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Statistical analysis of grain growth based on the Frieser-Eger film on development kinetics

Noreen Vredenburg

Sharon Perry

STATISTICAL ANALYSIS OF GRAIN GROWTH BASED ON THE FRIESER-EGER FILM ON DEVELOPMENT KINETICS

by

Noreen Vredenburg

Sharon L. Perry

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Thesis adviser: Dr. Burt Carroll

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ABSTRACT

Data were obtained from the Frieser-Eger[1] film on development kinetics for initiation times and for total development times of individual grains (times of complete development) in a lithographic developer and in a hydroquinone developer with normal sulfite level. Approximate areas were computed for each grain. The purpose of this investigation was to compare the process of development at the two sulfite levels and to determine if there is a functional relationship between total development time and grain size. Different relationships were expected for the two types of developers. This data analysis permits a better understanding of the differences between lithographic and normal hydroquinone developers.

The data were obtained by observing a number of grains throughout the development process. The film was run through the projector one frame at a time and each frame was counted so that the initiation times and times of complete development could be determined. The location of the grains in question was maintained by means of a grid. The areas were measured using the geometric shape of the individual grains. The shape of some irregular grains was approximated.

There were no functional relationships between grain size and times of complete development or initiation times for the two developers. There was, however, a significant difference between the two developers with respect to initiation times. The initiation period for the 0.5 g. sulfite developer is shorter than the 20g. sulfite developers initiation period. This difference is believed to be the result of different development mechanisms for the developers. The results of this evaluation are useful only as an example of a possible statistical analysis for films of a similar nature.

ACKNOWLEDGEMENTS

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INTRODUCTION

The process of development is often considered to exist in two phases. The first phase or initiation period is the initial stage of the reduction in which no microscopically visible reduction of the grain is apparent. The second phase or completion period of a grain is the microscopically visible growth of silver in the grain until no further silver growth is visible.

Meidinger[9] studied the kinetics of development of large individual silver bromide grains. Microscopically, he determined the initiation period and the rate of completion of development through-out a grain. He observed a decrease in initiation period with increase in exposure until a maximum was reached. The completion rate was independent of exposure. Both initiation period and completion rate decreased with increased bromide concentration in the developer. Both increased with increases in pH of the developer and both decreased when the developer was diluted with water. He found that the rate of propagation of development throughout the grain varied with the composition of the developer.

Freiser and Eger[1] studied the process of development by using infra-red microcinematography. The purpose of his investigation was to obtain qualitive information regarding photographic development. Eger investigated several different developers. Extended work on two of the developers Frieser and Eger used are studied in our thesis to obtain quantitative data.

The first was a litho type developer and the second was a normal hydroquinone developer. The only difference in the two being the amount of sulfite present. The litho type contains 0.5g of sulfite per liter and the normal hydroquinone developer contains 20.0 g of sulfite per liter. These two developers were selected for comparisons of initiation periods and periods of complete development. The data was collected so that any functional relationship between grain sizes and initiation periods and complete development times could be detected and differences between developers.

The sulfite content of a developer can change the developers properties. The sulfite in a hydroquinone black and white developer usually reacts with the oxidation products (quinone) to form sulfonates. These oxidation products usually have an undesirable influence throughout development, therefore the sulfite acts as a preservative for hydroquinone and its derivitives. Sulfite can have three functions; preservative, weak developing agent, and silver halide solvent.

The sulfite concentration in graphic arts developers is kept very low in order to utilize the phenomenon known as "infectious development" (the more rapid development of grains in the immediate neighborhood of already developing grains). Frotschen[10] in 1937 proposed that infectious development was due to the catalytic effect of oxidation products. Yule[11] postulated that the active catalyst was the semiquinone. The semiquinone concentration can build up only at low sulfite concentrations. The developing reaction is autocatalytic under these conditions. Yule[11] believes that the semiquinone is considerable stable by absorption on to the silver halide grain. This provides the right environment for infectious development.

Some compromise concerning sulfite concentration in a graphic arts developer is needed in order to obtain "good" dot quality in a graphic arts film. At low sulfite concentration, the lateral diffusion of hydroquinone oxidation products from the exposed area to developing grains leads to spreading of the dot image, as well as increasing the density within the dot. If the sulfite is completely absent, the excessive diffusion of oxidation products results in a large spread of the dot. The compromise sulfite concentration must be such that infectious development is promoted within the dot image, without any appreciable spread beyond the exposed area. Yule[11] found this compromise sulfite concentration to be around 1g. per liter of developer.

EXPERIMENTAL PROCEDURE

A 16mm Kodak Pagent Projector was modified so that the film could be advanced one frame at a time by turning a crank. As each frame was advanced, a counter was also advanced to keep track of the total number of frames that have been examined. Thus, initiation periods and periods of complete development can be measured in terms of the number of frames and by dividing by the number of frames exposed per second, we can calculate the times.

The projector was set up on a bench so that the image could be projected on the wall giving a projected image size of diameter 11.5 inches. The grains in question were located on a grid. The grid was 12 x 12 inches and divided into 1 inch squares. The grids were made on 97% reflectance, white cards. The grains in question were then outlined with marking pen and numbered. One grid was made for each run.

The grains selected for use in this analysis had to meet the following specification: 1) the grains must be completely in focus, and 2) the grains must not overlap or have a common border. These stipulations were necessary to avoid protruberances from one grain to start development in the next grain,

or the possibility that with a slightly out of focus grain, a development site might not be visible. Many grains had to be dropped from the analysis because they could not meet the requirements.

The approximate area for each grain was computed by using the area formula for its geometric shape, circular, triangular or hexagonal. All measurements were made using drafting dividers. These measurements were made using the outer edge of the grains. For grains with irregular shapes, approximations were made. That is, irregular shaped grains were called either triangles, circles or hexagons, whichever it most closely resembled.

Every grain in question was examined in the frame before progressing to the next frame. It was noted that just prior to the appearance of a development site, some grains were covered with a neutral density "cloud". We can find no explanation for this occurance.

It was noted during the examination of the 20g. of sulfite hydroquinone developer, that the runs varied in length. The runs and lengths are shown in the tables below.

20g. sulfite hydroquinine developer.	Run 1	7 ft.
	Run 2	6 ft.
	Run 3	19 ft.
	Run 4	10 ft.

0.5g sulfite litho developer	Run 1	6.5 ft.
	Run 2	5 ft.
	Run 3	6.5 ft.
	Run 4	4.5 ft.

Drs. Frieser and Eger were questioned, via letter, what the problem might be. They indicated that some of the runs were made at 3 frames per second and that others were made at 5 frames per second. They did not, however, know which were done at which frame rate. The film was then run through a normal 16mm. projector and by observing the "flicker" of the film, we were able to determine that the longer runs were made at 5 frames per second.

It was also noted that some of the grains were completely developed at the first frame. This was accounted for by Drs. Frieser and Eger. They said that the camera was not turned on immediately after the developer came in contact with the grains. They estimate that a period of about 10 seconds elapsed before the camera was started. This necessitated adding 10 seconds to each of the initiation periods. Since this is only an approximation, this analysis can be used only as an example of the method by which other such films can be analyzed. However, the results within a single run are valid.

