

#1102-8 THE INSTITUTE OF PAPER CHEMISTRY
(Physical Chemistry)
Project Reports (5)

Institute of Paper Science and Technology
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PROJECT REPORT FORM

Copies to: Central Records
John W. Swanson
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PROJECT NO. 1102-8
COOPERATOR The Institute of Paper Ch.
REPORT NO. 24
DATE January 13, 1969
* NOTE BOOK 1653:76, 77, 81-86, 98-103,
* 108-100, 114, 122-
* 108-100, 114, 122-
SIGNED *C. Y. Chu*
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*Also Notebook 2684:43-45, 49-52,
59-119

ORIENTATION STUDIES - COLLOID CHEMISTRY

STUDIES IN DEPOSITABLE PITCH

INTRODUCTION

One of the problems encountered in evaluating pitch control agents in papermaking systems is the matter of having a suitable reference pulp. In the past, Mitscherlich spruce sulfite pulp was used for this purpose but it has become increasingly difficult to obtain this pulp in suitable form for evaluation. Hence, a part of the present study was devoted to the preparation of an artificially induced pitchy pulp for use in the canister deposition technique.

The canister technique, as presently employed, has several serious drawbacks. The primary disadvantage is its cost. At best, two determinations can be made per day and, because of this time requirement, changes in the depositable nature of reference pulp frequently occur during the course of a series of tests. Hence, the need for a more rapid but precise method for measuring depositable pitch is apparent. The Meseran which measures the evaporation rate of a radiochemical has been examined for this purpose.

SUMMARY

In studies concerned with the preparation of a reference pitchy pulp it was found that incorporation of solvent solutions of several fatty acid and resinous products into Weyerhaeuser bleached sulfite pulp would provide satisfactory levels of deposit as measured by the canister technique. Included among these materials were Distal 42 (a commercial fatty acid product), a 3:1 mixture of Distal 42 and rosin, and the alcohol-benzene extract from Weyerhaeuser bleached sulfite pulp. In general, incorporation of 0.1 or 0.2% of these materials produced 25-60 milligrams of deposited pitch. The comparable addition of palmitic or oleic acids produced notably less pitch with the unsaturated acid showing the higher level of the two.

Subsequent tests utilizing induced pitchy pulp revealed that talc was not as effective in controlling pitch in such pulps as it is in natural pitchy pulp.

Orientation experiments with the Meseran show that the evaporative rate process is capable of detecting microgram quantities of deposited pitch but the reproducibility of the method was quite poor and would, therefore, not lend itself to a routine control test.

The major problem with the Meseran technique appears to be the reproducibility of the surface of the slide upon which the pitch is deposited. Other problems include the purity of the solvent used for desorbing the pitch from the slide and the thoroughness of the desorption process.

EXPERIMENTAL

I. INDUCED TROUBLESOME PITCH

- A. Preparation of Resinous Materials for Evaluation
- B. Dispersion of Talc
- C. Preparation of Pulp Slurry for Canister Technique
- D. Determination of Depositible Pitch by Canister Technique

II. DETERMINATION OF DEPOSITABLE PITCH BY MESERAN PROCEDURE

- A. The Meseran Measurement
- B. The Calibrations
- C. Preparation of Pitch Sample Drop
- D. Preparation of Mitscherlich Pulp Slurry for Meseran Determination

I. INDUCED TROUBLESOME PITCH

A. Preparation of Resinous Materials for Evaluation

1) Distal 42

Distal 42 is an Archer-Daniels-Midland product of unsaturated fatty acids. A 20% solution in pet ether was prepared.

2) Rosin

Rosin lumps were ground into powder, and dissolved in either ethyl alcohol or diethyl ether to provide 20% solution

3) Mixture of Rosin and Distal 42

A 20% solution of 1:3 rosin to Distal 42 in diethyl ether was prepared.

4) Weyerhaeuser Bleached Sulfite Extract

Pulp was torn into small pieces and extracted in a Soxhlet

for about eight hours with a 1:2 ratio of ethanol to benzene.

The extractives were concentrated in the following ways:

- a. To a point just short of precipitation, and
- b. To dryness, and then redissolved in diethyl ether.

5) Palmitic and oleic acid--20% solutions were prepared.

B. Dispersion of Talc

Mistron vapor talc was dispersed at 10% solids in distilled water with a Lightnin' stirrer for about 10 minutes.

C. Preparation of Pulp Slurry for Canister Technique

The pulp used for these experiments was Weyerhaeuser bleached sulfite (WBS) which was soaked in deaerated, distilled water for one-half hour and disintegrated with a Lightnin' stirrer at 3.3% consistency.

The pulp slurry was then adjusted to pH 7 by either diluted sodium hydroxide or acid. The pH value was also measured after stirring in the canisters.

D. Determination of Depositible Pitch by Canister Technique

The equivalent of 63 g. oven-dry pulp was weighed into each of two 3-liter beakers. Each batch of pulp was diluted with the distilled water which was boiled for five minutes in vacuo to a volume of 1900 milliliters. A Lightnin' stirrer was used to disintegrate the fibers. This was the point at which the resinous materials or talc was added. The pulp slurry was then transferred from the beakers to the canisters and locked into place in the stirring

apparatus in a water bath at 100°F. The stirring at 1100 r.p.m. lasted for exactly two hours. The pulp was then removed from the canisters and the walls of the canisters were rinsed with deionized water. After measuring the pH, the pulp was discarded.

An alcohol-benzene pre-extracted cotton swab and 100 ml. of 1:2 by volume of alcohol-benzene was then used to clean the canister walls, cover, and stirring propeller. The pitch solution was poured into a 600-ml. beaker. The canister walls, stirrer, and cover are swabbed twice more with the same cotton using 100 ml. of fresh solvent for each wash. The rinsings are added to the 600-ml. beaker. The cotton swab is then extracted with the mixture of alcohol-benzene for 1-1/4 hours in a Soxhlet extractor. The extracting liquid is then added to the 600-ml. beaker. The extracting flask was rinsed with some fresh solvent and the rinsings combined with the pitch solution. The pitch solution was filtered in vacuo through a funnel filled with a pad of celite filter aid. The beaker was rinsed with some fresh solvent. The filtered solution was then poured into a clean 600-ml. beaker and the flask was rinsed with fresh solvent. The pitch solution was concentrated to about 25 ml. and then transferred quantitatively to a tared 100-ml. beaker. The concentrated solution was cautiously further concentrated to almost dryness under a jet of air. The beaker was then placed in a vacuum desiccator over calcium chloride to constant weight.

II. DETERMINATION OF DEPOSITABLE PITCH BY MESERAN PROCEDURE

A. The Meseran Measurement (Ametek Corporation)

The sample surface to be analyzed is slipped under the dispersing pump, and .02 ml. of the test solution is metered onto the test surface. A special thin end-window Geiger-Mueller detector is then immediately positioned over the solution. Metered nitrogen gas is allowed to flow between the test surface and the detector window. The beta emissions from the labeled material remaining on the surface are monitored and the pulse data are fed into a small computer. The computer expresses it as either cumulative count or plots the data on a strip chart recorder.

Many test solutions are provided with this equipment, but only two were used for this study. They were:

1. TSBK - This solution contains a C_{14} radio Tridecane in the solvent cyclopentane
2. TSAj20p - This solution contains a C_{14} radio tetrabromoethane in the solvents 80% trifluorotrichloroethane and 20% tetrahydrofuran.

The conditions chosen for this study were as follows:

Test solution TSBK, TSAj20P

N_2 flow rate - 2.5/50; 2.5/15

Preset - 3 seconds

Temperature - 23.5°C.

B. The Calibrations

Benzene-alcohol extract from WBS pulp was used for both TSBK and TSAj20p test solutions.

C. Preparation of Pitch Sample Drop

A stainless steel slide, polished with Bon Ami or pumice, washed and boiled with deionized water, was dipped into a moving pulp slurry in a set angle for a given time. This slide was then extracted with the solvent. The solvent was concentrated to almost dryness and made up to 2 millileters with the solvent. Twenty-five λ of this concentrated solution was used to form a sample drop on the concave part of a glass spot plate for the Meseran test.

D. Preparation of Mitscherlich Pulp Slurry for Meseran Determination

Fresh Mitscherlich pulp obtained from Consolidated Papers, Inc. was beaten in the standard manner in our 1-1/2-lb. beater to a certain freeness. The unbeaten and beaten pulp slurries were stored in the cold room for further use with a few drops of formaldehyde added.

RESULTS AND DISCUSSION

I. INDUCED TROUBLESOME PITCH

Depositible pitch results for the various pitch-inducing agents are recorded in Tables I-III.

It is evident from the results in Table I that Distal 42, a 1:3 mixture of rosin and Distal 42, and the alcohol-benzene extract of Weyerhaeuser bleached sulfite pulp produce substantial levels of depositible material as measured by the canister technique. Past experience with Mitscherlich sulfite pulp as a reference has shown that the well beaten pulp will provide 30 to 40 milligrams of depositible pitch. The current results indicate that incorporation of 0.1-0.2% of the aforementioned materials (Distal, etc.) into Weyerhaeuser bleached sulfite pulp will provide comparable or higher amounts of pitch. However, incorporation of 0.2% of palmetic or oleic acids produced a notably lower level of pitch (Table II) with the unsaturated acid providing the higher level of the two.

From Table II, it is observed that the 0.2% addition of the mixture of rosin and Distal produced 51 and 57 mg. of deposit in duplicate determinations; however, the depositible pitch level decreased only to the range of 17-20 mg. with 2% talc addition. It is further evident that 3% of talc was of no advantage.

In the case of the ethanol-benzene extract from WBS, 2% talc to the 0.1% level of extract reduced the depositible pitch from 36 to 28 mg. When this extract was dispersed in ethanol-benzene rather than in ethyl ether, the depositible pitch at the 0.05% addition level was lowered only from 25

to 14 mg. with 2% of talc. At the 0.2% extract addition, the depositable pitch remained as high as 39 mg. in the presence of 2% of talc. Based on past experience with Mitscherlich pulp, the depositable pitch should be reduced to 10 mg. or less with 2% talc addition. Hence, talc does not appear as effective in the induced pitchy pulp.

Apparently, palmitic acid by itself is not a major contributing factor to a pitchy pulp. When added to the pulp at a 0.2% level, the depositable pitch was only 7 mg. The unsaturated acid, oleic acid, produced 21 mg. at 0.2% level, and was reduced to 13 mg. with 2% addition of talc.

Changing the order of addition of the resin and the talc did not produce consistent effects with respect to depositable pitch as shown in Table 3. These tests were included on the basis that talc may be incorporated into a papermaking system before the pulp is beaten and the pitch released thereby preventing deposition.

TABLE I
 DEPOSITABLE PITCH FROM TREATED WEYERHAEUSER
 BLEACHED SULFITE PULP

Additive, %, Based on wt. of fiber		Solvent	Depositabile Pitch, mg. av.	
Control		Pet ether	13, 9	11
Distal 42,	0.10	" "	24, 26	25
	0.20	" "	55, 59	57
	0.50	" "	119, 143	131
Rosin,	0.10	Ethanol	12, 13	13
	0.20	"	17, 12	15
	0.50	"	21, 14	18
Rosin,	0.10	Ethyl ether	14, 13	14
	0.20	" "	10, 11	11
	0.50	" "	32, 25	29
Mixture of 1:3 of rosin & Distal 42,		" "	26, 22	24
0.10	" "		(1)51, 50	51
0.20	" "		(2)65, 48	57
*Ethanol & benzene extracts from WBS		Mixture of 1:2 of ethanol:benzene	25, --	25
	0.05	"	50, 51	51
	0.20	"	53, 68	61
	0.50	"	178, 147	163
Ethanol & benzene extracts from WBS		Ethyl ether	39, 32	36

*The consistency of pulp slurry was run at 3.0% in this group rather than 3.3% in other trials.

TABLE II

THE EFFECTIVENESS OF TALC IN AN INDUCED PITCHY PULP
 (WBS)

Additive, %, Based on wt. of pulp		Solvent	Depositible Pitch, mg	
				av.
1:3 of Rosin:Distal 42	0.2	Ethyl ether	(1) 65, 48	57
" " "	0.2)	" "	(2) 51, 50	51
" " " + talc	2.0)	" "	(1) 18, 16	17
" " " + talc	2.0)	" "	(2) 20, 19	20
1:3 of Rosin:Distal 42	0.2)	" "	17, 21	19
" " " + talc	3.0)	" "		
Ethanol-benzene extract from WBS	.10	" "	39, 32	36
" " "	.10)	" "		
" " " + talc	2.00)	" "	29, 27	28
Ethanol-benzene extract from WBS	.05	Ethanol-benzene	25, --	25
" " "	.05)	" "	15, 12	14
" " " + talc	2.00)	" "		
" " "	0.20	" "	53, 68	61
" " "	0.20)	" "	41, 36	39
" " " + talc	2.00)	" "		
Palmitic acid	0.20	Ethyl ether	7, 7	7
" " "	0.20)	" "	7, 6	7
" " " + talc	2.00)	" "		
Oleic acid	0.20	" "	20, 22	21
" " "	0.20)	" "	12, 14	13
" " " + talc	2.00)	" "		

TABLE III

THE EFFECTIVENESS OF TALC AND THE ORDER OF MIXING
 (WBS)

Concentration, % on wt. fiber		Solvent	Depositible Pitch, mg.	av.
benzene				
0.1	Ethyl ether	39, 32	36	
0.1)	" "	29, 27	28	
2.0)				
+ Talc				
2.0)				
Talc +				
benzene	" "	22, 18	20	
.1)				
Distal 42	Ethyl ether	65, 48	57	
0.2)	" "	20, 19	20	
2.0)				
+ Talc				
2.0)				
Talc +	" "	22, 23	23	
Distal 42				
0.2)				
Distal 42	" "	26, 22	24	
0.1				
0.1)	" "	14, --	14	
2.0)				
+ Talc				
2.0)				
Talc +	" "	21, 20	21	
0.1)				

II. MESERAN MEASUREMENTS

Preliminary tests were carried out to test the response of the Meseran to microgram quantities of pitchlike deposits. The alcohol-benzene extract from WBS was used for this purpose. Either a flat surface or a concave slide may be used to hold the sample drop for the Meseran measurement. However, for the present work it was much easier to form an even drop in the concave part of a slide. Although the instrument supplier claims the total test time is less than two minutes, it was found that in many cases one or two intervals were not enough; in other words, the larger the sample size the longer the counting time required. From Figure 1, the data from four intervals (56 sec. is an interval) gave a much steeper slope than the data from one interval.

