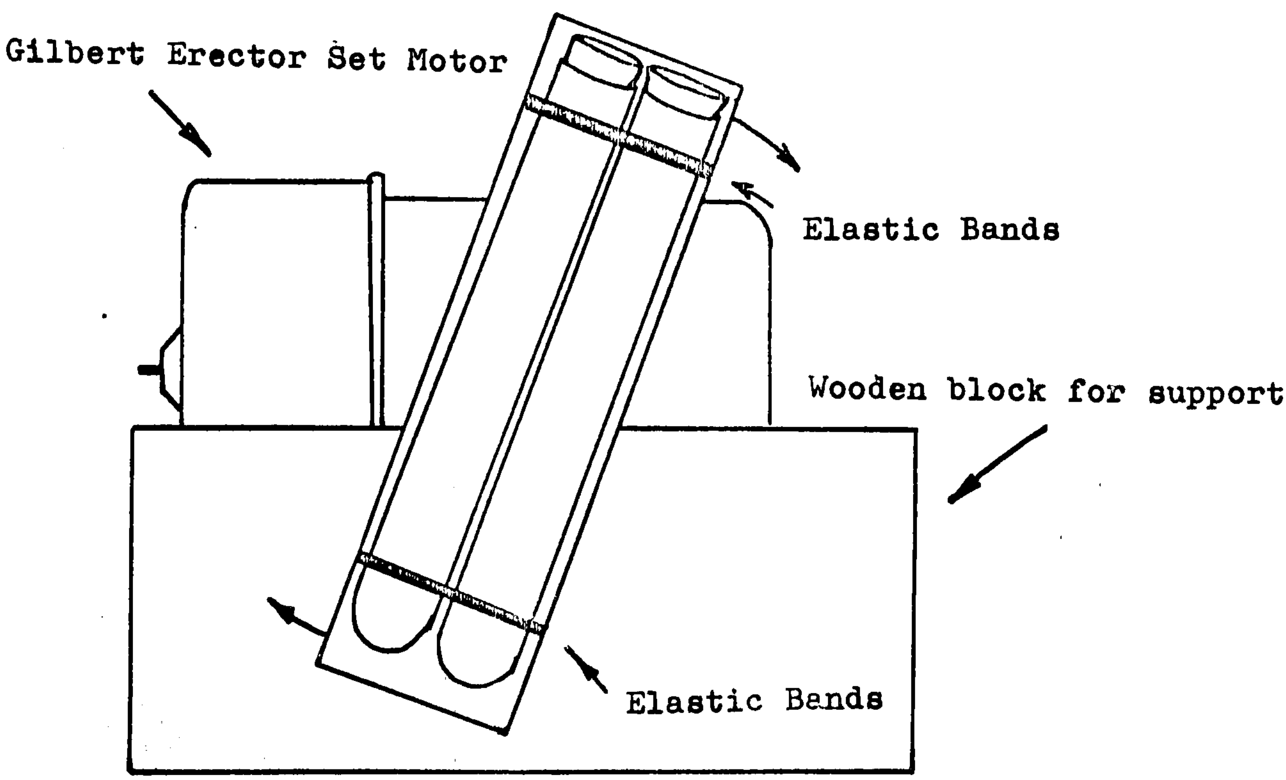
The two scales where cemented together to cut down on internal reflections which would cause errors in a sandwiched scale.

APPENDIX V

Orginally a "Jiggler" type test tube processor was designed for this project. It consisted of a light tight device which fitted over a Mag-mix[tm] and held a 100 ml. test tube upright. The film was attached to a magnet which jumped up and down in the test tube of solution. This type of processor is used at the Research Labatories at EG&G Inc. My version however proved to have considerable uneveness, and was discarded in favor of the "tumble" type processor. Appendix VI.

APPENDIX VI

The ~~jiggler~~ tumbler? type processor was made by attaching a 4x8 inch board to an Erector Set tm motor to which two elastic bands held two test tubes to it. The speed of the motor is 1 rps. and it gave very even results.