The data that was collected were analyzed statistically. Analysis of Variance (ANOVA) (Figs. 9-14), best line of fit curves (Figs. 3-6), and grain size distributions were applied to the data (Figs. 1 & 2).

An emulsion like that used in this film was prepared by Dr. Burt Carroll. The emulsion Dr. Eger used for his thesis is not chemically sensitized and consists of larger than normal grain sizes which are not typical of practical emulsions. Sensitometric evaluation of this emulsion gave a macroscopic view of the difference between developers as well as the abnormality of the emulsion.

Film samples were exposed to a Kodak step tablet by means of an EG & G sensitometer at 10^{-3} seconds.

The developers were prepared as stated in Dr. Egers thesis.

The "normal" hydroquinone developer was made up with little trouble. However, the pH was stated by Eger as being 11.2 and was found to be 10.8. The film was processed without any adjustments for pH. The litho developer, however, oxidized almost immediately. It was prepared several times without success. Dr. R. Francis was consulted and he suggested preparing the developer in two parts. The first part was 2.5g hydroquinone and 0.5g sodium sulfite and water to make 500 ml. The second part was 50.0g potassium carbonate and 1.0g potassium bromide and water to make 500 ml. Both parts were made in water at 70° F. The two parts were mixed in the darkroom

immediately before use. The exposed strips were developed for 30, 60, 90, 120 and 150 seconds with continuous rock agitation. The process was as below (at 70° F):

Litho or normal developer	30, 60, 90. 120, & 150 seconds
Water Stop Bath	30 seconds
Fixer (F. 5)	2 minutes
Wash (gentle agitation)	25 minutes
Dry at 100° F	

Since the emulsion does not contain a hardener, care was taken to avoid washing the emulsion off the base. The process was repeated several times, but uniform images could not be obtained. The density values for each step were read by means of a MacBeth TD-102 Densitometer with a 2mm. slit.

EXPERIMENTAL RESULTS

Grain size distributions (Figs. 1 & 2) were plotted for both the litho and the "normal" hydroquinone developers. These distributions were essentially the same indicating that the samples were adequate for showing the grain size distribution for the emulsion. When plotted on log-log paper they indicated a normal distribution.

Analysis of Variance (ANOVA) were run to determine whether or not there was a significant difference between the runs for each developer, between the various grain sizes and between the two developers. Each ANOVA was run with respect to initiation period and with respect to period of complete development. The results are shown in Figs. (9-14).

A computer program was used to plot the grain size vs. initiation period data and to determine the best line of fit for the data for the two developers. The same program was used for the period of complete development. Again the program was run for both developers. See Figs (3-6).

A development time series (Dlog E) was plotted from the sensitometric data obtained from the emultion prepared by Dr. Burt Carroll. Figs (7 & 8).

Pictures showing the different mechanisms of development for the two developers are in Figs (15 & 16).