It was found that glass spot plates with three rows of concave depressions on them are very helpful for these studies. Because of the thickness of the plate, it was necessary to adjust the detecting window 7/16 of an inch higher in order to have room for the plate underneath. Because of this, as can be seen from Fig. 2, the total count from the same concentrations of pitch from the glass spot plate is lower than from the ordinary glass slide. Results of preliminary calibrations (Fig. 1 and 2) were, in general, quite encouraging and, on this basis, more complete calibrations with the benzene-ethanol extract and TSBJ and TSAj20p test solutions were then undertaken. These results, presented in Fig. 3 and 4, were not as good as was expected, especially in Fig. 4 in the area of low concentrations when the TSAj20p test solution was used. It is assumed that at the high concentrations the film area was the same, but the film thickness different. Consequently,

K&S DATA BY THE CENTIMETER 46 1510
MADE IN U.S.A.
KODAK SAFETY FILM

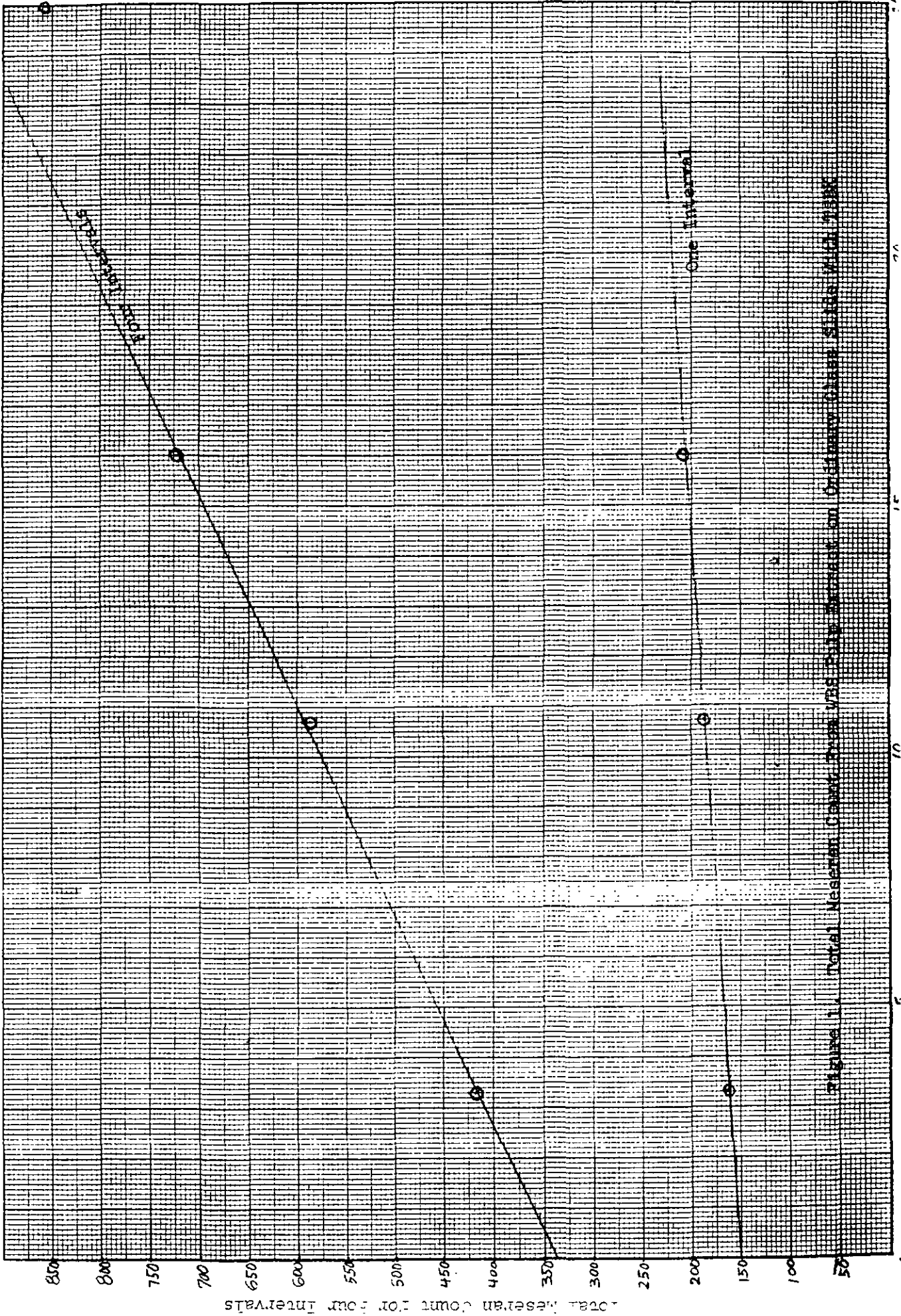


Figure 1. Total Meseran Count from 175-200 μm Interval on Ordinary Glass Slides with 110X

NO. 2
MADE IN U.S.A.
DATA CORRECTOR

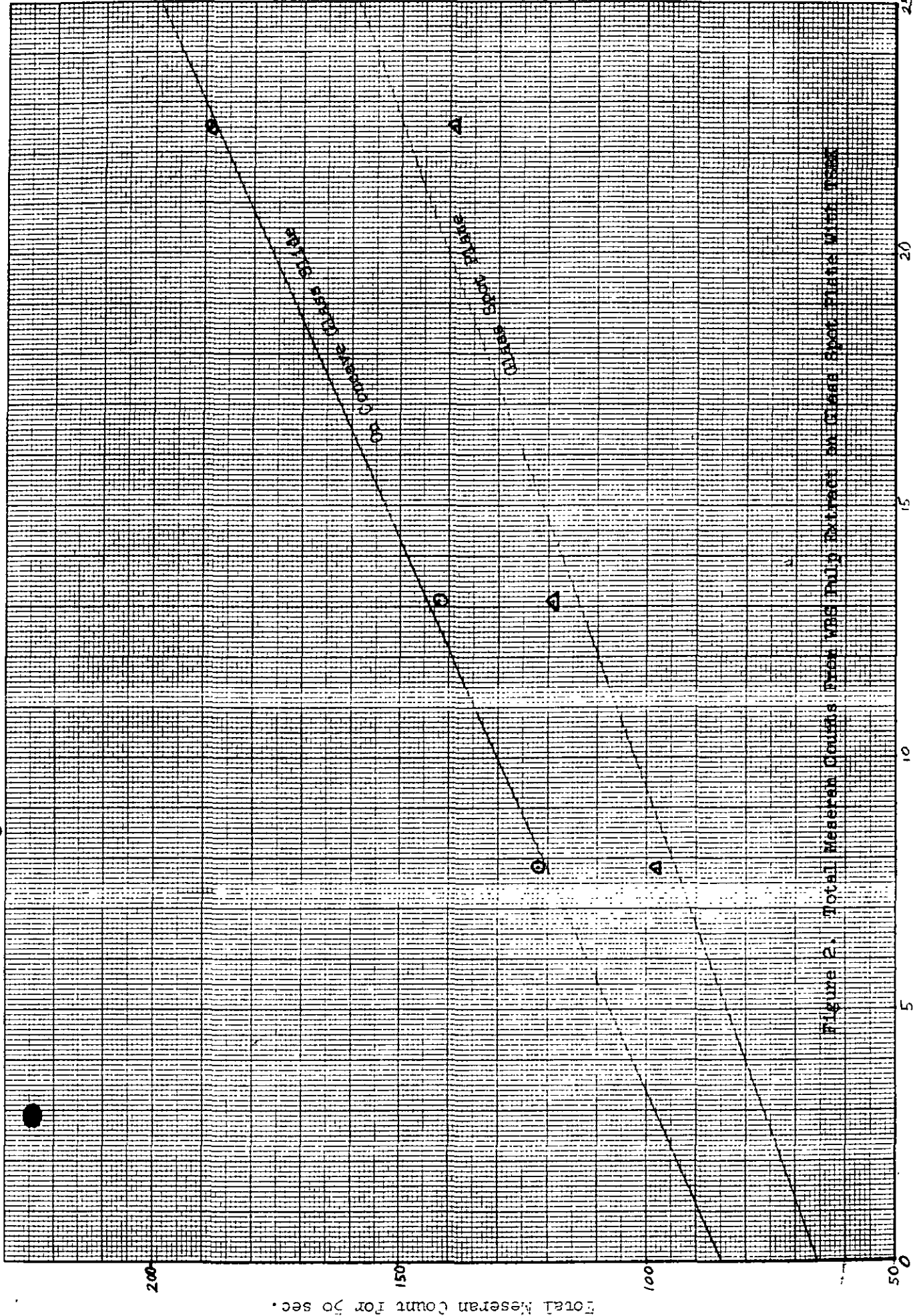


Figure 2. Total Meseran Counts From VBS Pulp Extract on Class Spot Plate With VBS

Total Meseran Count For 30 sec.

25
20
15
10
5
50
100
150
200

Model 46-1510
GEORGE EASTMAN COMPANY
PHOTOGRAPHY

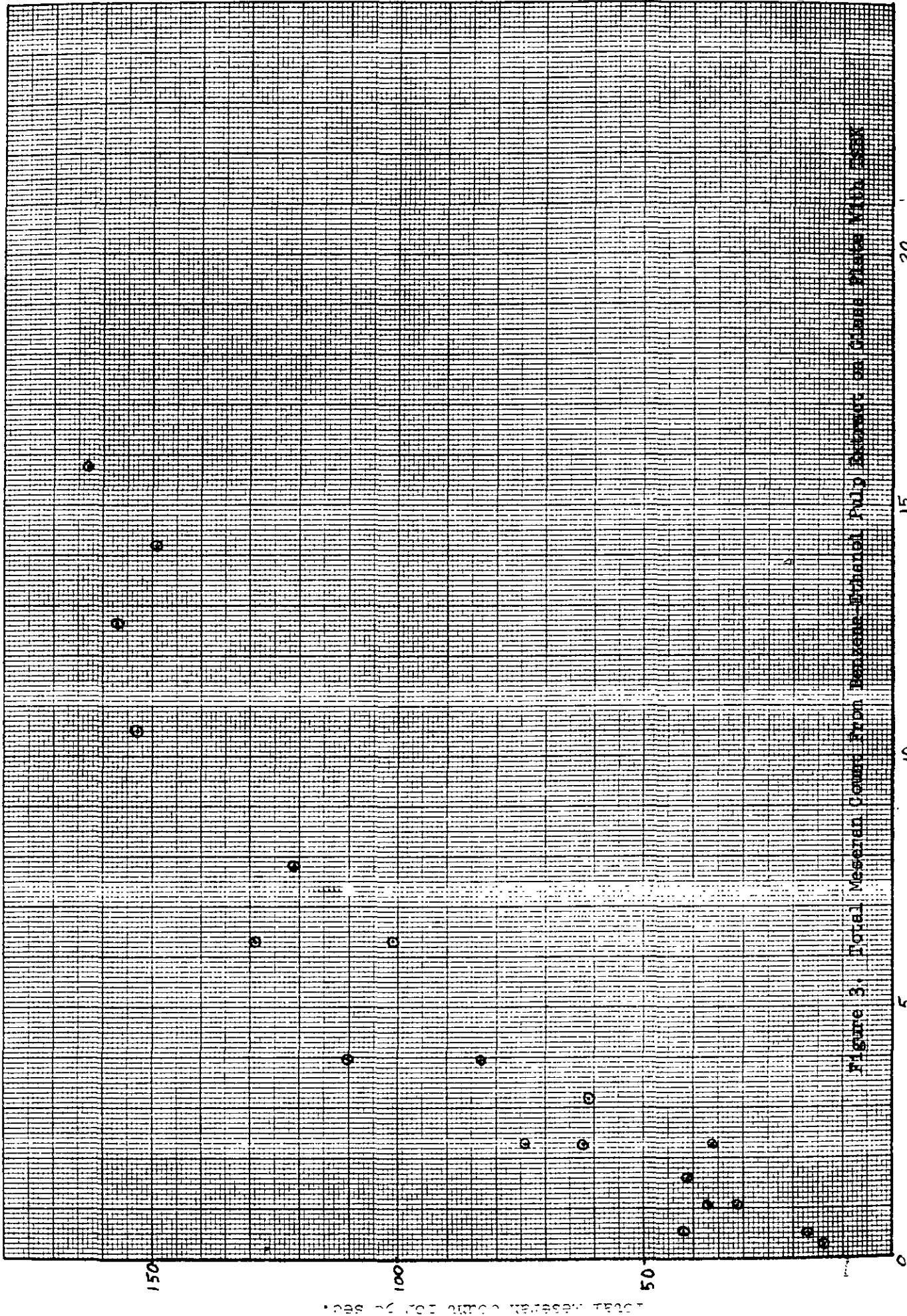


Figure 3. Total Meseren Count From Benzene-Soluble PULP Extract as Given Table VIII 1958

when the test solution was added, more radioactive chemical was trapped in the thicker film. However, when dealing with extremely low concentrations, the film area was much smaller due to the lack of residue; therefore almost no radioactive chemical was trapped and reliable readings could not be obtained.

In subsequent tests, efforts were made to deposit pitch from either WBS or fresh Mitscherlich sulfite pulp onto a stainless steel slide and to measure the amount of the deposit with the Meseran. A 1 x 3-inch slide was dipped in a suspension of the pulp contained in a glass battery jar. The stainless steel plate was immersed 2.5 inches into the pulp suspension which was agitated at a fixed speed with a Lightnin' stirrer at room temperature.

A. The Effect of Depositing Time

The benzene-alcohol extract from WBS was incorporated into a 0.5% slurry of unbeaten WBS and the Meseran count was measured as a function of contact time. The results are presented in Table IV. It was learned that even at five minutes depositing time, the difference was 40 counts between a pitchy pulp containing 2% benzene-ethanol extract and its control; 30 minutes depositing time didn't increase the count, but the difference in count increased to 98 at 120-minute level when compared to its control.

B. Method of Desorption

From Table V the results indicate desorption procedure No. I is much more effective than desorption procedure No. II. In Procedure I, the slide was desorbed repeatedly with fresh solvent and the washings were combined in a beaker. By comparing the depositing conditions from Tables IV and V, it is noted that pitch deposition favors the combination of higher pulp consistency and speed.

TABLE IV
 PITCH DEPOSITING TIME AND MESERAN COUNT

<u>Depositing Conditions</u>	<u>Measuring Conditions</u>					
Pulp consistency - 0.5%	Test solution - TSBK					
pH - 7	N ₂ flow rate - 2.5/15					
Benzene-ethanol extract - 2% (Based on the wt. of pulp)	Temperature - 23.5°C.					
Variac setting - 52	Preset - 3 seconds					
Depositing angle - 80°	Substrate - glass spot plate					
Substrate - stainless steel						
	<u>Control</u>			<u>2% Induced Pitch</u>		
Depositing time, in min.	5	30	120	5	30	120
Total count of first interval (56 sec.)	290	302	291	330	342	389
Counts due to pitch				40	40	98

TABLE V
 METHODS OF DESORPTION AND MESERAN COUNT

<u>Depositing Conditions</u>	<u>Measuring Conditions</u>			
Pulp consistency - 2%	Test solution - TSBK			
pH - 7	N ₂ flow rate - 2.5/15			
Benzene-ethanol extract - 0.5%	Temperature 23.5°C.			
Variac setting - 110	Preset 3 sec.			
Depositing angle - 90°	Substrate - glass spot plate			
Substrate - stainless steel				
	<u>Control</u>		<u>0.5% Induced Pitch</u>	
Depositing Time, in min.	5	5	5	5
Total counts of first interval (56 sec.)	382	422	402	402
Counts due to pitch		40	20	
Desorption procedure	1	1	2	2
Desorption Procedure No. 1 -- Flushed the slide with benzene-ethanol mixture from a wash bottle several times into a beaker.				
Desorption Procedure No. 2 -- Immersed the slide into a beaker full of benzene-ethanol mixture for about two hours.				

C. Application of the Meseran Technique to Mitscherlich Pulp

From Table VI, Part A, the results were irregular and unexplainable. The total count from the highly beaten pulp (S.-R. freeness = 90) was less than the unbeaten pulp. It was assumed that the error might be due to one of the following reasons: (1) Different surface phenomena on different slide surfaces, and (2) counting time of 56 seconds may not have been enough to reveal the true picture of the sample. Therefore, more trials in this direction were conducted. The results are presented in Table VI, Part B. From these results it was felt that another procedure for cleaning the slides was necessary. Also, a longer counting time was required if the data were to be meaningful.

D. Factors that Affect the Surface of a Stainless Steel Slide for Use in the Meseran Test

Variations in this study included smooth and dented stainless steel slides, Bon Ami and pumice cleaning powders, TSBK and TSAj2Op test solutions. The results presented in Table VII show that the solvent alone contributed quite a bit of residue. Counts that were due to Bon Ami cleaning powder particles on the dented slide were 326, it was 492 on the smooth slide. This indicates that the surface of this smooth slide (unfortunately we called this slide "smooth" at the beginning!) is actually rougher than the dented one. Therefore, more particles were held onto the rough surface than were on the dented slide. There were no discernible differences in using either Bon Ami or pumice for cleaning purposes.

At the suggestion of Dr. Anderson (Ametek Corp.), test solution TSAj2Op was included in subsequent tests.

TABLE VI

DEGREE OF BEATING OF A MITSCHERLICH PULP AND MESERAN COUNT

A.

<u>Depositing Conditions</u>	<u>Measuring Conditions</u>					
Pulp consistency - 1.57%	Test solutions - TSBK					
pH - 7	N ₂ flow rate - 2.5/15					
Variac setting - 115	Temperature - 23.5°C.					
Depositing angle - 80°	Preset - 3 seconds					
Substrate - stainless steel	Substrate - glass spot plate					
Degree of beating, as freeness in cc.	850		220		90	
	1	2	1	2	1	2
Depositing time, min.	5	5	5	5	5	5
Total count of first interval (56 sec.)	343	318	327	314	296	292

B.