APPENDIX VII

Stablizing Bath used:

Formaldehyde (37%)	15 ml.
Photo-flo Concentrate	2 ml.
Water to make	1 liter.

Taken from:
Physics II- Laboratory 1962
R.D. Zakia
H.N. Todd

APPENDIX VIII

STASTICAL EVALUATION

CALCULATED SILVER DENSITY (0.5 silver and dye density)

A N O V A

FACTOR	SS	df	MS	
CD-3	0.000	1	0.0000	
pH	3.040	3	1.0134	**
$Na_2S_2O_3$	1.7033	2	0.8514	**
CD-3/pH	1.7910	2	0.8950	*
CD-3/$Na_2S_2O_3$	0.3750	2	0.1875	
pH/$Na_2S_2O_3$	0.3467	2	0.1730	
Est.Error	0.7090	6	0.1181	
Total	7.965	18		

CALCULATED SILVER DENSITY (1.0 silver and dye density)

A N O V A

FACTOR	SS	df	MS	
CD-3	0.01650	1	0.01650	
pH	6.1785	3	2.05450	**
$Na_2S_2O_3$	2.985	1	2.985	**
CD-3/ pH	0.6710	2	0.3355	
CD-3/ $Na_2S_2O_3$	0.6705	2	0.3352	
pH/ $Na_2S_2O_3$	0.7025	2	0.3512	
Est. error	2.5650	5	0.5275	
	11.485	16		

RED UNBLEACHED DENSITY (0.5 silver and dye density)

A N O V A

FACTOR	SS	df	MS	
CD-3	0.4672	1	0.4672	*
pH	0.1733	3	0.05776	
$Na_2S_2O_3$	3.5833	2	1.7941	**
CD-3/pH	0.0305	2	0.0152	
CD-3/ $Na_2S_2O_3$	0.1455	2	0.0727	
pH/ $Na_2S_2O_3$	0.5643	2	0.2821	*
est. error	0.1209	6	0.0204	
total	5.085	18		

RED UNBLEACHED DENSITY (1.0 silver and dye density)

A N O V A

FACTOR	SS	df	MS	
CD-3	0.8559	1	0.8559	*
pH	0.6169	2	0.3084	
$Na_2S_2O_3$	1.1556	1	1.1556	**
CD-3/pH	0.5416	2	0.2708	
CD-3/$Na_2S_2O_3$	0.0154	2	0.0154	
pH/ $Na_2S_2O_3$	0.1419	2	0.0709	
est error	0.29205	5	0.0584	
total	3.70940	16		

APPENDIX IX

Orginally a wide range of concentrations of CD-3 were to be tried. However because the coupler came out of solution at these high concentrations and formed a yellow goo on the film,they could not be done.

It was discovered later in the project that high concentrations of Methonol would keep this from happening. further investigation in the a wide range of CD-3 concentrations using methanol will be interesting and

High concentrations of thiosulfate seem to promote the formation of yellow colloidal silver. further investigation into to this with CD-3 and other developers may make it possible to use the yellow quality of the image to gain printing density.