Fig. #1

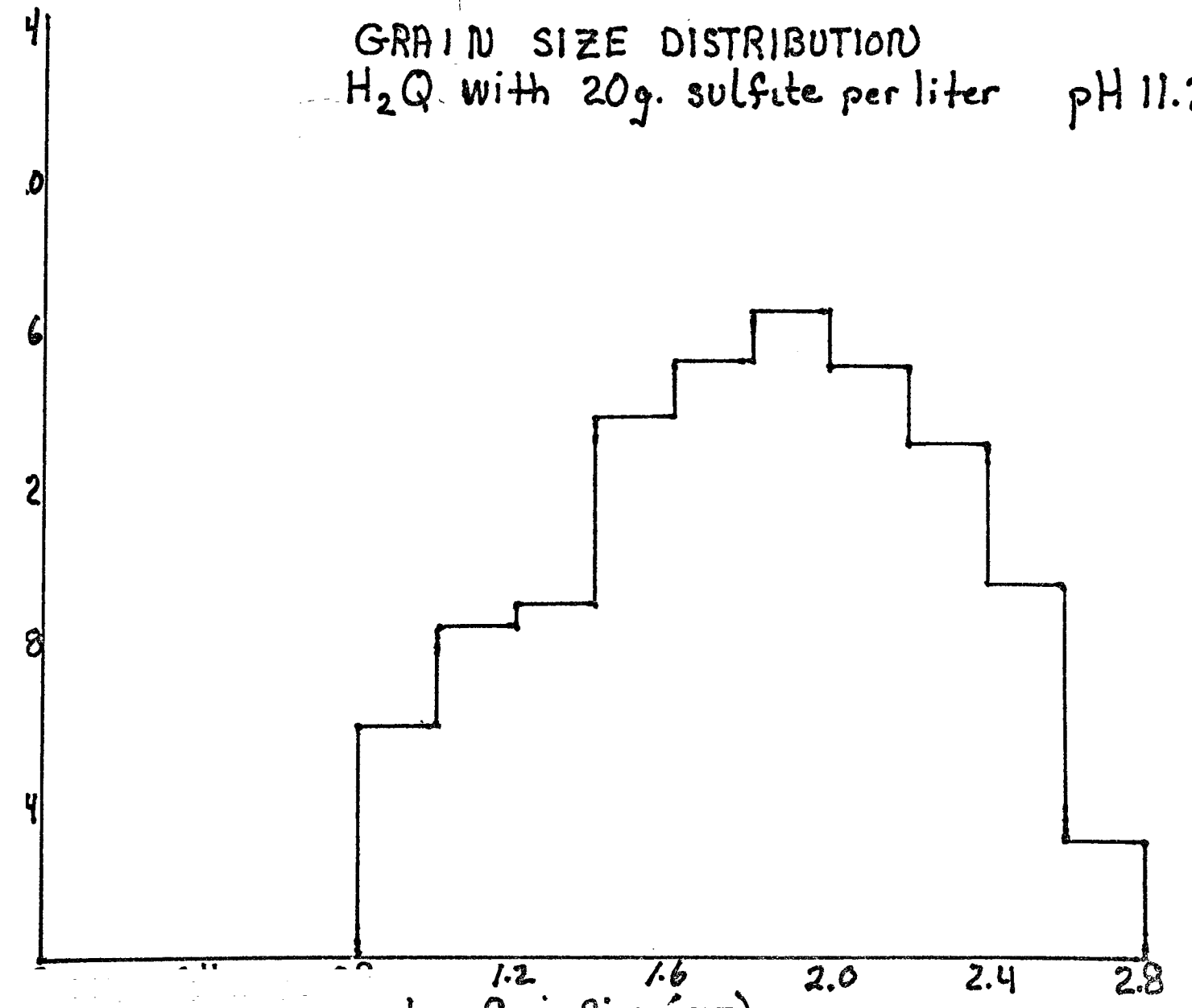
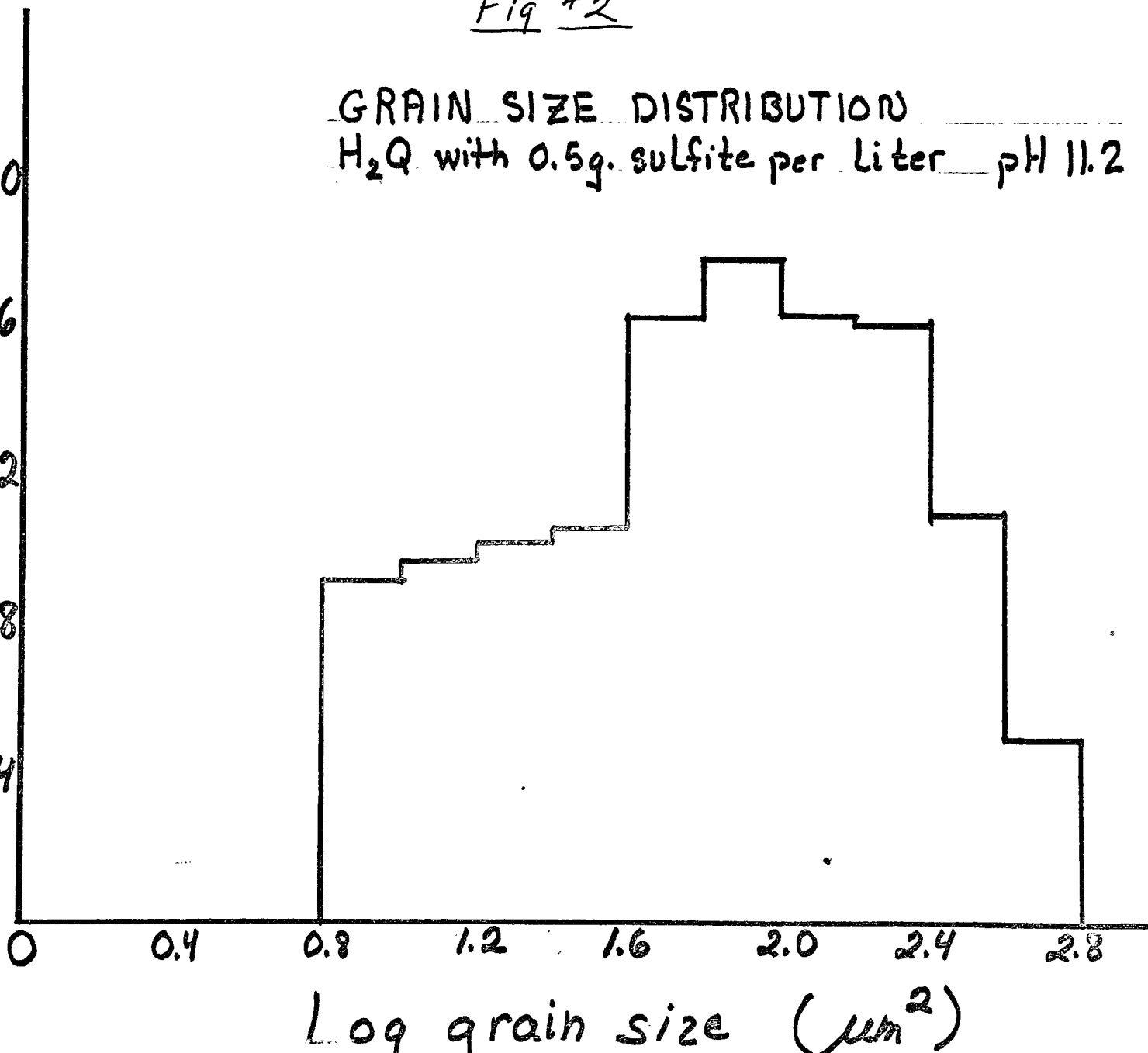
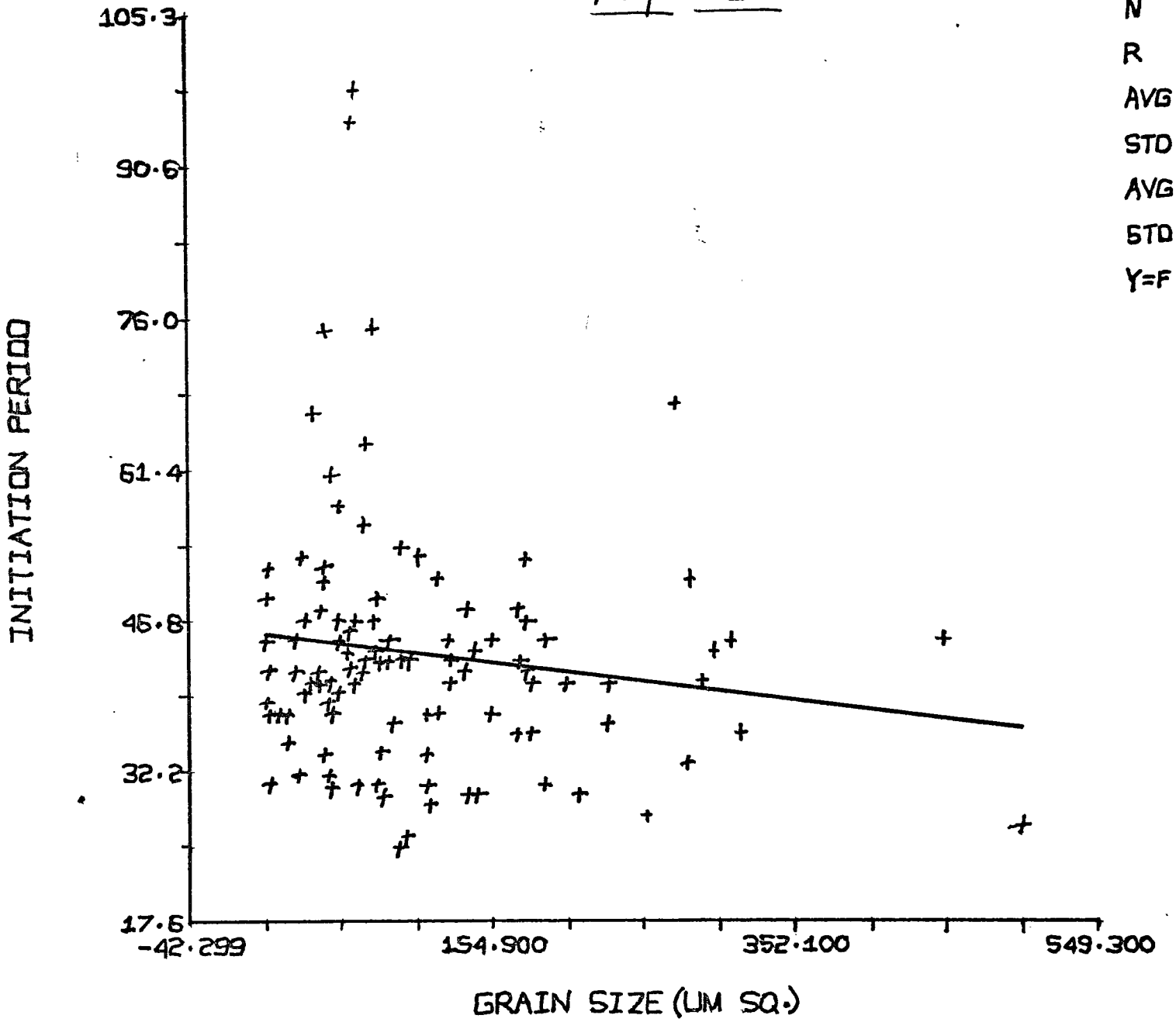