Same depositing and Meseran conditions as described in A except for using the same slide for depositing for all trials

	Cleared Slide			Cleared Slide		
Degree of beating, as freeness in cc.	--	850	90	--	850	90
Depositing time, min.	--	5	5	--	5	5
Total count of first interval (56 sec.)	370	396	340			
Total count of 8 intervals (448)				1010	779	1170

TABLE VII

COMPARISON OF VARIOUS SURFACE PHENOMENA OF
 A STAINLESS STEEL SLIDE AND THE CORRESPONDING MESERAN COUNTS

Measuring Conditions:

Test solution	TSBK, TSAj20p
N ₂ flow rate	2.5/15
Preset	3 seconds
Temperature	23.5°C.
Count	8 intervals

Test Solution	TSBK	TSBK	TSBK	TSBK	TSAj20p	TSAj20p
Type of Slide (stainless steel)	--	Dented	Dented	Smooth	--	Smooth
Type of Cleaning Powder	--	Bon Ami	Pumice	Bon Ami	--	Bon Ami
Total Meseran Count of Eight Intervals	987	1313	1312	1479	546	573
Counts Due to Cleaning Particles	--	326	325	492	--	27
Remarks	270 ml. solvent			270 ml. solvent		

Modified procedure used for these trials for cleaning the slide:

1. Polish the slide with Bon Ami or pumice powder
2. Wash the polished slide with deionized water from a wash bottle
3. Boil the polished and washed slide with deionized water for about 1/2 hr.

Modified procedure used for these trials for preparation of sample solution:

1. Extract the slide three times with fresh hot solvent (10 min. each)
2. Filter the total amount of extract
3. Evaporate the total filtrate to about dryness, then make up to 2 ml. with the mixture of ethanol-benzene

It is noticed in Table VIII that there was no resinous material deposited on the stainless steel slide for the unbeaten pulp because the count from that sample was as low as the count from the combination of cleaned slide and the same amount of solvent used for the pulp sample. For the beaten sample, the final result has yet to be checked because the readings from two separate runs did not coincide. For unknown reasons, one was as low as the control and the other was about 167 counts higher than the control or unbeaten sample. Unfortunately, the data fall in the low concentration range in the calibration curve where accuracy is in question.

Further studies in this area might utilize a sample size which is five to eight times larger than that used in these experiments. In this size range, the total count from Meseran measurement for eight or more intervals can then be expected to be in the range of 1000 to 1500 counts where accuracy is more dependable.

CONCLUSION

The Meseran instrument is relatively simple to operate and requires only a few micrograms of sample. Because of this, the method of preparing the sample for testing is very critical and painstaking. The surface roughness of the slide changes every time it is cleaned, and there is an uncertainty concerning the complete absence of cleaning powder particles on the slide surface. These are the two most difficult factors to combat among those factors which affect the rate of evaporation.

On the basis of these experiments, it is concluded that the Meseran technique is of doubtful applicability in practical pitch determinations.

TABLE VIII

<u>Depositing Conditions</u>	<u>Measuring Conditions</u>			
Pulp consistency, 0.75%	Test solution, TSAJ20p			
pH, 7	N ₂ flow rate, 2.5/15			
Variac setting, 100	Temperature, 23.5°C.			
Depositing angle, 85	Preset, 3 sec.			
Substrate, stainless steel (same slide was used for all trials)	Substrate, glass spot plate			
	Count, 8 intervals			
	<u>Slide & Solvent</u>	<u>Unbeaten</u>	<u>Beaten</u>	
Beating Degree, as freeness in cc.	--	380	50	
Depositing Time, min.	--	10	10	
Total Count of 8 Intervals	576	(1) 576 (2)545	(1)743 (2)574	
		561 av.		
Counts Due to Pitch		None	167	
			--	
Depositible Pitch by Canister Technique, mg.		9	30	

APPENDIX

DATA FOR FIGURE 1

Measuring Conditions:

Substrate - ordinary glass slide

Test solution - TSBK

N₂ flow rate - 2.5/50

Temperature - 23.5°C.

Preset - 3 seconds

Concentration of Pitch, micrograms	Total Meseran Count for Four Intervals
0	199
3.3	616 (417)
10.7	785 (586)
16.0	921 (722)
25.0	1036 (856)

	Total Meseran Count for One Interval
0	171
3.3	332 (161)
10.7	357 (186)
16.0	378 (207)
25.0	352

DATA FOR FIGURE 2

Measuring Conditions:

--Substrate - concave glass slide

Test solution - TBSK

N₂ flow rate - 2.5/50

Temperature - 23.5°O.

Preset - 3 seconds

Concentration of Pitch, µg	Total Meseran Count for 56 sec.
0	173
7.8	292 (122)
13.1	312 (142)
22.5	359 (189)

Substrate - glass spot plate
detecting window adjusted to 7/16" higher

7.8	271 (98)
13.1	292 (119)
22.5	312 (139)

DATA FOR FIGURE 3

Calibration:

Resinous materials --benzene-ethanol pulp extract

Test solution - TSBK

N₂ flow rate - 2.5/15

Temperature - 23.5°C.

Preset - 3 seconds

Concentration of Pitch, μg	Total Count of One Interval
Solvent	126
0.263	140 (14)
0.525	(1) 168 (42) (2) 143 (17)
1.050	(1) 157 (31) (2) 163 (37)
1.580	167 (41)
2.250	(1) 200 (74) (2) 162 (36) (3) 188 (62)
3.15	187 (61)
3.95	(1) 209 (83) (2) 236 (110)
6.30	(1) 227 (101) (2) 255 (129)
7.80	247 (121)
10.50	279 (153)
12.63	283 (157)
14.18	275 (149)
15.75	289 (163)

DATA FOR FIGURE 4

Calibration:

Resinous materials - C₆H₆ - C₂H₅ - OH extract from WBS
Test solution - TSAj20p
N₂ flow rate - 2.5/15
Temperature - 23.5°C.
Preset - 3 sec.

Concentration of Pitch, µg	Total Count in 8 Intervals
0	345
0.25	
.525	
1.05	561 (216)
1.58	567 (222)
2.25	526 (181)
3.15	1225 (880)
3.95	1490 (1145)
6.30	1915 (1570)
7.80	2124 (1779)
10.50	1589 (1244)

PROJECT REPORT FORM

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✓ PROJECT NO. 1102-8
COOPERATOR Institute of Paper Chemis-
REPORT NO. 23
DATE October 2, 1968
NOTE BOOK 2684
PAGE 53 TO 58
SIGNED *George E. Lauterbach*
George E. Lauterbach

ORIENTATION STUDIES ---COLLOID CHEMISTRY

STARCH XANTHIDE FROM TEE-PAK'S DRY POWDER STARCH XANTHATE

SUMMARY

Starch xanthide prepared from the powdered starch xanthate of Tee-Pak Inc. (acid modified starch base) is comparable to the United States Department of Agriculture (U.S.D.A.) starch xanthate solution used in Project 2580 in regard to dry tensile strength development. It is, however, inferior in regard to wet tensile strength (0.16 vs. 0.24 lb/in wet tensile per grams added).

The Tee-Pak product can be cross-linked without coagulation at, at least, 2 to 3 times the concentration possible with the U.S.D.A. xanthate. This could avoid the use of high-ionic strength white water to dilute the xanthate.

INTRODUCTION

Tee-Pak, Incorporated provided us with a sample of starch xanthate which was a dry powder rather than a solution such as was provided by the U.S.D.A. for Project 2580. In powder form, starch xanthate is more easily transported and handled by potential users in the paper industry.

In order to gain some familiarity with the Tee-Pak product (and possibly uncover the basis for a cooperative project), handsheets were prepared with starch xanthide obtained by oxidizing the starch xanthate sample provided by the manufacturer. The methods used were those developed for cooperative Project 2580 (U.S.D.A.) outlined in Report Nine, pages 49-51. The control data are those obtained in the earlier work.

The original design of the experiment included cross-linking at 0.167, 0.33, and 0.67% concentrations (as received basis). Inasmuch as the treatment at 0.67% produced a clear, uncoagulated starch xanthide dispersion, the lower concentrations were not run.

Materials Used

Sodium Starch Xanthate, Tee-Pak, Inc.:
Acid Modified, D.S. 0.14, 4.37% Xanthate Sulfur,
76% Starch Base, Lot No. D1597. (Stored in refrigerator
for several weeks before being used.)

Rayonier Bleached Softwood Kraft Whole Pulp
Beaten to 690 ml. Schopper-Riegler freeness
Dewatered and aged several weeks in cold room (24.74% solids)

Deionized Water

EXPERIMENTAL PROCEDURES

STARCH XANTHIDE PREPARATION

Sodium starch xanthate (15.00 g. as is) was dispersed in deionized water (2500 ml.) for five minutes by means of an Eppenbach Homogenizer. Acetic acid (5% to pH 5.0-5.2, 9.3 to 9.6 ml.) and potassium iodide (4 ml., 5% W/V) were then blended with the xanthate solution. Sodium hypochlorite (1% (50 ml. Hi-lex diluted with 150 ml. water, adjusted to pH 5.0-5.2 with 20% acetic acid, 11.6 to 12.0 ml., then made up to 250 ml.) was added rapidly to the xanthate solution to produce a blue color persisting at least one minute (55.7, 66.2, and 50.0 ml. dilute Hi-lex used for three preparations). The Eppenbach Homogenizer was operated at full speed during the addition of acidified Hi-lex (i.e., hypochlorous acid). The clear blueish-pink xanthide dispersion was diluted to 3000 ml. and used within 45 minutes.

HANDSHEET PREPARATION

Starch xanthide (0.50% as is basis) was added to about five liters of stock containing 30.0 g. dry fiber and 6.0 ml. 10% alum (W/V). Following the addition of the starch xanthide (5, 10, and 15% as is dry basis of dry fiber weight) the stock was made up to 6.00 liters and agitated for 15 minutes.

Noble and Wood handsheets (eight 8 by 8-inch, 500-ml. stock per sheet) were prepared, couched, wet pressed (5 min., 50 p.s.i.g.) and dried on the couch blotter, blotter side down, for seven minutes on a drum containing steam at 3 p.s.i.g. The 15% addition set of handsheets were dried between the wire and couch blotters after pressing, wire blotter down, for two minutes. The couch blotter was removed, and drying then completed (5 min.) with the wire blotter next to the dryer surface.

RESULTS AND DISCUSSION

Data in Table I and Figure I show the results of the experimental work.

Starch xanthide prepared from Tee-Pak's starch xanthate equals the dry tensile strength performance, on similar preparations of the same pulp, as the starch xanthate (D.S. 0.13) provided by the U.S.D.A. for Project 2580. The Tee-Pak product is inferior to the U.S.D.A. product in regard to wet tensile strength (16-hour soak). The Tee-Pak product produced but 0.16 lb/in wet tensile strength per gram of xanthide starch compared to 0.24 lb/in for the U.S.D.A. product.

The Tee-Pak product could be effectively cross-linked at 0.51% consistency (as starch, 0.67% as received) whereas the U.S.D.A. xanthate cannot be oxidized effectively at 0.33%. (A consistency of 0.167% was established as the standard cross-linking condition for U.S.D.A. starch xanthate for Project 2580). It is likely that the Tee-Pak product could be oxidized at even higher concentrations. This is an obvious advantage since cross-linking at 0.167 to 0.20% consisting in low ionic strength solutions disrupts the normal water balance in large scale papermaking. The use of high ionic strength white water for dilution defeats the purpose of that dilution which is to reduce the ionic strength of the cross-linking medium.

ACKNOWLEDGEMENT

Donald Gilbert performed most of the work involving the xanthide and handsheet preparation.

TABLE I

PERFORMANCE OF STARCH XANTHIDE PREPARED FROM TEE-PAK POWDERED STARCH XANTHATE

Starch Xanthate, %:	as is as starch	Tee-Pak Xanthate					U.S.D.A. Xanthide ^a						
		0	5	10	15		0	5	10	15	0	10	
		0	3.8	7.6	11.4		(Fines-free pulp)				(Whole pulp)		
				% Con- trol	% Dry Con- trol								
Basis wt.: lb/ream(25x40/500)		45.9	46.9	47.6	50.3	110	110	46.9	50.5	48.2	48.7	44.7	47.4
	g./m ²	64.6	66.0	66.9	70.7	--	--	--	--	--	--	--	--
Thickness:	mils	4.9	4.8	4.8	5.0	--	--	--	--	--	--	--	--
	micrometers	124	122	122	127	--	--	--	--	--	--	--	--
Density:	lb/ream/mil	9.4	9.8	9.9	10.1	107	107	9.4	10.1	10.0	10.4	9.9	10.8
	g./cm. ³	0.521	0.541	0.548	0.557	--	--	--	--	--	--	--	--
Dry Tensile ^b :	lb/in.	21.3	26.5	28.9	32.2	152	152	17.2	28.4	29.2	33.0	20.6	31.8
	kg/cm.	3.80	4.73	5.16	5.75	--	--	--	--	--	--	--	--
Wet Tensile ^c :	lb/in.	0.83	1.35	1.95	2.64	318	12.4	0.65	2.43	2.98	4.68	0.84	4.38
	kg/cm.	0.148	0.241	0.348	0.471	--	--	--	--	--	--	--	--
Dry T.E.A. ^b :	in.-lb/in. ²	0.70	0.89	0.94	1.16	166	166	--	--	--	--	--	--
	g.-cm./cm. ²	124	158	167	208	--	--	--	--	--	--	--	--
Wet T.E.A. ^c :	in.-lb/in. ²	0.020	0.030	0.047	0.067	335	9.6	--	--	--	--	--	--
	g.-cm./cm. ²	3.57	5.36	8.48	12.0	--	--	--	--	--	--	--	--
Dry Et. ^b :	lb/in.	2080	2310	2340	2380	114	114	--	--	--	--	--	--
	kg/in.	372	412	419	425	--	--	--	--	--	--	--	--
Wet Et. ^c :	lb/in.	77.4	111	112	120	155	5.8	--	--	--	--	--	--
	kg/cm.	13.8	19.8	20.0	21.4	--	--	--	--	--	--	--	--

^aProject 2580, Report Nine, p. 51 (Dec. 27, 1967).

