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#1395 THE INSTITUTE OF PAPER CHEMISTRY 1950-51
(Prehydrolysis of Wood-Kraft Odor Problem)
Project Reports

PROJECT REPORT FORM

PROJECT NO 1395
COOPERATOR Pool
REPORT NO 6
DATE March 3, 1950 (Typed 4/15/5
NOTE BOOK 860 and 944
PAGE ____ TO ____
SIGNED J. R. Peckham

Copy to: Files
Dr. Forman
Mr. Peckham
Pulping Lab.

Notebook 944
Pages 8-27

Notebook 860
Pages 125
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INTRODUCTION

Previous project reports were summarized in Progress Report One. This report will cover various prehydrolysis experiments which were underway at the time the progress report was written and some which were conceived after issuance of the report.

EXPERIMENTAL

The equipment and techniques used in the following work have been described in previous reports.

Cook 40 was made as a result of a memorandum from L. V. Forman to J. R. Peckham under date of April 2, 1949. The cooking conditions are shown in Table I. The basis for the procedure used was an observation that the odor attendant to the kraft pulping of a series of water extracted southern hardwoods was not particularly objectionable. Therefore, it was proposed that a kraft cook be made on southern pine chips which had been subjected to a hot water extraction.

A digester charge of chips was placed in a stainless steel cylinder having a perforated cone bottom. This container was suspended over a tank of hot water maintained at a temperature of about 90° C. by an immersed lead steam coil. Water was pumped in the top of the container

TABLE I

COOKING CONDITIONS AND PRODUCT VARIABLES OF SOUTHERN PINE

Cook	40	51	53	55	56	57	58	59	60	60-A
Pretreatment	Water Soak	None	None	None	None	None	None	None	Yes	None
Type of chemical									Ammonia	
Prehydrolysis	None	None								None
Steam pressure, p.s.i.			110	120	120	120	120	110	100	
Time to attain pressure, min.			2	2	2	2	25	15[c]	3	
Time at pressure, min.			60	15	15	15	0	0	15	
Time to relieve to inject, min.			3	4	3	3	3	3	3	
Injecting time, min.			5	6	5	5	5	7	5	
Kraft cooking										
Time to max. temp., min.	60	60	20	75	75	75	75	60	60	60
Maximum temperature, °C.	172	172	172	172	172	172	172	172	172	172
Time at max. temp., min.	60	68	75	40	40	40	40	60	68	68
Blowdown time, min.	15	15	15	15	15	15	15	15	15	15
Total cooking time, min.	135	143	110	130	130	130	130	135	143	143
Active Alkali as NaOH, %	23.0	24.75	22.5	22.9	21.0	18.0	19.0	22.0	25.25	25.25
Sulfidity, %	25.0	20.0	33.3	33.3	33.3	33.3	33.3	33.3	20.0	20.0
Water ratio (ovendry chip basis), cc./g.	4.5	4.5	3.5[a]	3.5	3.5[a]	3.5[a]	3.5[a]	3.5[a]	3.5[a]	4.5
Permanganate number	31.9	33.4	22.1	23.8	30.4	54.5	—	22.3	24.4	24.9
Unscreened yield, %			35.8	38.8	39.2	45.8[b]	42.4[b]	39.0	43.7	47.2
Screened yield, %			32.8	36.8	38.8	45.2	42.1	38.0	43.4	46.6
Screenings, %			8.31	4.38	1.25	1.60	0.65	1.64	0.58	1.53

TABLE I (CONT.)

COOKING CONDITIONS AND PRODUCT VARIABLES
OF SOUTHERN PINE

Cook	40	51	53	55	56	57	58	59	60	60-A
Black liquor analysis										
pH			12.1	11.3	12.2	11.8	11.7	12.5	12.4	12.9
Total alkali as Na_2O, g./l.			35.4	35.8	36.3	29.6	31.8	31.4	46.3	39.2
Active alkali as Na_2O, g./l.			10.0	11.7	5.4	5.3	5.1	7.8	16.4	15.7
Prehydrolysis condensate data										
Volume of top relief, cc.			6060	1125	1090	1540	1950	600	1100	
pH of top relief			3.55	4.0	4.1	4.2	6.4	4.8	8.8-6.9-5.8[d]	
Volume of bottom relief, cc.			18,500	7730	7550	9360	7900	7440	10,550	
pH of bottom relief			3.95	3.8	4.1	4.0	4.0	3.7	9.9-9.8-9.5[d]	
Odor evaluation	Fairly Strong Kraft	Strong Kraft	Faint Burnt Sugar	Faint Kraft	Faint Kraft	Faint Kraft	Faint Kraft	Fairly Strong	Kraft + Ammonia	Kraft