GRAIN SIZE DISTRIBUTION
H2Q with 20g. sulfite per liter pH 11.
4
0
6
2
8
4
1.2
1.6
2.0
2.4
2.8

Fig #2

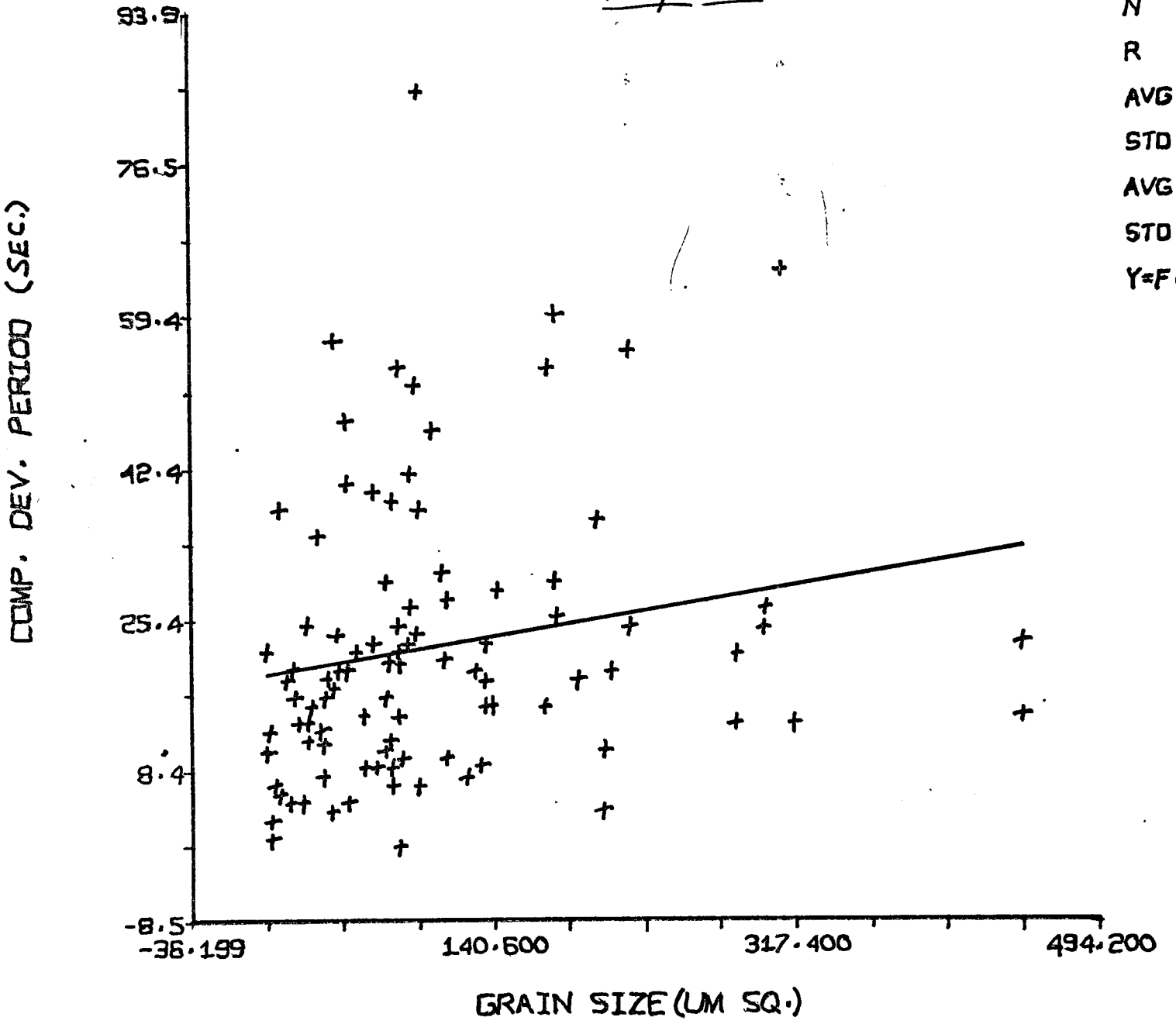
GRAIN SIZE DISTRIBUTION
H_2Q with 0.5g. sulfite per Liter pH 11.2