^bDry = 50% R.H.
Wet = 16-hr. soak

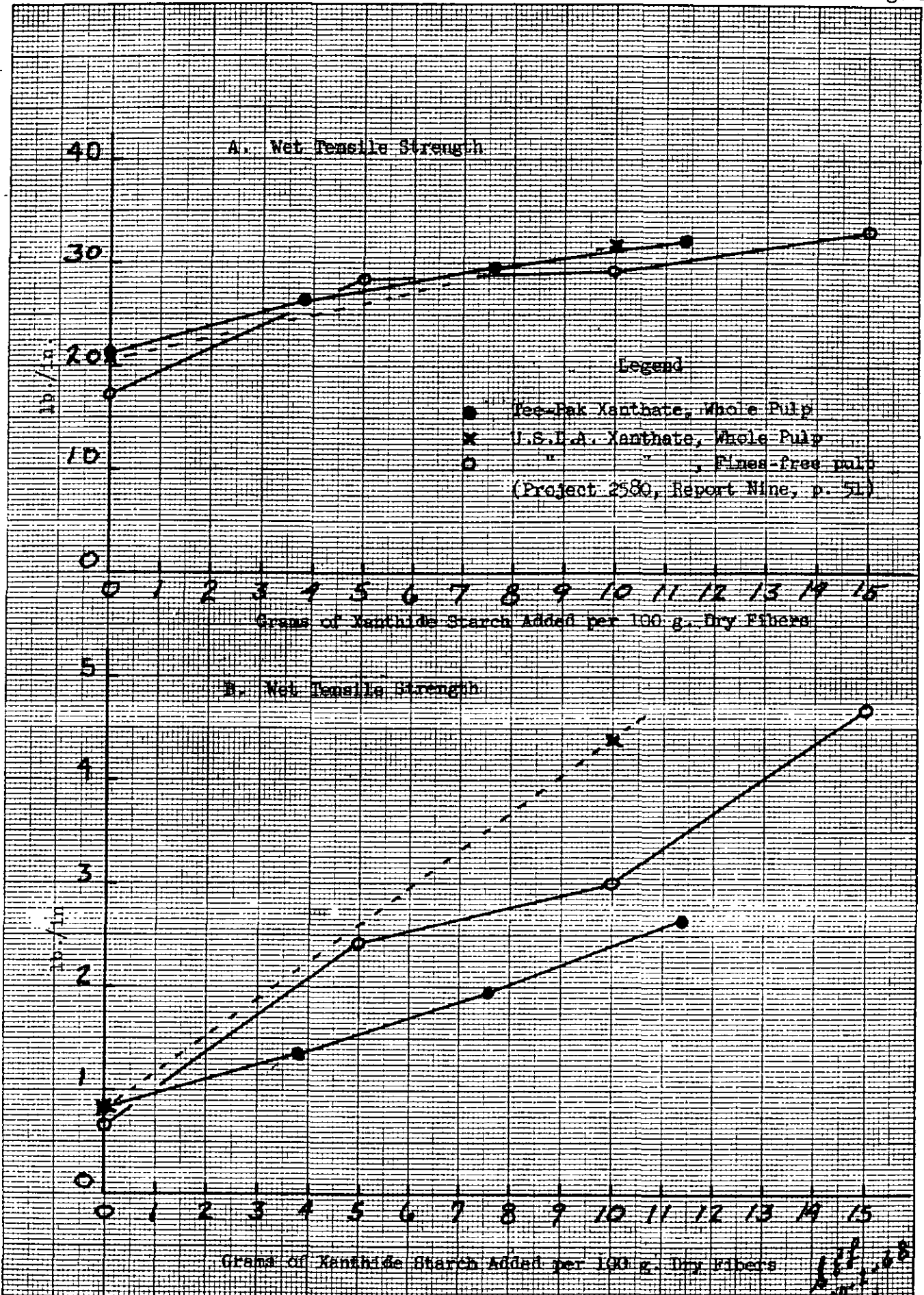


Figure 1. Tensile Strength as a Function of Xanthide Added

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PROJECT NO. 1102-8
COOPERATOR Institute of Paper Chemist
REPORT NO. 22
DATE July 24, 1968
NOTE BOOK 1653:104-6, 111-3
PAGE 2605:155-7
SIGNED S. C. Nagel
S. C. Nagel
Robert M. Leekley
Robert M. Leekley

ORIENTATION STUDIES

DETERMINATION OF THE PORE SIZE DISTRIBUTION OF A PAPER PAD BY MERCURY INTRUSION

INTRODUCTION

The suitability of papers for adhesive binding of books or edge padding of business forms is dependent upon the pore size distribution of the paper pad. Intrasheet pores in the edges of the sheets and intersheet pores between the sheets are both of importance. These pores should be subject to measurement in the mercury porosimeter provided that the sheets can be held face-to-face in pad form in the penetrometer tube.

SUMMARY

Pore size distribution measurements have been made with the mercury intrusion porosimeter upon a pad of paper. The pad was placed on a stainless steel cylinder within the penetrometer tube. The buoyancy of the steel floating in mercury and a stainless steel spring applied a compressive force which held the paper together in pad form against the cover of the penetrometer tube.

Comparison of measurements made on the paper pad and upon single sheets held in the usual way show that surface roughness is filled at a higher pressure when the sample is in pad form. It is believed that the

pore size distribution determined with the sample in pad form may be a better indicator of suitability for adhesive binding than measurements made in the usual way.

During the course of these experiments a Plexiglas cylinder was used at first. However, after apparently normal operation, the porosimeter counter suddenly started to run continuously and did not stop until it reached its limit. This had occurred previously only when samples of coatings on polyethylene were tested. It is now hypothesized that these plastics contain some slightly volatile material which contaminates the penetrometer stem wall during evacuation. This material is then believed to contaminate the mercury meniscus to the extent that alcohol bypasses the mercury in the stem and breaks the circuit which would otherwise stop the counter drive. Bench-top experiments with purposely contaminated penetrometer tubes give some support for this hypothesis.

EXPERIMENTAL RESULTS

Pore size distribution curves for determinations made on separate sheets and on pads using the steel and Plexiglas cylinders are shown in Figures 1-5. These plots show that surface roughness is detected at consistently higher pressure (smaller effective pore diameter) when the sample is in pad form.

PROCEDURES

The paper used was a high bulk paper D-2 which had been used in Project 2690. Separately mounted specimens were strips 1/2 x 1-inch with their bottom ends held in the spring holder.

Specimens in a pad were squares $3/8 \times 3/8$ -inch with machine directions oriented in the same direction and felt sides facing the same way. The pad was held against the penetrometer cap by a spring acting against a cylinder as illustrated in Figure 6. The spring was necessary to hold the paper in pad form during handling before the mercury was introduced. Total pressure acting on the pad due to the spring and the bouyant effect of the mercury on the cylinder is estimated at not more than 1.6 p.s.i., which is considerably less than the 8 p.s.i. used for determining the bulking thickness of paper (IPC method 505).

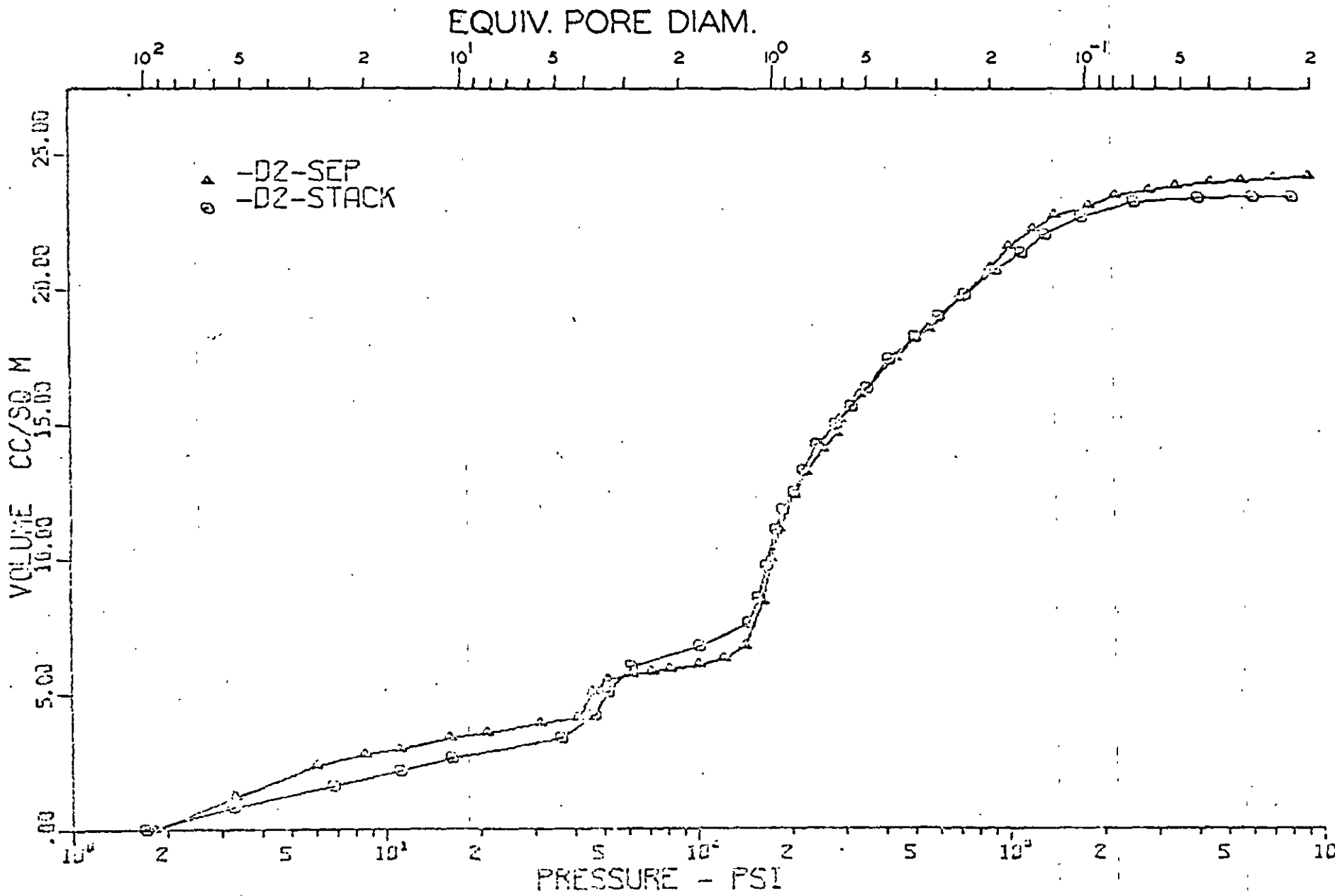
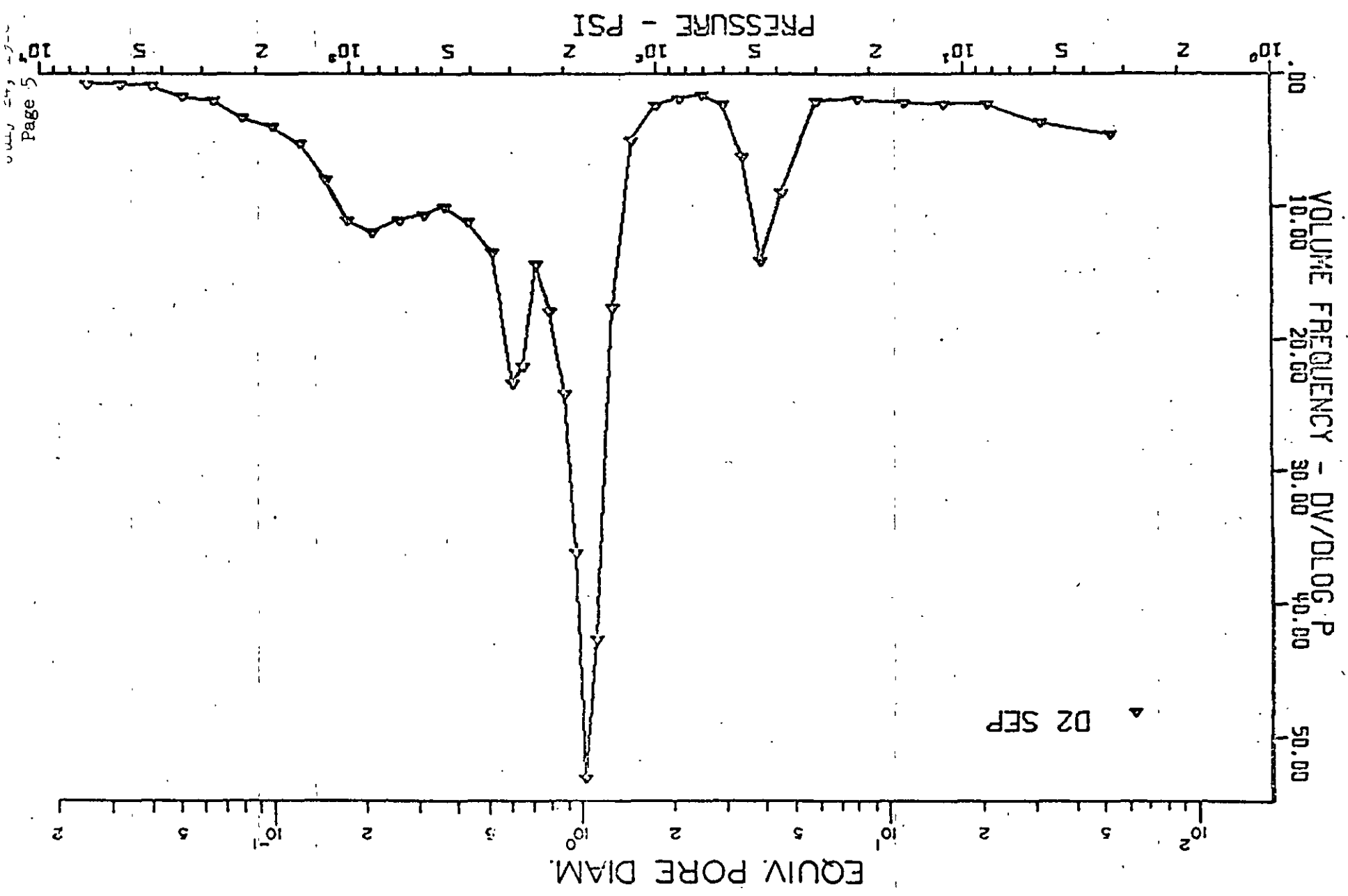


Figure 1. Mercury Porosity of Low Bulk Paper D-2. Effect of Mounting in a Pad. (Steel Cylinder).

Figure 2. Pore Volume Frequency of Low Bulk Paper D-2.



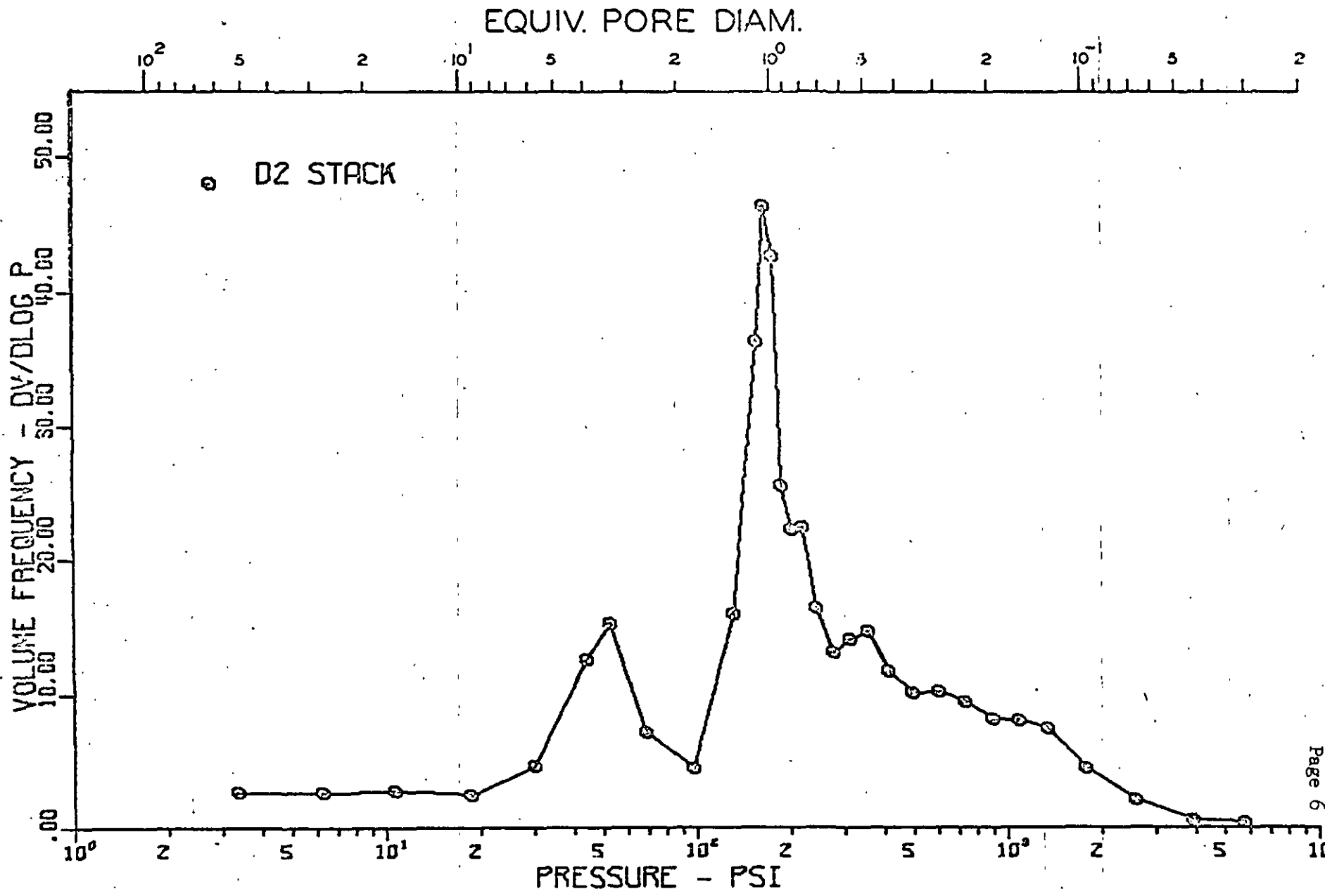


Figure 3. Pore Volume Frequency of Low Bulk Paper D-2 in a Pad. (Steel Cylinder).