Notes:

[a] Disregarding water absorbed by chips during prehydrolysis
[b] Pulp put through Bauer pulper before washing and screening
[c] 5 min. to 80 p.s.i., 5 min. at 80 p.s.i., 5 min. from 80 p.s.i. to 110 p.s.i.
[d] First 5 minutes, second 5 minutes, and third 5 minutes of steaming
[e] These data taken from another project

of chips and drained out the bottom. This operation was allowed to progress over a week end. However, sometime during this period the steam coil broke and the temperature of the water returned to about 20° C. These leached chips were cooked by a typical kraft schedule. The odor of kraft was apparent. A permanganate number determination was made but the pulp was not saved.

Cook 51 was made in No. 3 iron digester to obtain a sample of black liquor typical of a kraft operation. The black liquor was used in the chemical evaluation of odor described on pages 20 to 24 in Progress Report One. The pulp was discarded.

Cook 53 embodied a 60-minute prehydrolysis period at 110 p.s.i. steam pressure. The cook was brought to maximum temperature in 20 minutes after addition of the chemical. The result was a pulp of low yield and high screenings content. The odor was reminiscent of burnt sugar but there was little-or-no-mercaptan odor.

Cooks 55 through 59 were made with a view to producing a prehydrolyzed kraft pulp having yield and screening content similar to those of a normal kraft cook, without regard to the permanganate number range. Cook 55 utilized a prehydrolysis period of 15 minutes at 120 p.s.i. steam pressure, and a period of 75 minutes to reach maximum temperature after addition of the liquor. The kraft odor was negligible. The permanganate number was 23.8, the unscreened yield was 38.8, and the screenings were 5.38%.

Cook 56 was made under conditions very similar to those used in Cook 55. However, the active alkali was reduced from 22.5% to 21% in an effort to increase the yield and permanganate number. These conditions resulted in a pulp with considerable material which failed to pass a 0.010-in. cut screen plate. The rejects were quite soft however, and about 80% of the material was accepted by the screen after it had been stirred in the British disintegrator for 25,000 stirrer revolutions. The two accepted fractions were not combined but they were both included in the screened yield determination. On this basis, the unscreened yield was 39.2% and the screenings 1.2%. The permanganate number was 30.4. The pulp which was beater evaluated and on which the permanganate number test was performed did not include the disintegrated and screened rejects.

Cook 57 was made in the same manner as Cooks 55 and 56, but with active alkali further cut to 18.0%. The resultant pulp had the appearance of being quite raw, but the blow gases were considered to be free of kraft smell. Before screening the blown stock was put through the Bauer pulper at 0.005 inch clearance, feed rate 7, at a consistency of about 6%, which produced a load of 350 amps. The Bauer was fitted with B957 plates. The pulp was washed, screened, and yield was determined. On an unscreened basis, the yield was 45.8% and the screenings were 1.6%. A permanganate number test, which was run using a 60-cc. basis, indicated a figure of 54.5. The pulp was beater evaluated.

Cook 58 was made under conditions which duplicated most of those used in making Cook 57. The main difference lay in the fact that the prehydrolysis step embodied a 25 minute steaming wherein the pressure was

brought to 120 p.s.i. in a straight line rise. The active alkali used was 19%. The blow gases from this cook were considered to be quite free of kraft smell. The chips were poorly pulped and were passed through the Bauer pulper once at 8% consistency, .008" clearance between B957 plates, feed rate 7, and load of 180 amps. The pulp was then washed, screened, and the yield was determined. The unscreened yield was 42.4% and the screenings were 0.6%.

Cook 59 was also made using many of the conditions of Cook 57. The differences were (1) prehydrolysis, which in this case was done in steps as follows: 5 minutes from zero pressure to 80 p.s.i., 5 minutes at 80 p.s.i., and 5 minutes from 80 p.s.i. to 110 p.s.i., and (2) active alkali which was increased to 22.0%. The odor was typical of prehydrolysis kraft cooks. The permanganate number was determined to be 22.3 and the unscreened yield 39.0%. 1.6% screenings were retained on .010" cut screen.