N	107
R	-0.14320
AVG X	110.78
STD DEV X	91.65
AVG Y	43.59
STD DEV Y	11.96
Y=F(X) PCT	2.05

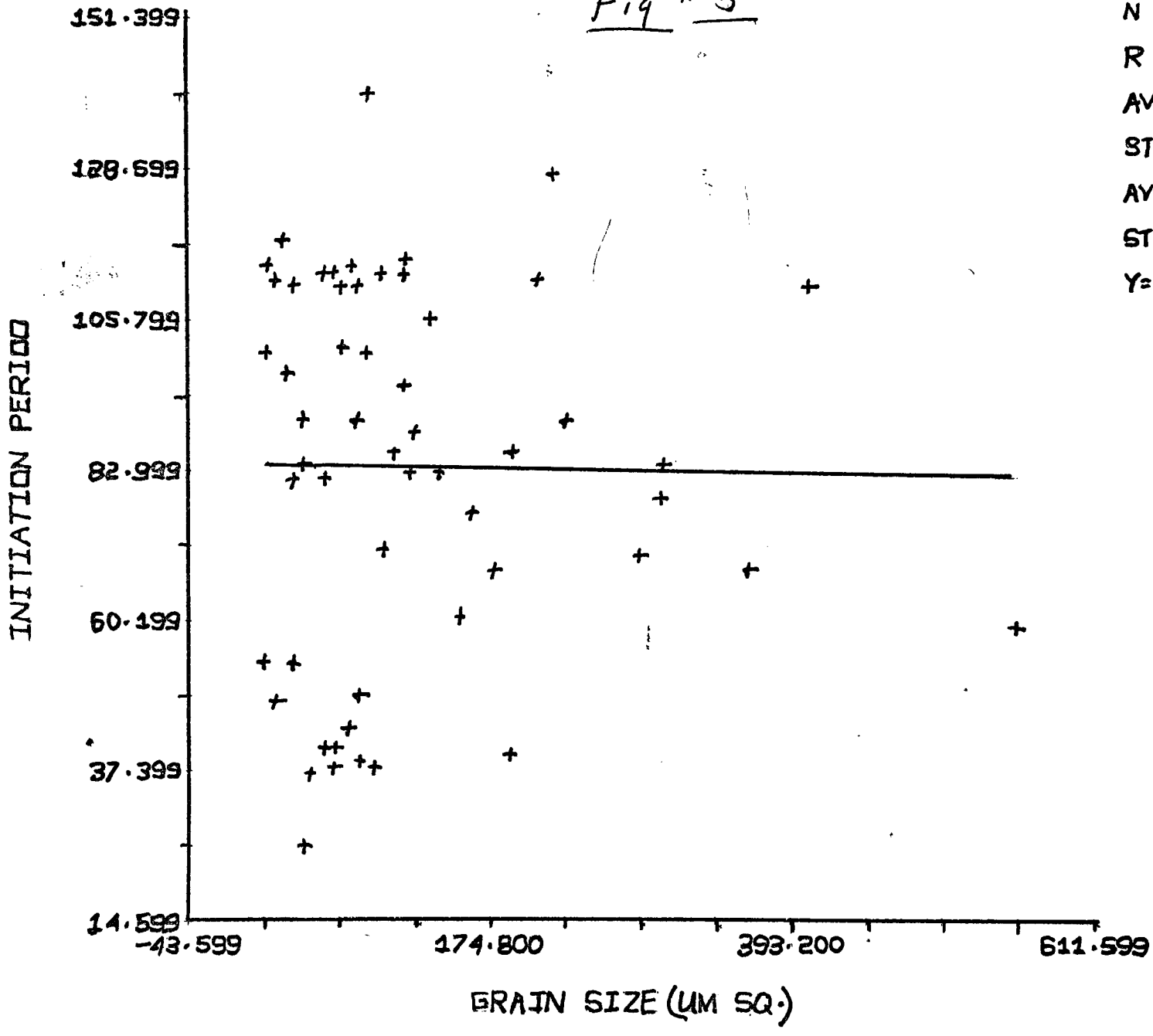
Fig #4



N	96
R	0.188166
AVG X	105.895
STD DEV X	90.054
AVG Y	22.427
STD DEV Y	15.634
Y=F(X) PCT	3.540

206. SULFITE

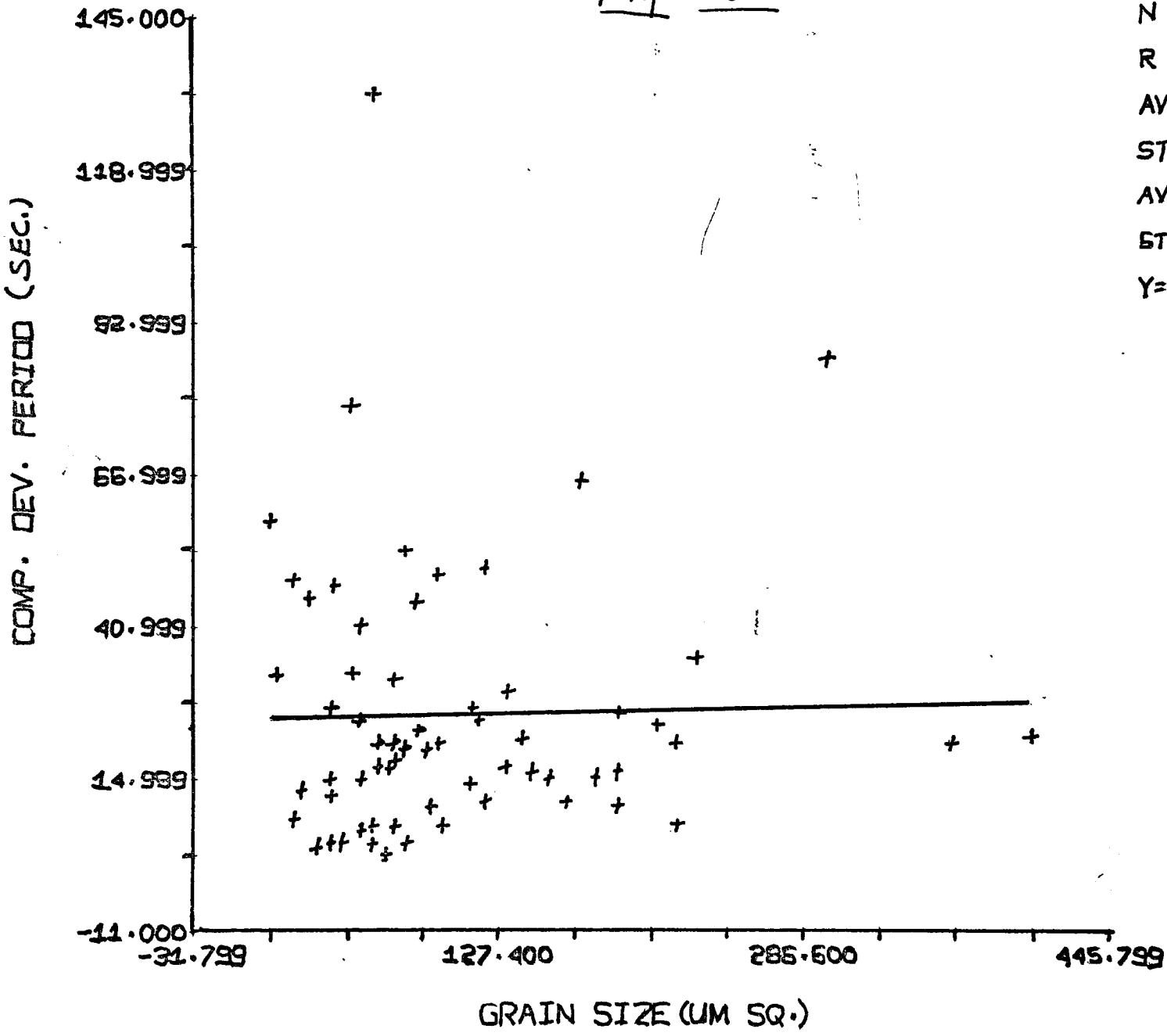
Fig #5



N	55
R	-0.013180
AVG X	117.745
STD DEV X	108.422
AVG Y	83.400
STD DEV Y	28.617
Y=F(X) PCT	0.017