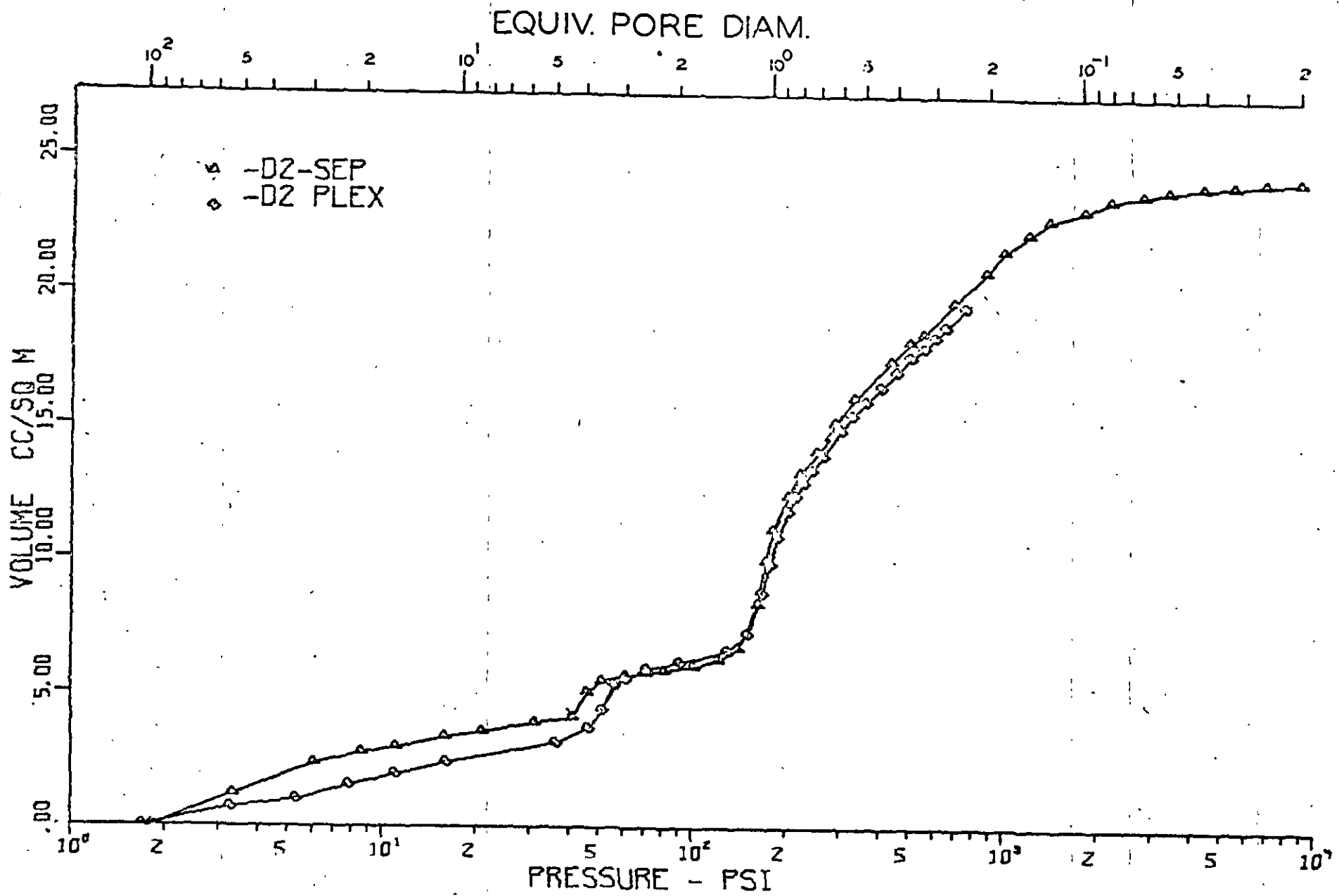


Figure 4. Mercury Porosity of Low Bulk Paper D-2. Effect of Mounting in a Pad. (Plexiglass Cylinder).

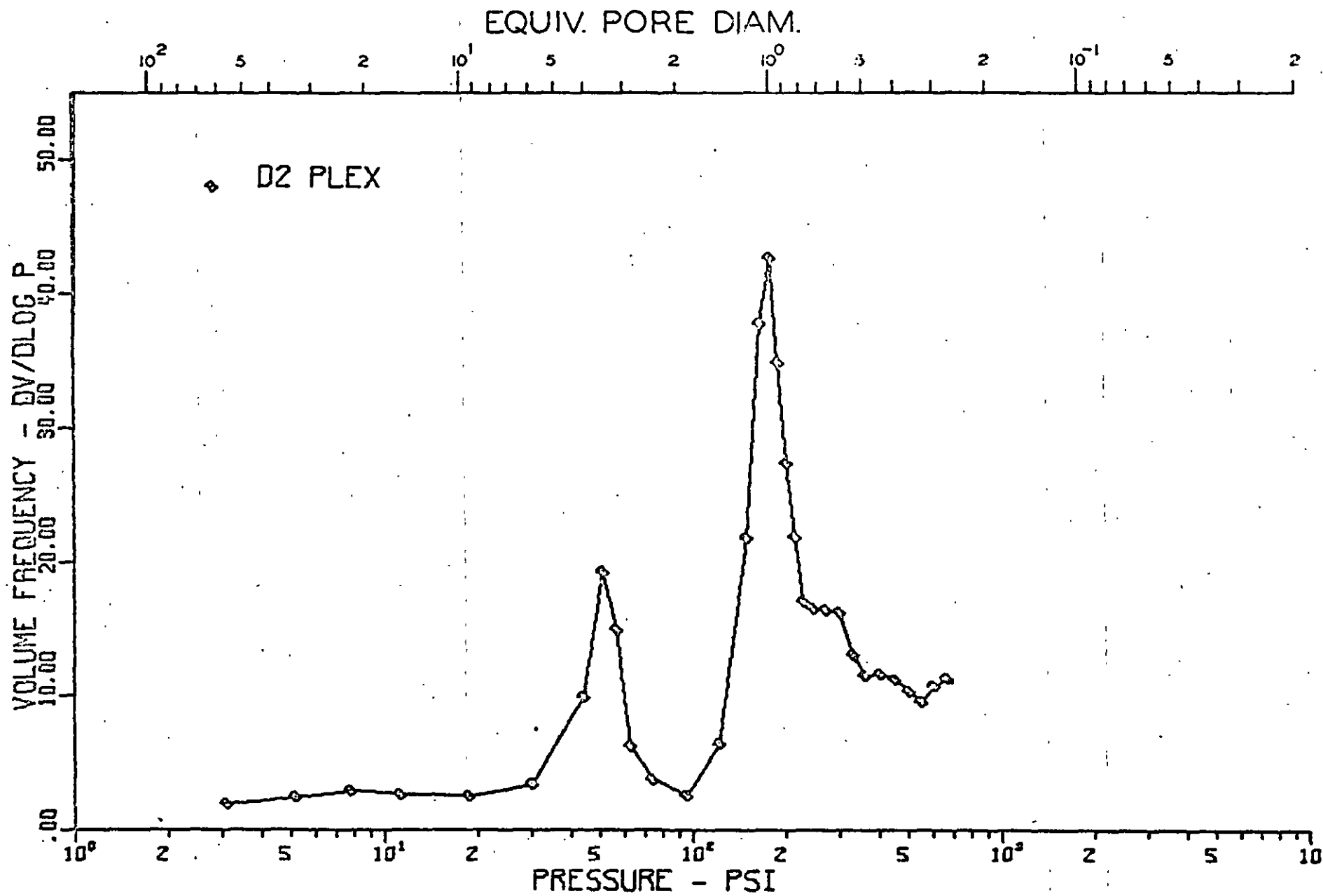


Figure 5. Pore Volume Frequency of Low Bulk Paper D-2 in a Pad. (Plexiglass Cylinder).

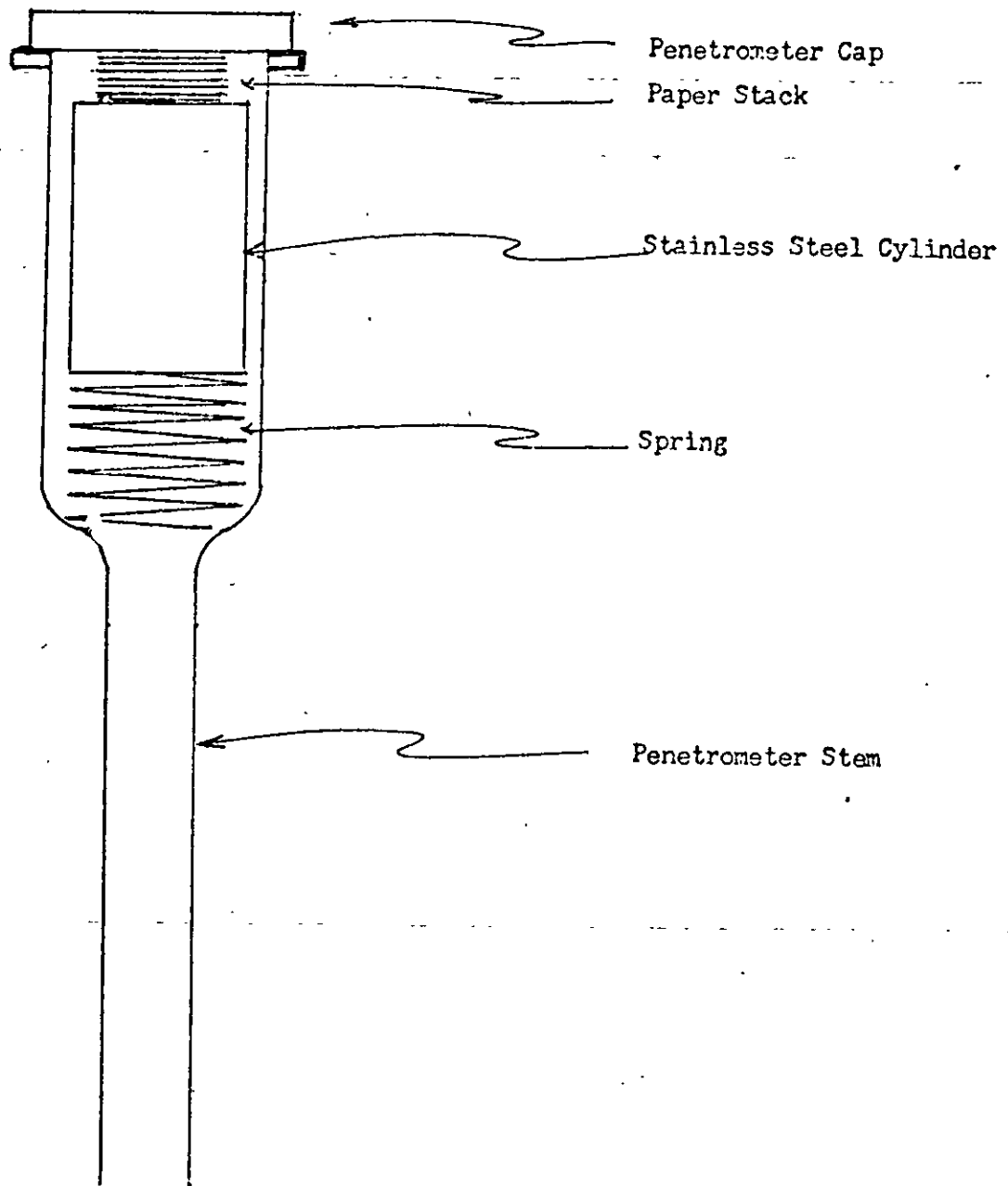


FIG 6. Arrangement of Stacked Paper Samples in the Penetrometer

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PROJECT NO. 1102-8
COOPERATOR Institute of Paper Chemist
REPORT NO. 21
DATE July 15, 1968
NOTE BOOK 1109
PAGE 77 TO 80
SIGNED *Carlton W. Denzer*
Carlton W. Denzer
Robert M. Leekley
Robert M. Leekley

ORIENTATION STUDIES

MEASUREMENT OF REFLECTION OF LIGHT FROM PAPER SURFACES. SEPARATION
OF INTERNAL DIFFUSE AND SURFACE REFLECTIONS

SUMMARY

Goniophotometer measurements using polarized light have been made in order to calculate the diffuse and surface components of light reflected from glossy black and white and matte black and white papers. The distribution of surface inclination for the papers has been calculated on the assumption that the spatial distribution of the surface reflection is due to the inclination of small elements of the surface relative to the nominal plane of the paper. Each element is assumed to reflect light specularly in accordance with Fresnel's law.

INTRODUCTION

When a beam of light is incident upon a paper surface, part is reflected from the upper surface at an angle equal to the angle of incidence in accordance with Fresnel's law and part is diffusely reflected due to scattering within the surface layer. It is only the diffusely reflected light that is attenuated by absorption by the colorants within the sheet. Therefore the light reflected from the surface is "white light" even when the paper is printed with colored ink.

If the paper is optically smooth, all elements of the surface will lie in the same plane and make the same angle with the direction of the incident beam. The light reflected from the surface will therefore all be directed at the same angle of reflection. The extent to which this surface reflection is confined to the area of a small aperture at this angle is a measure of the gloss of the sample.

When a viewer looks at a glossy print, he unconsciously adjusts the angle of incidence of the light and his viewing angle to avoid having the glare from the surface enter his eye. Under this viewing condition, the colors of the print can appear highly saturated and the blacks can be very dark. However, if the print has a matte surface, the individual surface elements lie at a range of angles relative to the plane of the sheet and intercept parts of the incident beam at a range of angles of incidence. The light reflected from the surface is therefore distributed over such a wide range of angles that there is no viewing geometry under which this unwanted white light can be avoided. For this reason, the color saturation and black density of matte prints is severely limited. Because of this relationship of print gloss to the possible range in color saturation and density, gloss measurements of paper and printed ink are widely used to indicate the suitability of paper for high quality printing. However, a measure of the extent to which surface reflection can be avoided would seem to be a better quality indicator where papers of moderate gloss are concerned. This should be particularly true for embossed and textured papers for which gloss measurements are difficult to interpret.

This report summarizes a feasibility study of a proposed method for determining angular distribution of the surface and diffuse internally reflected light.

DISCUSSION OF PROPOSED METHOD

Fresnel's law,

$$I = I_0 \left[\frac{\sin^2 (i-r)}{\sin^2 (i+r)} + \frac{\tan^2 (i-r)}{\tan^2 (i+r)} \right]$$

where i and r are the angles of incidence and refraction, respectively, describes the surface reflection from a dielectric surface. The first term, $\frac{\sin^2 (i-r)}{\sin^2 (i+r)}$, represents the reflection from the surface for the component of the incident light which is polarized with electric vector perpendicular to the plane of the incident and reflected beams and the second term, $\frac{\tan^2 (i-r)}{\tan^2 (i+r)}$, represents the reflection for the component of the incident light with electric vector parallel to this plane. Light reflected from the surface is not depolarized, but internally diffusely reflected light is completely depolarized. Therefore, if light is plane polarized (either parallel or perpendicular to the plane of the incident reflected beams), reflected from paper, and detected with a polarizing analyzer over the receptor, the degree of depolarization is related to the relative amounts of diffuse and surface reflections. One half of the depolarized light will be detected with the analyzer oriented to exclude the incident light. The other half of the depolarized light and all of the light which is reflected without change in polarization will be detected with the analyzer oriented to accept the incident light. The angular distribution of both components therefore can be determined

with a goniophotometer. Distribution curves applying to ordinary, nonpolarized light, can be computed from the sum of the intensities found in two experiments with incident light polarized in the parallel and perpendicular positions relative to the plane of the incident and reflected beams.