Cook 60 entailed the use of ammonia gas as an alkali present during the prehydrolysis step, the theory being that the ammonia would neutralize the organic acids as fast as they were formed and thus keep the hydrolysis reaction alkaline. The introduction of the ammonia was accomplished by filling the cone of the digester with 28% ammonium hydroxide solution up to the level of the pulp plug. The chips, which were southern pine from another project, were charged to the digester and the cover was bolted in place. A vacuum line was attached to the top relief valve and the air was evacuated, allowing ammonia fumes to rise up into the chips. When the vacuum was released, the relief line was

inserted in the top of a partially filled ammonia bottle to increase the fumes present in the digester. The digester stood all night without further attention. Prehydrolysis conditions were 100 p.s.i. steam for 15 minutes. Because of the possibility of pressure due to the ammonia gas, the prehydrolysis was controlled by maintaining the temperature at 170° C. Relief was constant from both top and bottom of the digester. The condensate was divided into the following samples for testing purposes: (1) Top relief--time to attain pressure and the first 5 minutes of relief, (2) Second 5 minutes of top relief, (3) Third 5-minute period of top relief, (4) Bottom relief--time to attain pressure and first 5 minutes at pressure, (5) Second five minutes of bottom relief, and (6) Third 5 minutes of bottom relief. The pH values of the different samples were (1) 8.8, (2) 6.9, (3) 5.85, (4) 9.9, (5) 9.8, and (6) 9.5, the latter three being tested with a blue point electrode.

The cooking conditions used duplicated those employed on another portion of these chips in work done on another project. 25.25% active alkali as NaOH, with a sulfidity of 20%, was applied after the steaming by injecting it into the circulating line. The water ratio, disregarding the moisture pickup during hydrolysis, was 3.5 to 1. Maximum temperature of 172° C. was attained in 60 minutes and held for 68 minutes. The blow gases from this cook were particularly obnoxious, being a combination of ammonia and mercaptan. Tests made on a black liquor samples taken just prior to blowing indicated that 1 gram of NH_3 per liter of the liquor was present. The pulp was washed and screened and the yield was determined.

The pulps from Cook 55 through 60 were beater evaluated according to Institute methods 403 and 411. The results of these tests, along with pulp test results on the duplicate cooks which were comparable to Cook 60, appear in Table II and graphically in Figures 1 through 6.

Pulps from Cooks 53 and 55 through 60 were evaluated for alpha cellulose, lignin, and pentosan content. The results of these tests are shown in Table III along with similar data from Cooks 28 and 29 which, although reported previously, are included for purpose of comparison.

TABLE II

PHYSICAL CHARACTERISTICS OF KRAFT PULPS

Cook		55	56	57	58	59	60	Composite
Prehydrolysis pressure, p.s.i.		120	120	120	120	110	100	--
Prehydrolysis time, min.		15	15	15	0	0	15	--
Permanganate number		23.8	30.4	54.5	—	22.3	24.4	24.9
Schopper-Riegler freeness, cc.	0	875	875	870	875	880	900	880
	5	870	865	865	870	875	870	880
	15	850	840	830	860	815	860	860
	30	755	720	660	705	725	760	740
	50	500	470	420	435	445	440	420
	70	340	305	280	265	245	260	210
Basis weight (24 x 36--480), lb.	0	37.9	37.9	38.6	36.9	37.4	38.1	37.9
	5	38.2	39.0	39.4	38.5	37.4	39.8	38.5
	15	38.6	38.8	39.0	38.0	39.6	36.7	38.7
	30	38.1	38.9	39.1	38.7	39.9	38.0	39.4
	50	38.3	37.9	38.8	37.1	38.9	37.4	38.9
	70	38.0	38.5	37.9	39.4	38.0	36.1	38.7
Caliper, in.	0	0.0044	0.0046	0.0043	0.0049	0.0051	0.0053	0.0057
	5	0.0038	0.0040	0.0041	0.0045	0.0045	0.0047	0.0049
	15	0.0035	0.0036	0.0038	0.0040	0.0041	0.0038	0.0042
	30	0.0033	0.0033	0.0035	0.0038	0.0038	0.0036	0.0040
	50	0.0031	0.0030	0.0032	0.0034	0.0034	0.0034	0.0036
	70	0.0029	0.0029	0.0029	0.0036	0.0032	0.0032	0.0034
Apparent density	0	8.6	8.2	9.0	7.5	7.3	7.2	6.6
	5	10.1	9.8	9.6	8.6	8.3	8.5	7.8
	15	11.0	10.8	10.3	9.5	9.7	9.7	9.1
	30	11.5	11.8	11.2	10.2	10.5	10.6	10.0
	50	12.4	12.6	12.1	10.9	11.4	11.0	10.8
	70	13.1	13.3	13.1	10.9	11.9	11.3	11.6

TABLE II (CONT.)