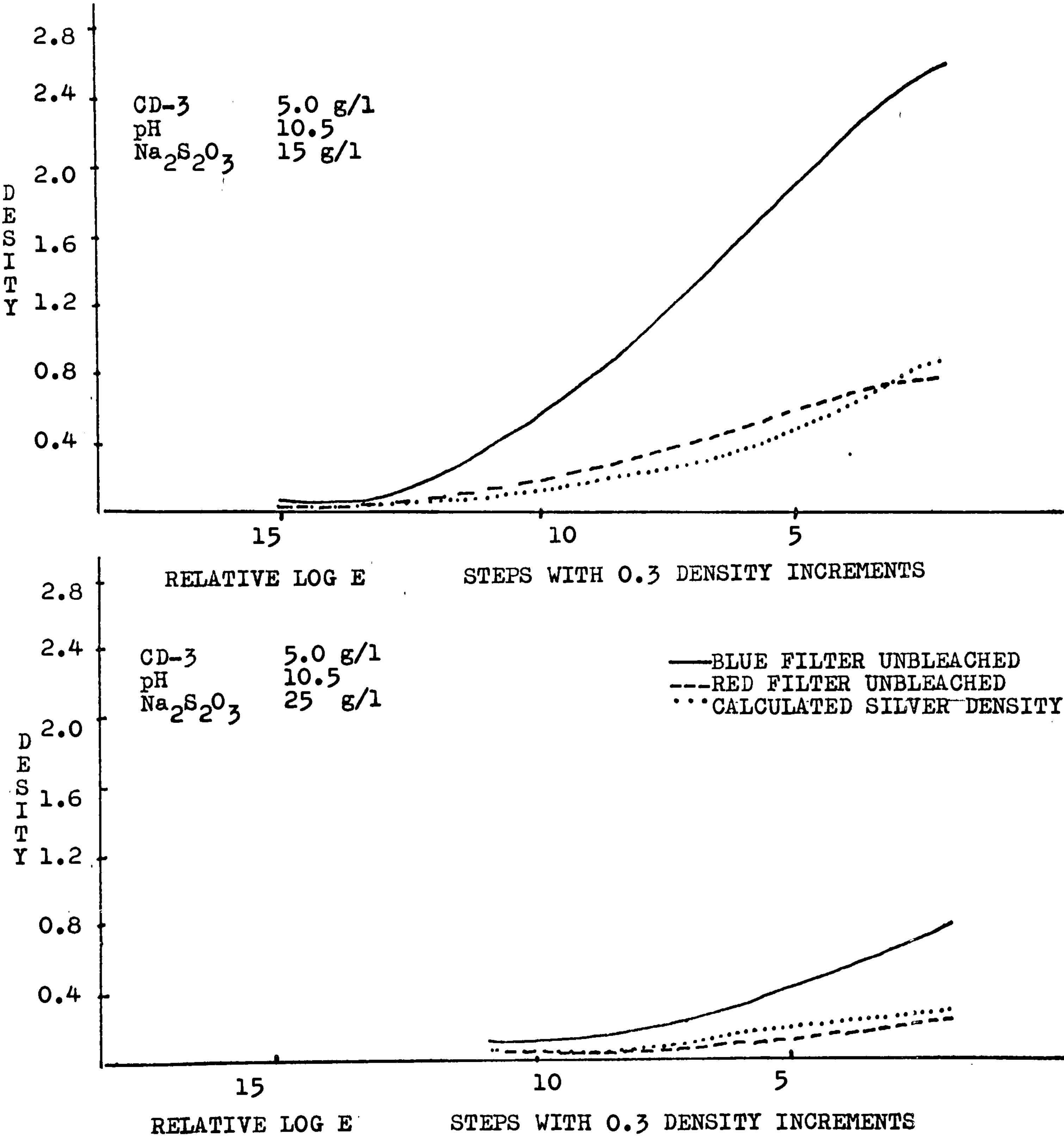
APPENDIX X

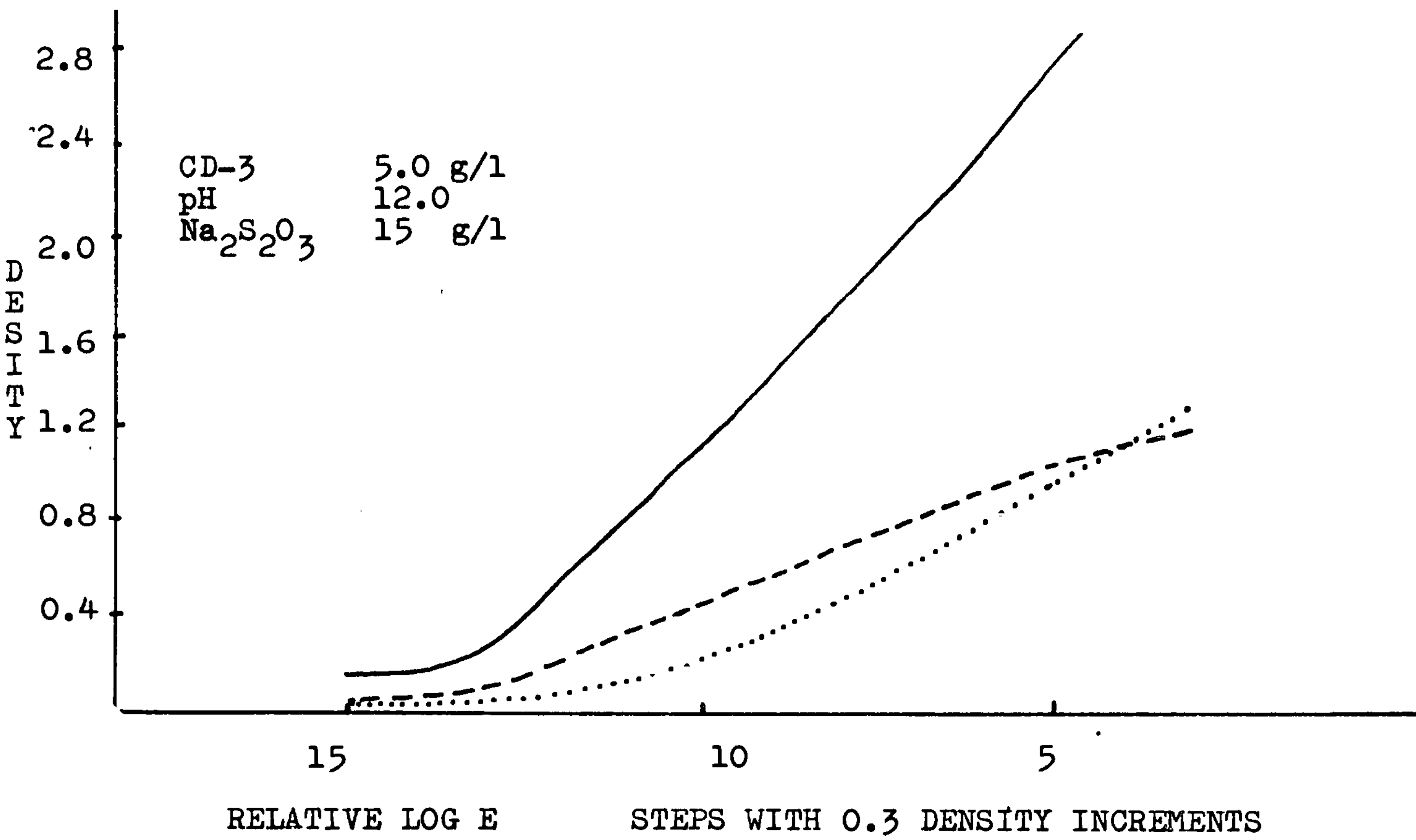
J.C. Barnes* states that when adding sodium thiosulfate to a developer there is first a great increase in the amount of silver formed, and even an increase in optical speed, it them falls off drastically. He found that under his conditions of a very active developer he got the highest silver formation at about 8 g/l when using Fine Grain Positive.