EXPERIMENTAL DETAILS

The goniophotometer developed under Project 2518 was modified by introduction of a smaller aperture in the light source, addition of an auxilliary lens to image the aperture at the light receptor and installing rotatable polarizing filters over the light source and receptor. The orientation of the polarizing filters was adjusted by placing a glossy specimen on the holder and setting the angle of incidence at 57° (which is approximately the Brewster angle) and the receptor angle at 57° . The polarizing filter at the light source was then rotated until minimum light was detected at the analyzer because light polarized parallel to the plane containing the incident beam and the normal to the surface should have zero surface reflection under these conditions. Orientation of the polarizer at 90° to this direction corresponds to light polarized perpendicularly to this plane. The proper orientation of the polarizing film at the detector and minimum was determined by adjustment to give maximum/response to suitably polarized incident light.

Samples of paper for study were prepared by exposing one-half each of two sheets of photographic paper to light. After development and fixing, one sheet was dried on a ferrotype plate to produce a glossy finish and the other was dried to give a dull or matte finish. The black and white, glossy and dull specimens were mounted on the goniophotometer holders with epoxy resin.

Measurement of all four papers were made with incident beam at 45° because it was desired that the results be applicable to $45-0^\circ$ viewing conditions. In each case measurements were made with incident beam polarized in the parallel and perpendicular direction with the analyzer both parallel and perpendicular to the direction of incident beam polarization. To prevent confusion, the symbols $I_{\perp\perp}$, $I_{\perp=}$, $I_{==}$, and $I_{=\perp}$ are used for the light intensities detected at the receptor. The subscript symbols \perp and $=$ indicate that the polarizing filters were oriented to transmit light polarized perpendicularly or parallel, respectively, to the plane containing the incident and reflected beams. The first subscript designates the orientation of the polarizing filter in the light source; the second subscript designates the orientation of the polarizing filter on the light receptor. The intensity of surface reflection determined for light polarized perpendicularly to the plane of the incident and reflected beam is then $I_{\perp S}$ and is given by the equation

$$I_{\perp S} = I_{\perp\perp} - I_{\perp=}$$

Similarly,

$$I_{=S} = I_{==} - I_{=\perp}$$

$$I_{\perp D} = 2I_{\perp=}, \text{ and}$$

$$I_{=D} = 2I_{=\perp},$$

where the subscript D designates diffuse reflection. The intensities for ordinary (not polarized) light reflected from the surface and diffusely from the interior are then I_S and I_D , respectively, and are given by the equations

$$I_S = I_{\perp S} + I_{=S} \quad \text{and}$$

$$I_D = I_{\perp D} + I_{=D} .$$

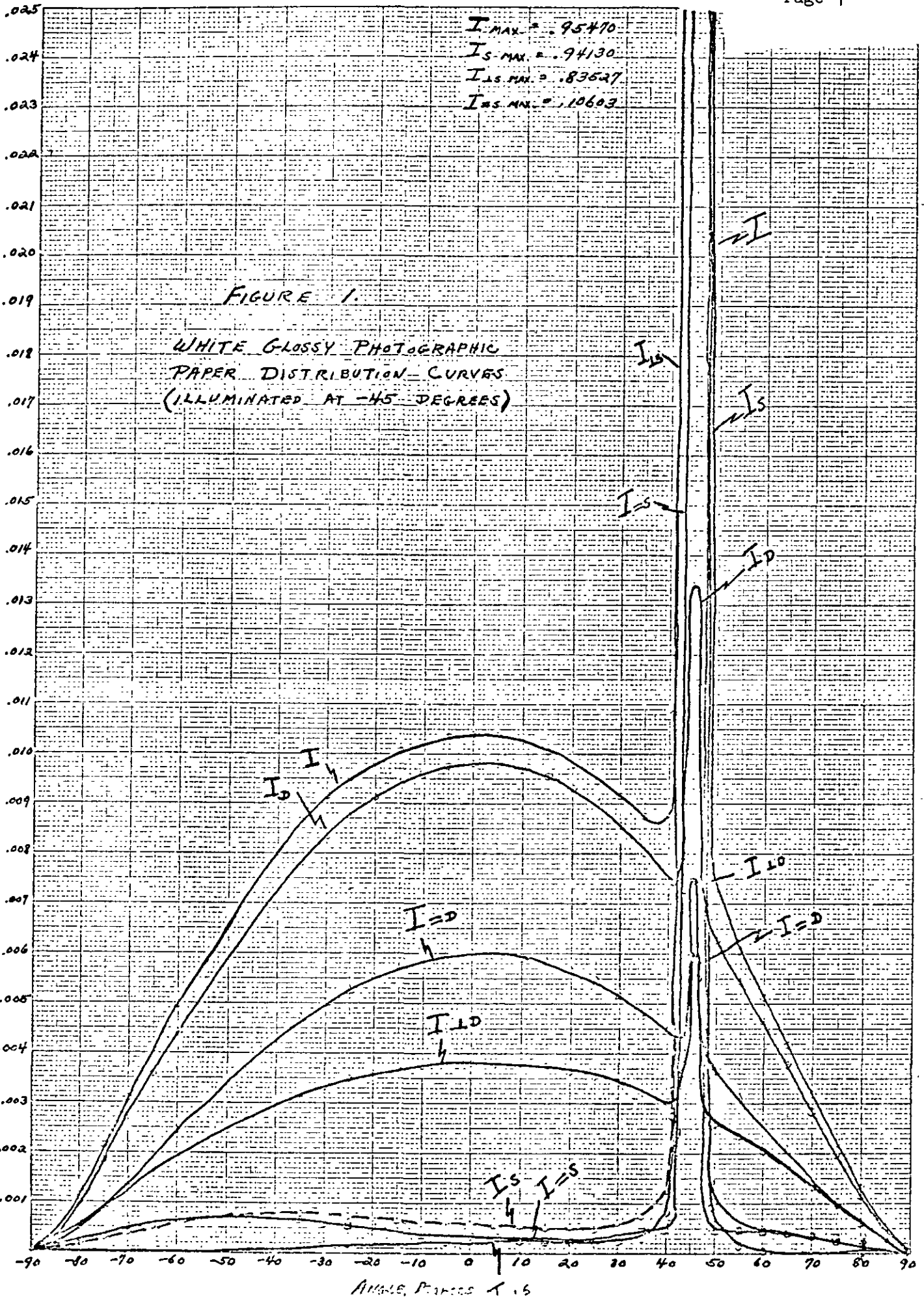
The sum of I_S and I_D is designated as I and should be proportional to goniophotometer measurements made with ordinary light.

Tables I-IV give the experimentally observed values for I_{11} , $I_{1=}$, $I_{=}$, and $I_{=1}$ at various receptor angles for the four papers. Values of I_{1S} , $I_{=S}$, I_{1D} , $I_{=D}$, I_S , I_D , and I derived from the above experimentally observed values are also given. Figures 1 through 4 show plots of the derived I , I_S , and I_D values and their component parts for the four papers.

The values for the white matte paper are plotted in polar coordinates in Figure 5 to show how well the diffuse reflection, I_D , conforms to the spherical distribution described by Lambert's law for a perfectly matte surface. This indicates that the measurement method employed does separate the internal diffuse and surface reflections. However, the diffuse reflection curves for the glossy papers, Figure 1 and 2, have maximum at 45° . This is due to the imperfect behavior of the polarizing filter at the receptor which transmits a small fraction of the very strong peak of surface reflection occurring at this angle. In future work, it is planned to substitute Nicol prisms for the polarizing filters.

KE 10 X 10 TO THE CENTIMETER 46 1510
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Intensity, meter reading

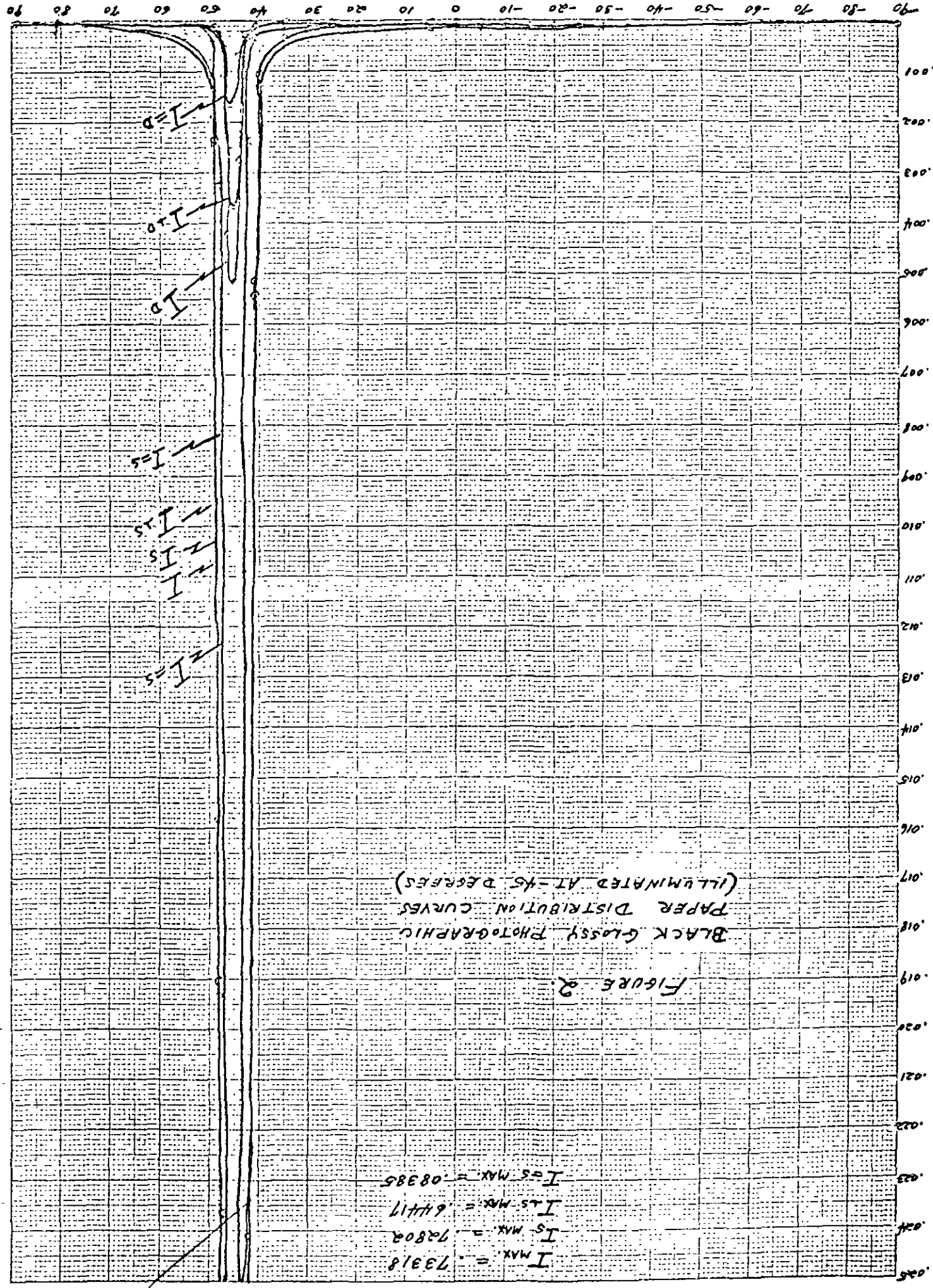


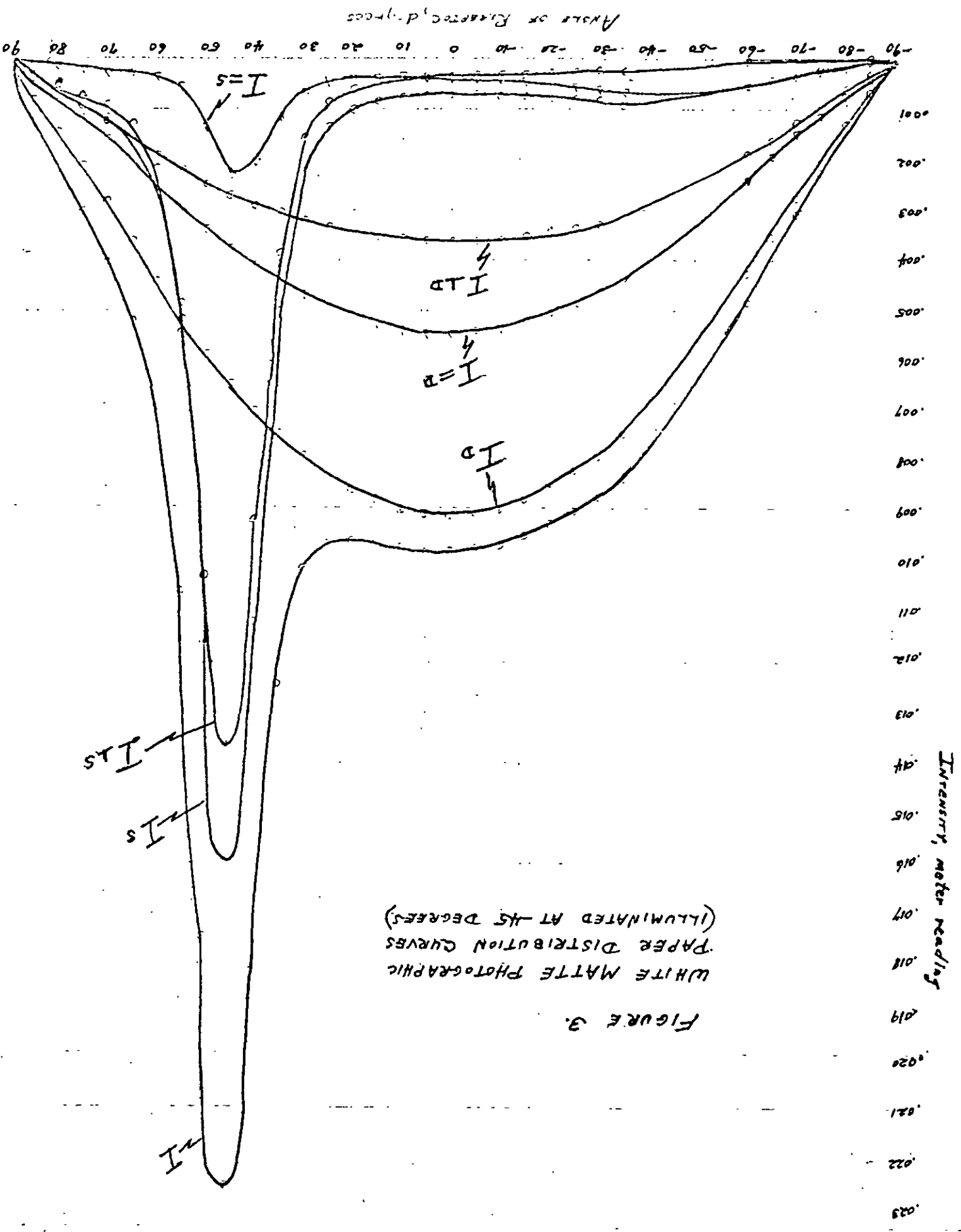
Intensity, meter reading

BLACK GLOSSY PHOTOGRAPHIC
 PAPER DISTRIBUTION CURVES
 (ILLUMINATED AT 45 DEGREES)

FIGURE 2.

$I_{MAX} = .73318$
 $I_{S MAX} = .72802$
 $I_{LS MAX} = .64417$
 $I_{OS MAX} = .08385$





WHITE MATTE PHOTOGRAPHIC
PAPER DISTRIBUTION CURVES
(ILLUMINATED AT 45 DEGREES)

FIGURE 3.

K₁E 10 X 10 TO THE CENTIMETER 46 1510
19 X 25 CM.
KEUFFEL & ESSER CO

Intensity, meter reading

.016
.015
.014
.013
.012
.011
.010
.009
.008
.007
.006
.005
.004
.003
.002
.001

FIGURE 4.