20G. SULFITE

Fig #6



N	65
R	0.025201
AVG X	103.707
STD DEV X	79.598
AVG Y	25.738
STD DEV Y	22.737
Y=F(X) PCT	0.063

0.5% sulfite per liter

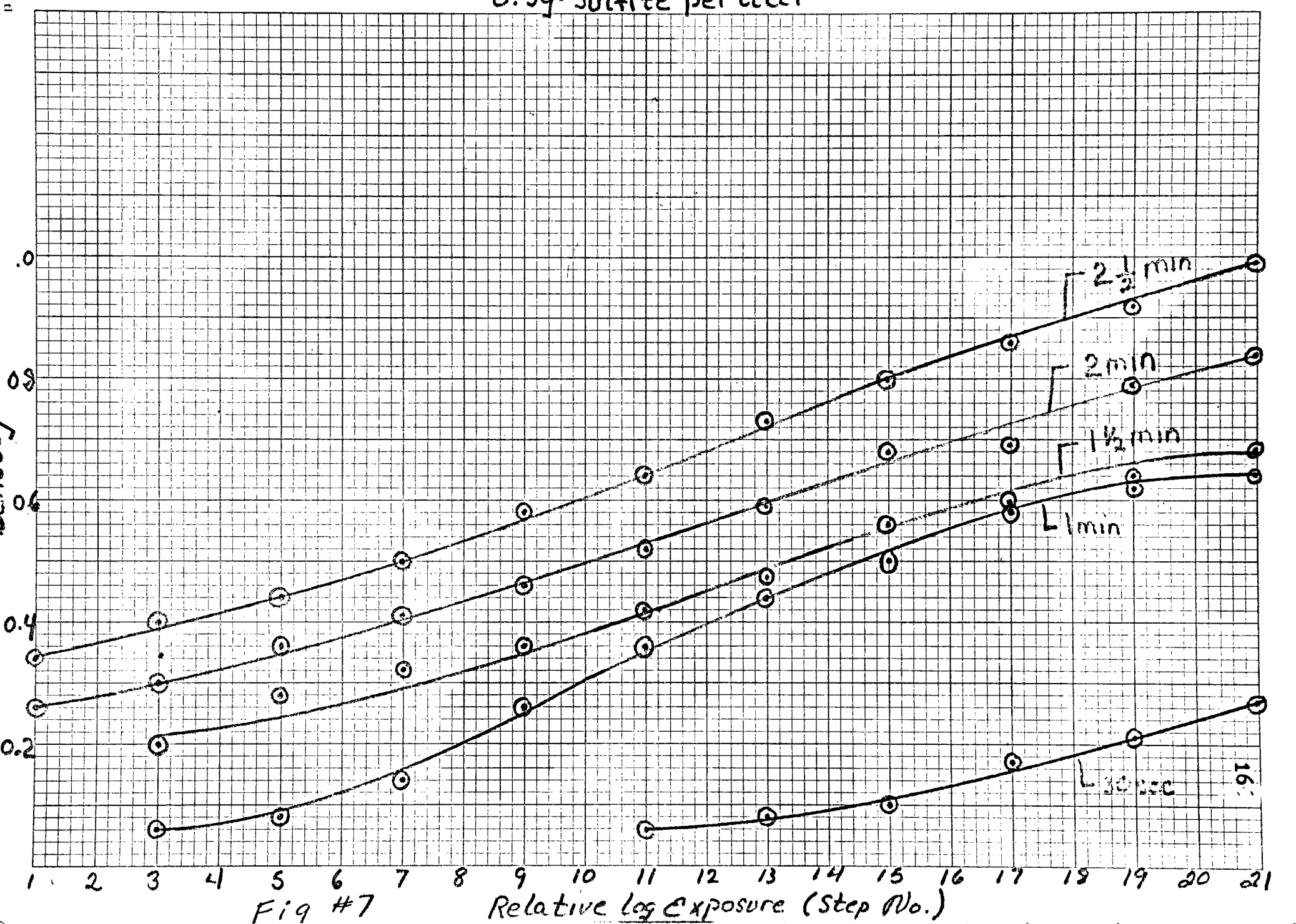


Fig #7

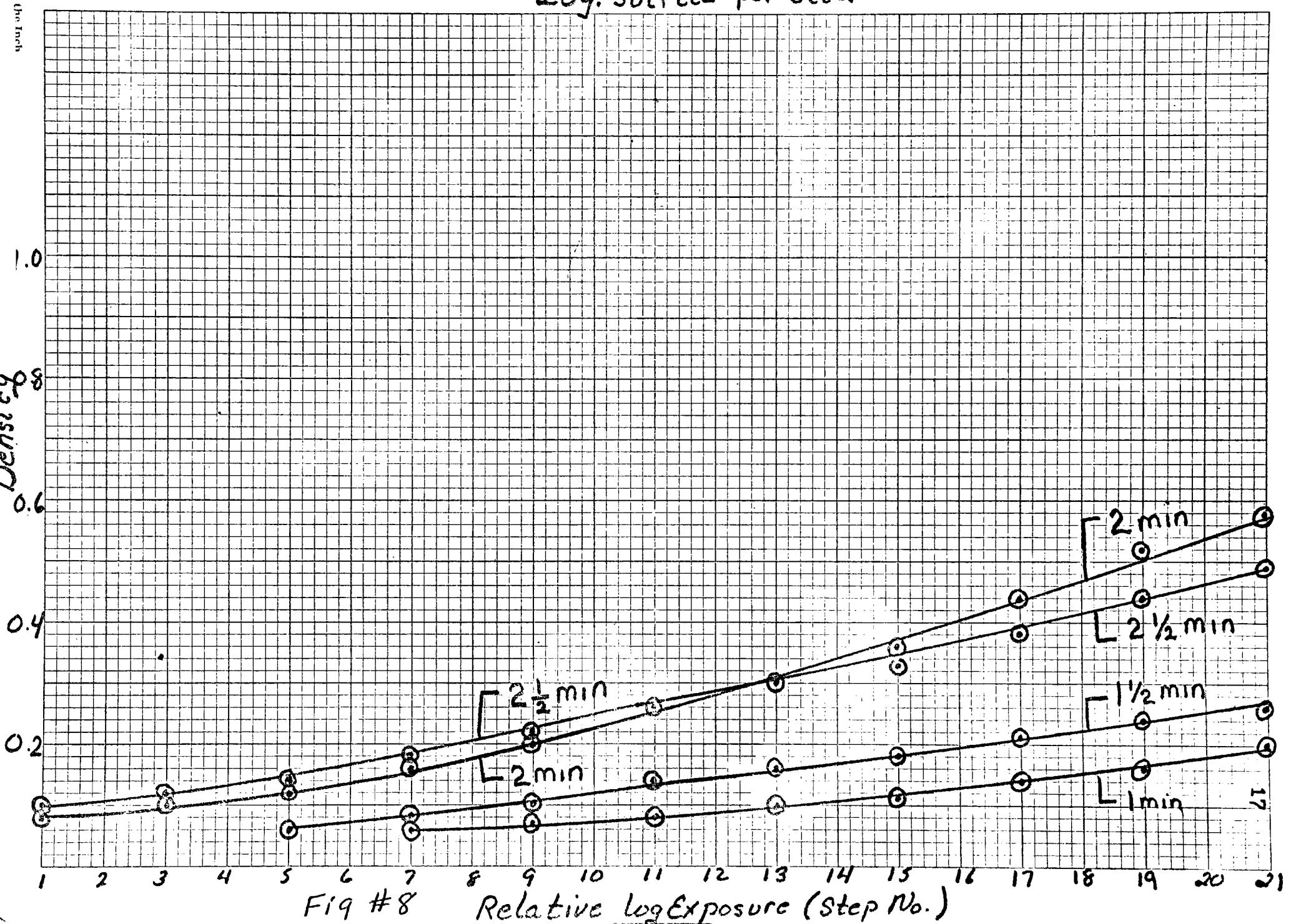

Log. Subject per Step
Density
1.0
.8
0.6
0.4
0.2
2 min
2½ min
2½ min
2 min
1½ min
1 min
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Relative log Exposure (Step No.)