PHYSICAL CHARACTERISTICS OF KRAFT PULP

Cook		55	56	57	58	59	60	Composite
Bursting strength pt./100 lb.	0	54	49	63	44	40	50	44
	5	101	105	97	73	78	91	86
	15	147	148	124	106	120	136	134
	30	171	162	142	120	148	162	165
	50	172	157	145	123	147	174	177
	70	165	159	125	128	147	164	167
Tear factor	0	3.54	3.06	3.50	4.01	3.45	4.78	3.92
	5	3.80	3.33	2.89	3.77	3.90	4.75	4.94
	15	2.80	2.76	2.36	2.89	3.18	3.41	3.38
	30	2.26	2.24	1.97	2.48	2.73	2.71	2.76
	50	2.01	1.95	1.49	1.97	2.24	2.19	2.16
	70	1.87	1.51	1.37	1.88	2.11	2.08	1.83

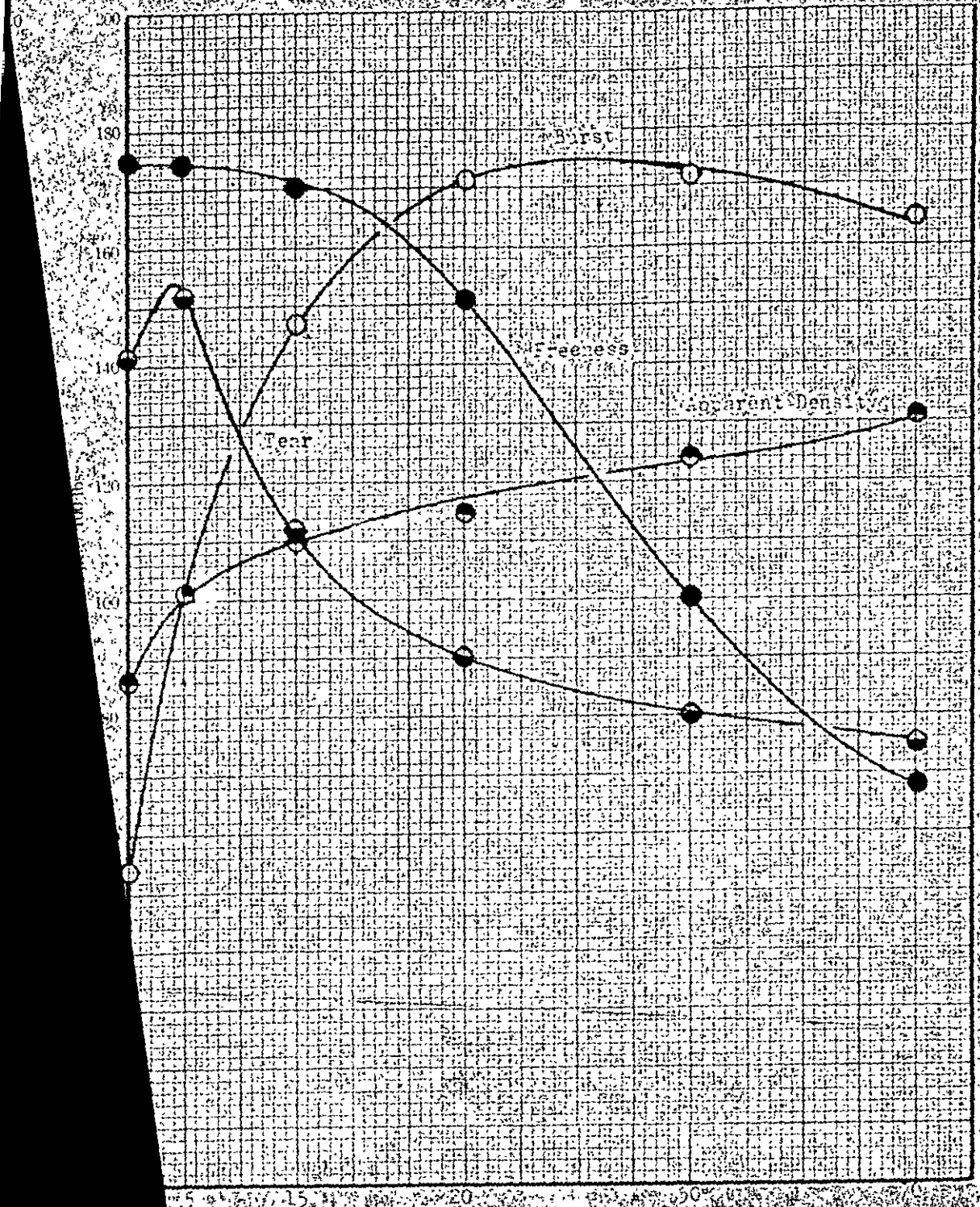
BEATING CURVES

Project 1395 Date

File No. Type of Pulp Prehydrolyzed kraft

Cook 55

Figure 1



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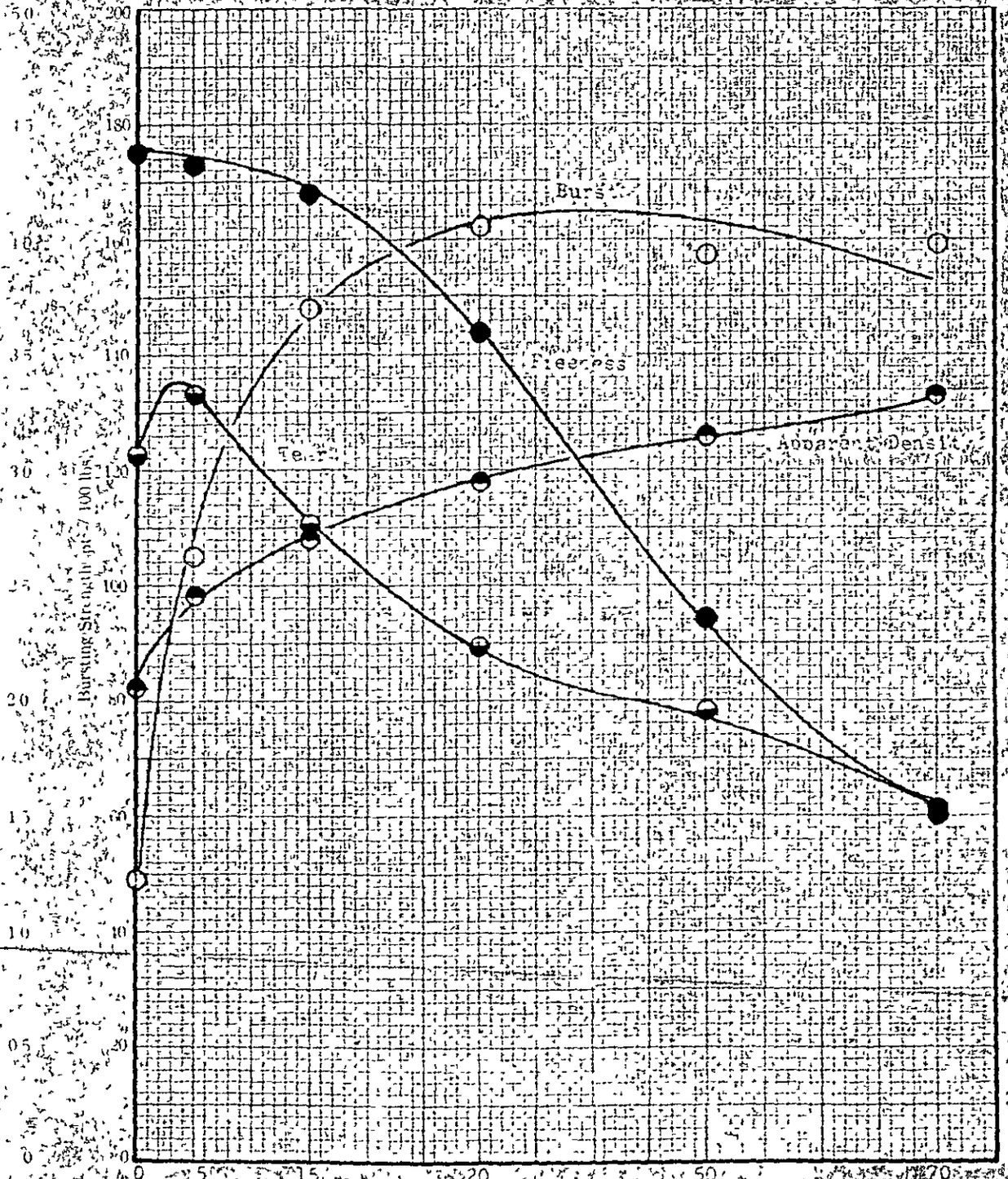
BEATING CURVES