BLACK MATTE PHOTOGRAPHIC
PAPER DISTRIBUTION CURVES
(ILLUMINATED AT 45 DEGREES)

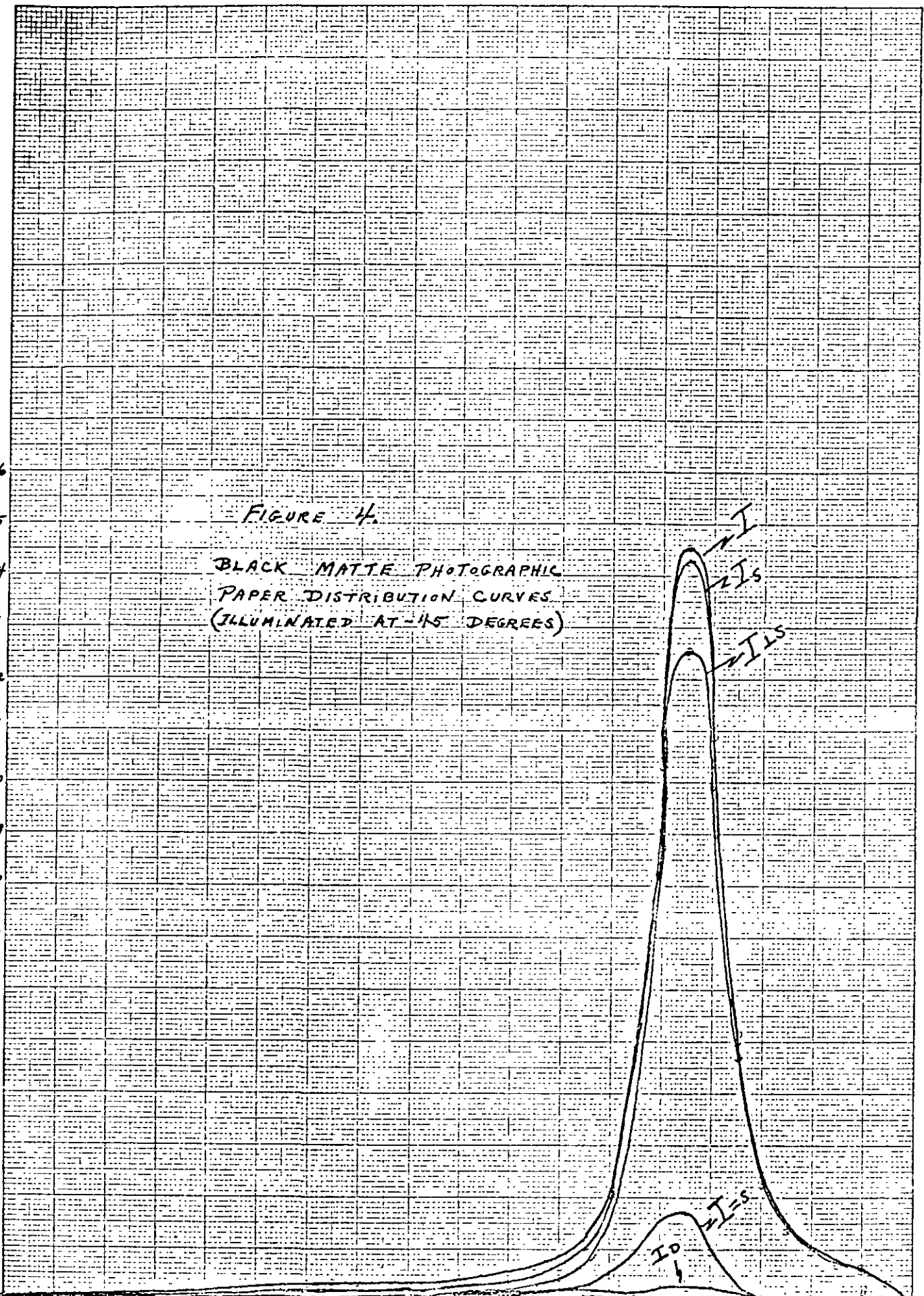
I
I₁
I₂

I₀
I₁
I₂

-90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90

Avg. of Reflection degrees

T. T



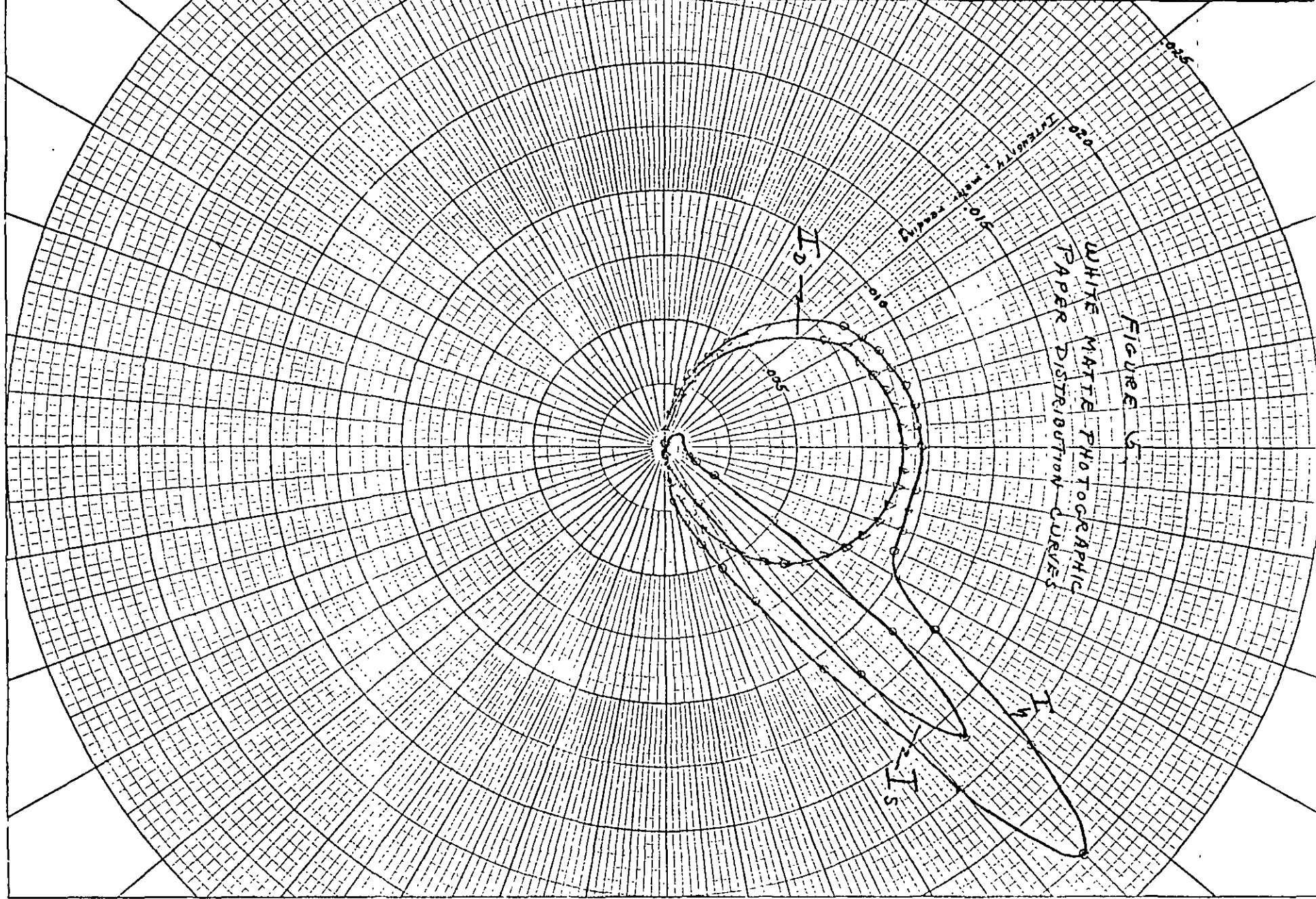
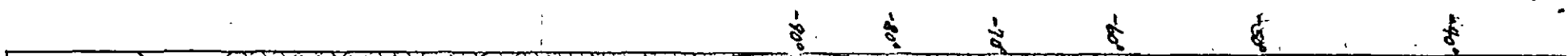
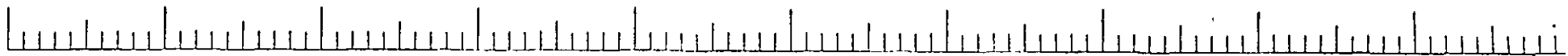
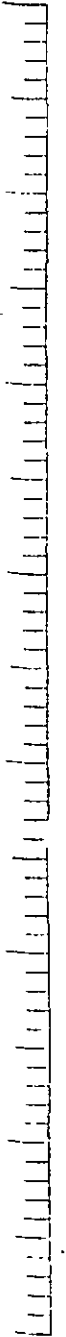
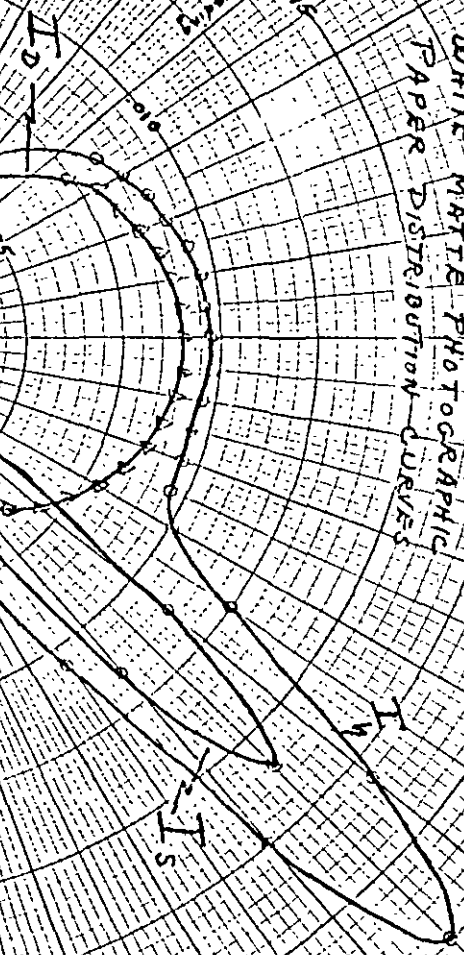


FIGURE 5
WHITE MATIC PHOTOGRAPHIC
PAPER DISTRIBUTION CURVES



CALCULATION OF THE DISTRIBUTION OF SURFACE INCLINATION

The distribution of surface inclination was calculated from the surface reflection values, $I_{\perp S}$, but the method could also be applied to values of $I_{=S}$.

The surface of the paper is assumed to be comprised of elements which are tilted at angles \underline{t} relative to the nominal plane of the specimen. Only those elements tilted in a direction such that the perpendicular to the surface lies in the plane of the incident beam need be considered because only these can provide surface reflections which will be detected by the receptor which lies in this same plane. The angle of tilt, \underline{t} , and the actual angle of incidence \underline{i} are related to the nominal angle of incidence, which in these experiments is 45° by the expression

$$i = 45 + t.$$

If \underline{a}_t is the fractional area of the cross section of the incident beam intercepted by elements tilted at angle \underline{t} , the actual area of such elements, \underline{A}_t , is proportional to $\underline{a}_t / \cos \underline{i}$ and the projected area on the nominal plane of the specimen, \underline{A}_{tp} , is proportional to $\underline{a}_t \cos \underline{t} / \cos(45 + \underline{t})$. If no shadowing of the incident beam occurs the summation of \underline{A}_{tp} over all angles of tilt and all directions of tilt should equal the geometric area of the illuminated spot on the specimen. Therefore,

$$\underline{A}_{tp} = \underline{a}_t \cos \underline{t} / \cos(45 + \underline{t})$$

can be considered to be the fractional area of the specimen, measured by projection on the plane of the specimen, which is tilted at angle \underline{t} in a direction to provide surface reflection in the plane traversed by the receptor. The experimentally determined value of $I_{\perp S}$ determined with receptor at angle \underline{R}

represents the surface reflection due to elements at the angle, \underline{t} , where

$$t = \frac{R - 45}{2} .$$

The intensity of this reflection is a measure of \underline{a}_t since

$$a_t = \frac{I_{\perp S}}{I_{\perp S}(\max)}$$

where $I_{\perp S}(\max)$ is the maximum value of $I_{\perp S}$ which would be detected if the specimen were optically flat and was tilted at angle \underline{t} . Therefore,

$$A_{tp} = I_{\perp S} \cos t / I_{\perp S(\max)} \cos(45 + t).$$

The function $I_{\perp S(\max)}$ was determined by determining $I_{\perp S}$ for the glossy photographic paper at several angles of incidence and fitting the Fresnel expression for perpendicularly polarized light,

$$I = I_o \frac{\sin^2(1 - r)}{\sin^2(i + r)}$$

to the experimental points as shown in Figure 6. Figures 7 and 8 show plots of \underline{A}_{tp} vs. \underline{t} for the photographic papers.