Fig #8

ANOVA - FIG #9

$\alpha = .05$
response variable = initiation period
0.5g. sulfite - hydroquinone developer

SOURCE	SS	γ	MS	RATIO	SIGN.
Runs	884.3	3	294.8	1.85	no
Grain Size	485.8	4	121.5	.76	no
Interaction	866.5	12	72.2	.45	no
Error	9081.8	57	159.3		
TOTAL	11318.4	76			

ANOVA - FIG #10

$\alpha = .05$
response variable = period of complete development
0.5g. sulfite - hydroquinone developer

SOURCE	SS	γ	MS	RATIO	SIGN.
Runs	718.4	3	239.5	2.07	no
Grain Size	959.2	4	239.8	2.07	no
Interaction	320.9	12	26.7	.23	no
Error	5316.3	46	115.6		
TOTAL	7953.1	65			

ANOVA - FIG #11

$\alpha = .05$
response variable = initiation period
20g. sulfite - hydroquinone developer

SOURCE	SS	γ	MS	RATIO	SIGN.
Runs	6680.85	2	3340.4	3.29	no
Grain Size	857.59	4	214.4	.21	no
Interaction	9986.82	8	1248.4	1.23	no
Error	31429.11	31			
TOTAL	48954.37	45			

ANOVA - FIG #12

$\alpha = .05$
response variable = period for completion of development
20g. sulfite - hydroquinone developer

SOURCE	SS	γ	MS	RATIO	SIGN.
Runs	1831.40	3	610.47	2.32	no
Grain Sizes	63.927	4	15.98	.061	no
Interaction	5672.5	12	472.71	1.80	no
Error	9993.2	38	262.98		
TOTAL	17561.09	57			

ANOVA - FIG #13

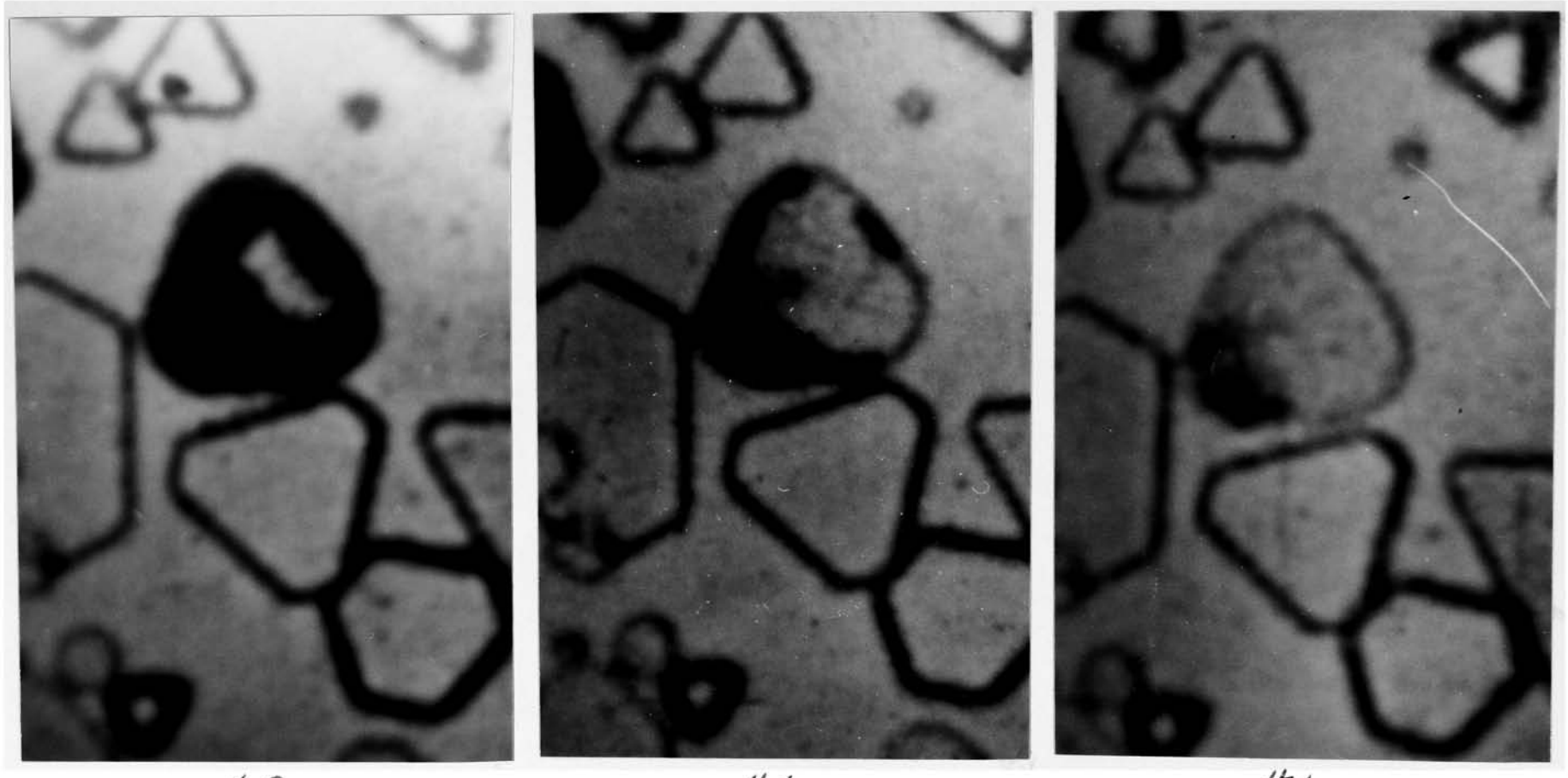
$\alpha = .05$
response variable = initiation period
0.5g sulfite developer vs. 20g sulfite developer

SOURCE	SS	γ	MS	RATIO	SIGN.
Developers	8528.5	1	8528.5	17.09	yes
Error	8980.1	18	498.9		
TOTAL	17508.5	19			

ANOVA - FIG #14

$\alpha = .05$
response variable = period of complete development
0.5g sulfite developer vs. 20g sulfite developer

SOURCE	SS	γ	MS	RATIO	SIGN.
Developers	16.2	1	16.2	.113	no
Error	2562.6	18	142.36		
TOTAL	2578.8	19			