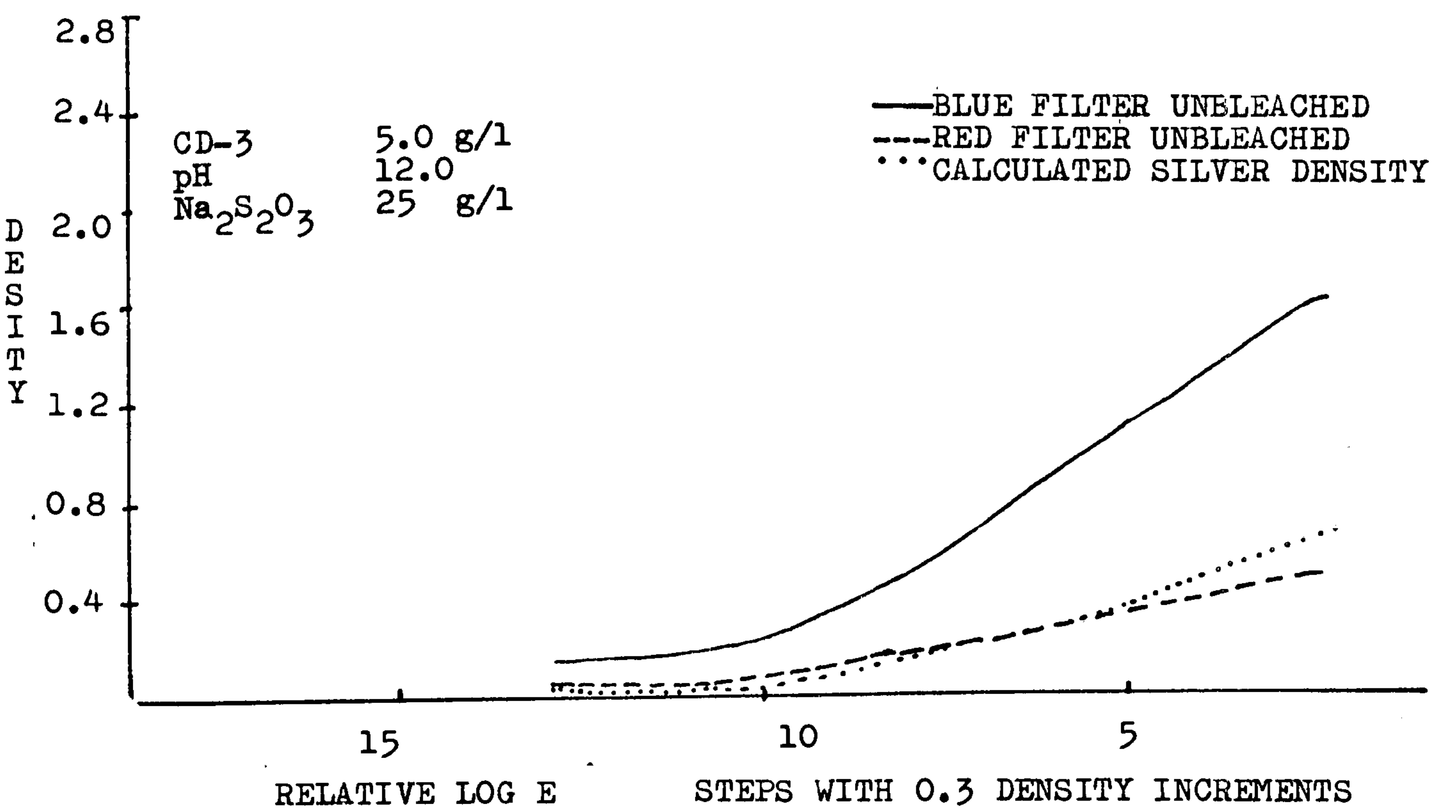
He also found that optical density however falls off much more rapidly. The data found in this project seemed to support this. I believe that from the data that an even more active developer would increase the results.

* Mechanism of Development in Monobaths Containing Thiosulfate Ion, J.C. Barnes. Photographic Science and Engineering Vol. 5 4: July-Augest 1961

Selected grafted data to show the dye relationships to silver over the whole exposure range.




2.8
2.4
2.0
1.6
1.2
0.8
0.4
DESITY
CD-3 5.0 g/l
pH 12.0
$Na_2S_2O_3$ 15 g/l
15
10
5
RELATIVE LOG E
STEPS WITH 0.3 DENSITY INCREMENTS


2.8
2.4
2.0
1.6
1.2
0.8
0.4
DESITY
CD-3 5.0 g/l
pH 12.0
$Na_2S_2O_3$ 25 g/l
BLUE FILTER UNBLEACHED
RED FILTER UNBLEACHED
CALCULATED SILVER DENSITY
15
10
5
RELATIVE LOG E
STEPS WITH 0.3 DENSITY INCREMENTS