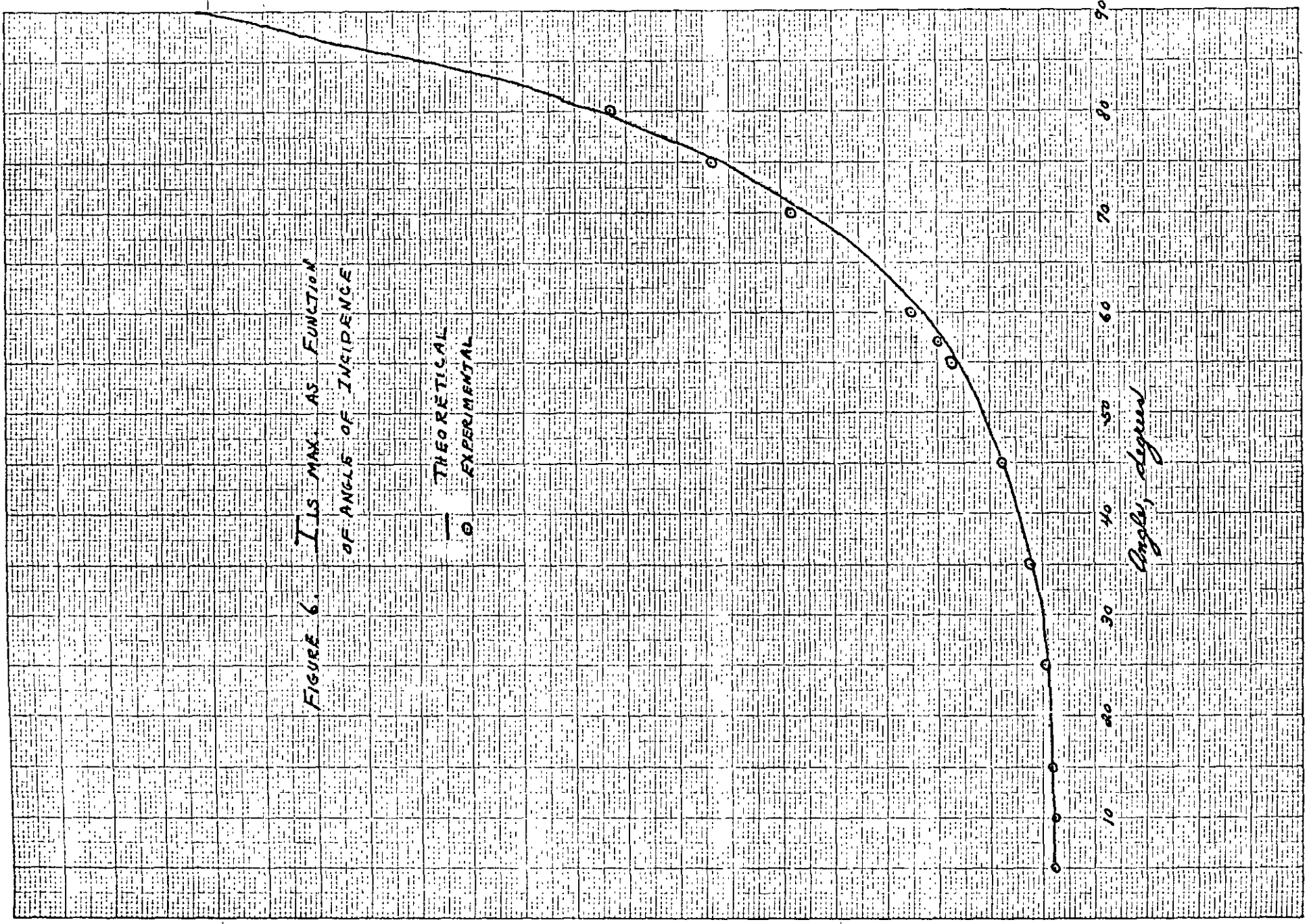
FIGURE 6. I_{115} MAX. AS FUNCTION
OF ANGLE OF INCIDENCE

— THEORETICAL
○ EXPERIMENTAL

Intensity, meter reading

Angle, degrees

10 X TO THE CENTIMETER 40 1510
MADE IN U.S.A.
KEUFFEL & ESSER CO.



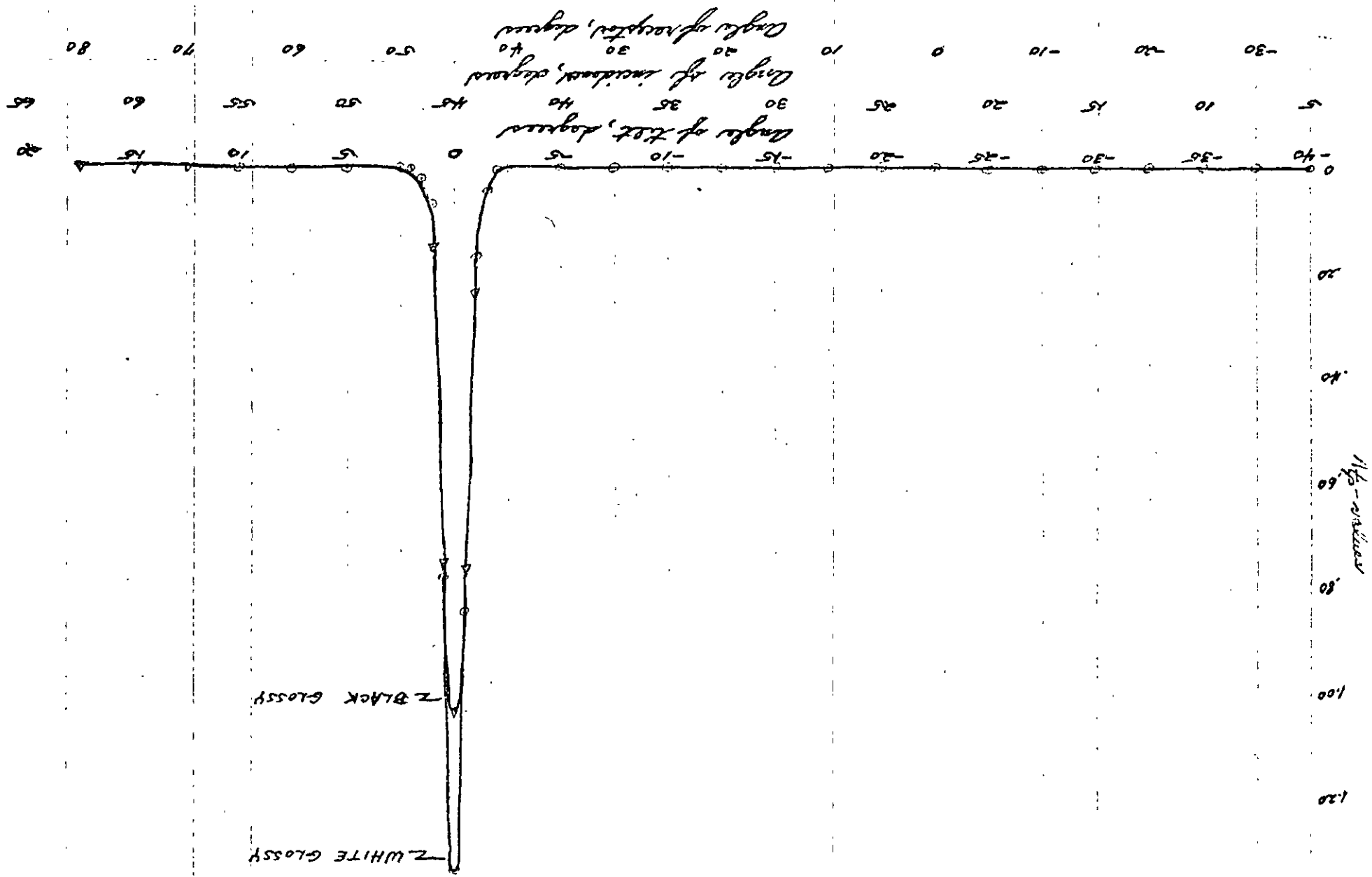


FIGURE 7. DISTRIBUTION OF TILED AREAS FOR GLOSSY-FINISH PHOTOGRAPHIC PAPER

FIGURE 8. DISTRIBUTION OF TILTED AREAS FOR DULL-FINISH PHOTOGRAPHIC PAPER.
 (NOTE CHANGE IN SIDE SCALE AS COMPARED TO FIGURE 7.)

BLACK MATTE
 WHITE MATTE

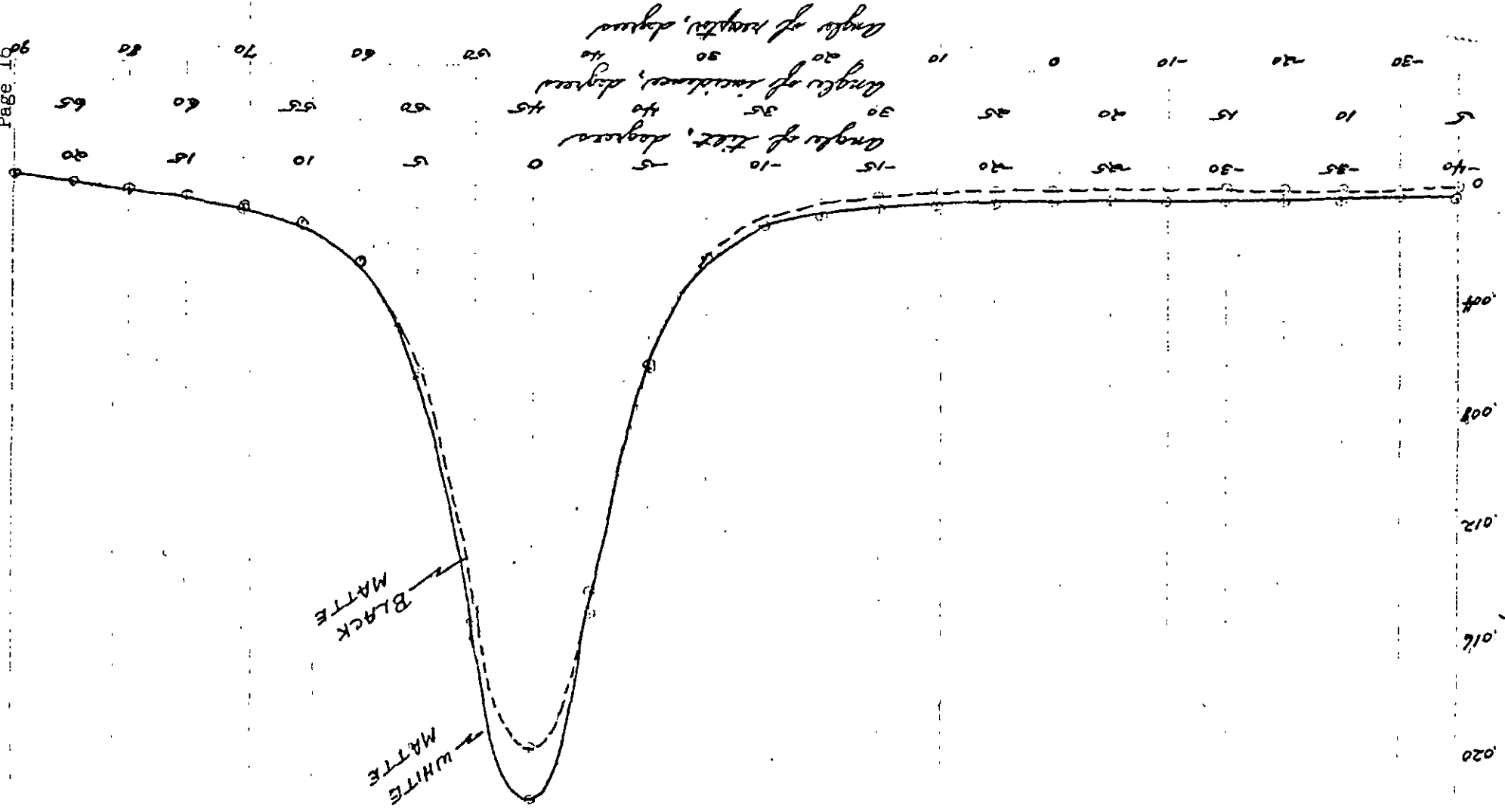


TABLE I
WHITE GLOSSY PHOTOGRAPHIC PAPER ILLUMINATED AT -45°

Angle of Receptor, degrees	Intensity, meter reading $\times 10^5$									
	I_{111}	I_{11-}	I_{1-1}	I_{1-}	I_{1S}	I_{1D}	I_{1D}	I_{1G}	I_{1D}	I_{1D}
-90	1	1	1	0	1	2	0	1	2	3
-85	7	9	16	-2	10	18	12	8	30	38
-80	19	27	49	-8	25	54	48	17	102	119
-75	36	47	85	-11	39	94	92	28	186	214
-70	54	66	120	-12	50	132	140	38	272	310
-65	74	83	154	-9	58	166	192	49	358	407
-60	93	98	186	-5	64	196	244	59	440	499
-35	173	159	301	14	67	318	468	81	786	867
-30	186	167	310	19	60	334	500	79	834	913
-25	193	175	319	18	56	350	526	74	876	950
-20	202	181	325	21	50	362	550	71	912	983
-15	206	185	329	25	44	370	570	65	940	1005
-10	212	187	330	25	37	374	586	62	960	1022
-5	214	191	336	23	40	382	592	63	974	1037
0	215	191	334	24	35	382	598	59	980	1039
5	216	190	331	26	31	380	600	57	980	1037
10	213	190	328	23	32	374	592	55	972	1027
15	208	187	320	21	29	374	582	50	956	1006
20	205	182	309	23	26	364	566	49	930	979
25	197	178	300	24	28	356	544	47	900	947
30	193	170	295	23	37	340	516	60	856	916
35	189	161	285	28	45	322	480	73	802	875
40	232	153	271	79	48	306	446	127	752	879
41	429	152	282	277	62	304	440	339	744	1083
42	2820	159	462	2661	245	318	434	2906	752	3658
43	10700	180	945	10520	728	360	434	11248	794	12042
44	52500	296	5450	52204	5206	592	488	57410	1080	58490
45	83900	373	10900	83527	10603	746	594	94130	1340	95470
46	49500	276	10500	49224	10203	552	594	59427	1146	60573
47	4760	151	2870	4589	2652	302	436	7241	738	7979
48	1500	140	636	1360	442	280	388	1802	668	2470
49	222	133	240	89	53	266	374	142	640	782
50	189	131	228	58	46	262	364	104	626	730
55	132	117	200	15	44	234	312	59	546	605
60	107	102	174	5	44	204	260	49	464	513
65	83	85	146	-2	42	170	208	40	378	418
70	62	66	114	-4	38	132	152	34	284	318
75	40	49	82	-9	32	98	100	23	198	221
80	22	29	50	-7	20	58	60	13	118	131
85	7	10	21	-3	8	20	26	5	46	51
88.7	1	2	7	-1	1	4	12	0	16	16

Note: Light is blocked by receptor between -60 and -35° . The receptor could not reach 90° due to an obstruction. See text for symbol identity.

TABLE III

WHITE MATTE PHOTOGRAPHIC PAPER ILLUMINATED AT -45°

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Angle of Receptor, degrees	Intensity, meter reading $\times 10^5$										
	I_{11}	I_{12}	I_{13}	I_{14}	I_{15}	I_{16}	I_{17}	I_{18}	I_{19}	I_{20}	I_{21}
-90	1	2	1	2	-1	-1	4	4	-2	8	6
-85	15	15	24	18	0	6	30	36	6	66	72
-80	29	30	52	35	-1	17	60	70	16	130	146
-75	44	48	79	55	-4	24	96	110	20	206	226
-70	61	63	110	74	-2	36	126	148	34	274	308
-65	78	81	140	96	-3	44	162	192	41	354	395
-60	99	94	170	120	5	50	188	240	55	428	483
-35	178	154	284	218	24	66	308	436	90	744	834
-30	187	164	290	231	23	59	328	462	82	790	872
-25	194	167	296	242	27	54	334	484	81	818	899
-20	199	171	301	251	28	50	342	502	78	844	922
-15	206	176	306	261	30	45	352	522	75	874	949
-10	212	180	309	268	32	41	360	536	73	896	969
-5	213	181	309	269	32	40	362	538	72	900	972
0	215	181	309	272	34	37	362	544	71	906	977
5	219	180	308	272	39	36	360	544	75	904	979
10	220	178	304	269	42	35	356	538	77	894	971
15	224	176	300	262	48	38	352	524	86	876	962
20	232	171	296	257	61	39	342	514	100	856	956
25	253	166	293	247	87	46	332	494	133	826	959
30	315	160	300	234	155	66	320	468	221	788	1009
35	534	151	336	220	383	116	302	440	499	742	1241
40	1060	145	407	204	915	203	290	408	1118	698	1816
45	1500	135	418	188	1365	230	270	376	1595	646	2241
50	1150	124	303	169	1026	134	248	338	1160	586	1746
55	596	110	203	147	486	56	220	294	542	514	1056
60	314	96	158	124	218	34	192	248	252	440	692
65	209	79	131	102	130	29	158	204	159	362	521
70	153	62	107	79	91	28	124	158	119	282	401
75	117	47	79	59	70	20	94	118	90	212	302
80	87	31	57	42	56	15	62	84	71	146	217
85	47	15	31	25	32	6	30	50	38	80	118
88.7	12	4	12	11	8	1	8	22	9	30	39

TABLE IV

BLACK MATTE PHOTOGRAPHIC PAPER ILLUMINATED AT 45°

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Angle of Receptor, degrees	Intensity, meter reading $\times 10^5$										
	I_{11}	$I_{1=}$	$I_{=}$	$I_{.1}$	$I_{.5}$	$I_{.S}$	$I_{.S}$	$I_{.D}$	$I_{.D}$	I	
-90	1	2	0	0	-1	0	4	0	-1	4	3
-85	2	2	1	0	0	1	4	0	1	4	5
-80	2	2	2	0	0	2	4	0	2	4	6
-75	3	2	2	0	1	2	4	0	3	4	7
-70	4	2	3	1	2	2	4	2	4	6	10
-65	5	3	4	1	2	3	6	2	5	8	13
-60	5	3	5	1	2	4	6	2	6	8	14
-35	9	4	12	3	5	9	8	6	14	14	28
-30	11	4	13	3	7	10	8	6	17	14	31
-25	12	5	14	4	7	10	10	8	17	18	35
-20	13	4	15	3	9	12	8	6	21	14	35
-15	13	4	15	4	9	11	8	8	20	16	36
-10	14	4	14	4	10	10	8	8	20	16	36
-5	15	4	17	4	11	13	8	8	23	16	39
0	19	4	17	3	15	14	8	6	29	14	43
5	21	5	17	4	16	13	10	8	29	18	47
10	25	5	20	4	20	16	10	8	36	18	54
15	35	4	22	5	31	17	10	10	48	18	66
20	47	4	26	5	43	21	8	10	64	18	82
25	77	5	35	4	72	31	10	8	103	18	121
30	157	4	54	4	153	50	8	8	203	16	219
35	380	4	96	3	376	93	6	6	469	14	483
40	878	6	166	6	872	160	12	12	1032	24	1056
45	1260	7	180	6	1253	174	14	12	1427	26	1453
50	999	6	100	5	993	95	12	10	1088	22	1110
55	475	5	32	3	470	29	10	6	499	16	515
60	229	3	10	2	226	8	6	4	234	10	244
65	135	3	5	2	132	3	6	4	135	10	145
70	94	2	4	1	92	3	4	2	95	6	101
75	71	2	3	1	69	2	4	2	71	6	77
80	57	2	4	1	55	3	4	2	58	6	64
85	31	1	2	0	30	2	4	0	32	6	34
88.7	8	1	1	0	7	1	2	0	8	2	10