#3 #2 #1

Fig. #15 Mechanism of "Litho" developer

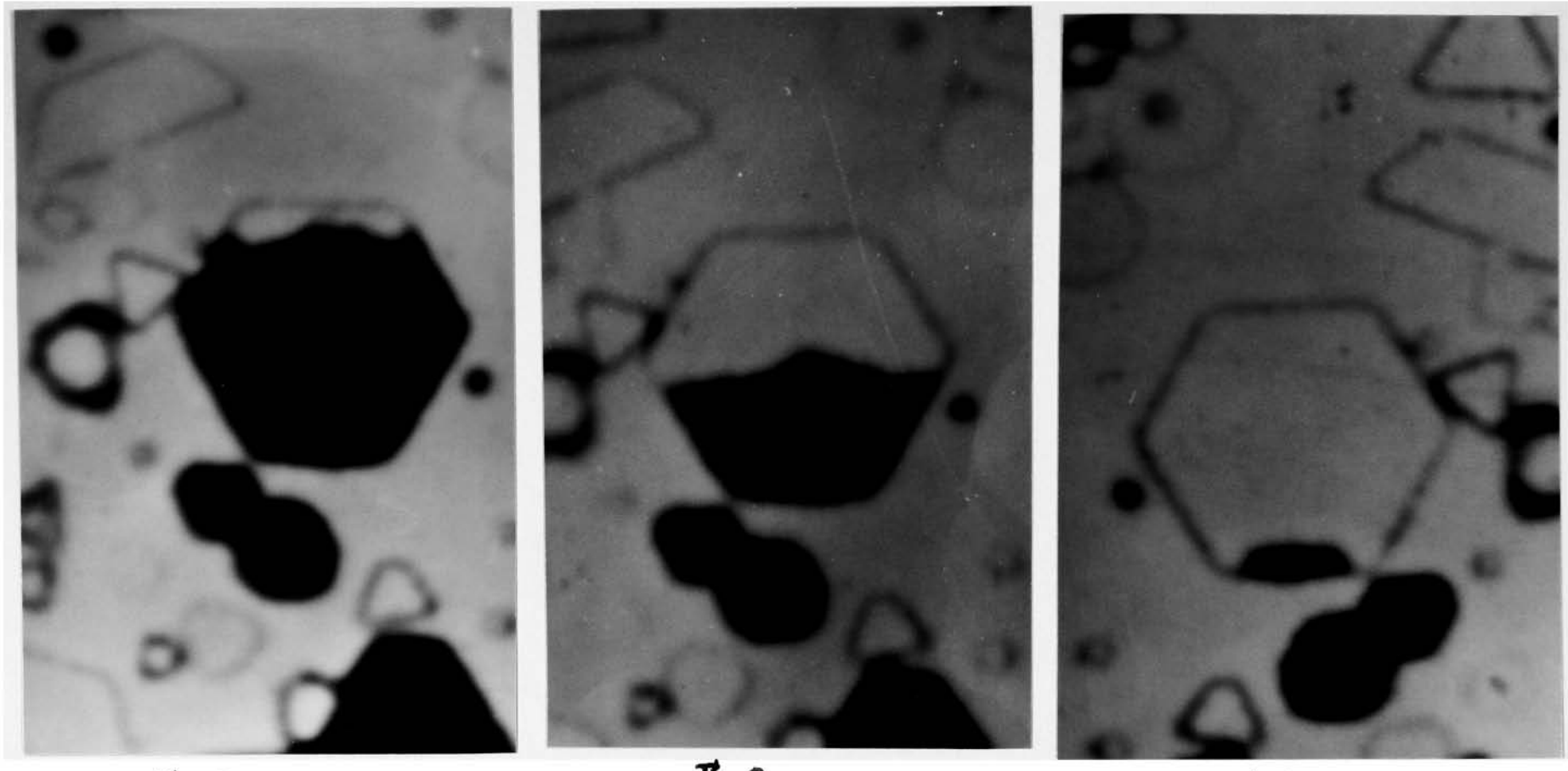


Fig. #16 Mechanism of Normal Developer

SUMMARY AND CONCLUSIONS

The sensitometric curves do show, on a macroscopic scale, a significant sensitometric difference betwen the two developers.

Through the use of the statistical tool, the analysis of variance it was determined that there was no significant difference between runs for either developer using the initiation period or the period of complete development as response variables.

There were no functional relationships between grain sizes and initiation periods for the 0.5g and 20g. sulfite hydroquinone developers, nor were there functional relationships between grain sizes and periods of complete development for the same developers.

There is a significant difference between the 0.5g sulfite developer and the 20g sulfite developer with respect to initiation period. The average initiation period for the 0.5g sulfite is 44 sec. as compared with the 83 sec. average initiation period for the 20g sulfite. Turbide and Williams found just the opposite of this result. As the sulfite level

increased the initiation period decreased. A guess as to why the difference might be explained by the difference in development mechanism for the two developers (Figs. 15 & 16). There is no significant difference between the 0.5g sulfite developer and the 20g sulfite developer with respect to period of complete development.

Dr. Eger[1] described two types of development which are dependent upon the composition of the developer and to some extent on the exposure conditions. The first type is the "accretion development" which spreads throughout the grain from one or a few initiation points. Accretion development occurred when there was a small number of active nuclei and the developer showed marked initiation period. Accretion development was noticed in the runs for the 20g sulfite-hydroquinone developer. The second type is Dr. Eger's "infectious development" in which protruberances from one developing grain start development in another. This definition of "infectious development" was not seen in the runs for the 0.5g sulfite developer.

The litho type developer attained a greater gamma as compared with the normal hydroquinone developer after 1 minute development. This suggests that the rate of development for the litho developer is greater than for the normal developer. This agrees with our previous results, the litho developer had a shorter initiation period than the normal developer.

The results of this evaluation are useful only as an example of a possible statistical analysis for films of a similar nature. This particular emulsion has definite drawbacks- its large grains are not typical of practical emulsions, and it is not chemically sensitized.

LITERATURE REFERENCES

[1]Hans Eger, "Infrared Microcinematographic and radiochemical investigations of Photographic Development," Dissertation, Tech. Hochschule Munchen, 1969.

[2]Gorokhovskii, Polovtseva, Shamsheva, Ushechi Nauchn, "Kinetics of the Initial Stage of Photographic Development," FOT 13 3041, 1968.

[3]Zwicky, H., "The Mechanism of Litho Development," Photo. Korr. v. 107, 1971.

[4]James, T.H., "The charge Effect in Relation to the Kinetics of Photographic Development III, The Abnormal Behavior of Sulfite-Free Caustic HQ Developers," J. Franklin Inst. 240, 1945.

[5]James, T.H., "The Initiation of Development," J. Photo. Sci. v19, 1971.

[6]Karrer, J., Berg W.F., "The Induction Period of Photographic Development," SPSE Conference Summary, May 1970.

[7]Zwicky, H., "Some Studies of Litho Development," Photo. Korr., 1966.

[8]Jaenicke, W., "Mechanism of the Development of Single Grains," Photographic Science, Zurich, 1961.

[9]Meidinger, "Studies of the Photographic Development Process," Physik z36, 1935.

[10]Frotschner, H., Photogr. Korr., 27, 801, 1937.

[11]Yule, J.A.C., J. Frank. Inst., 239, 221, 1945.