Project 1395 Date

File No. Type of Pulp Archangel Kraft

Cook 50

Figure 2



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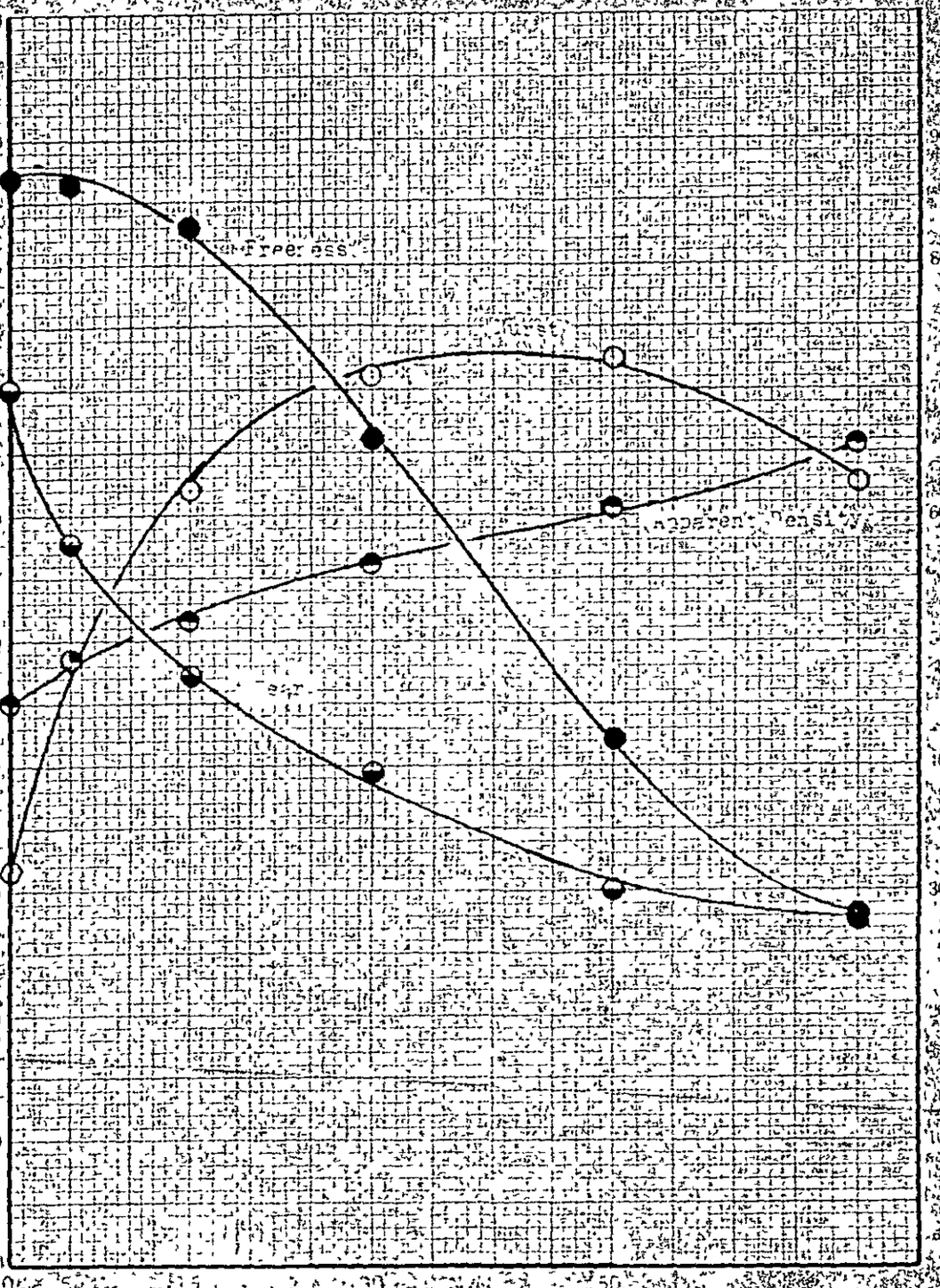
BEATING CURVES

Project 1395 Date

File No. Type of Pulp Prehydrolyzed Kraft

Cook 57

Figure 1



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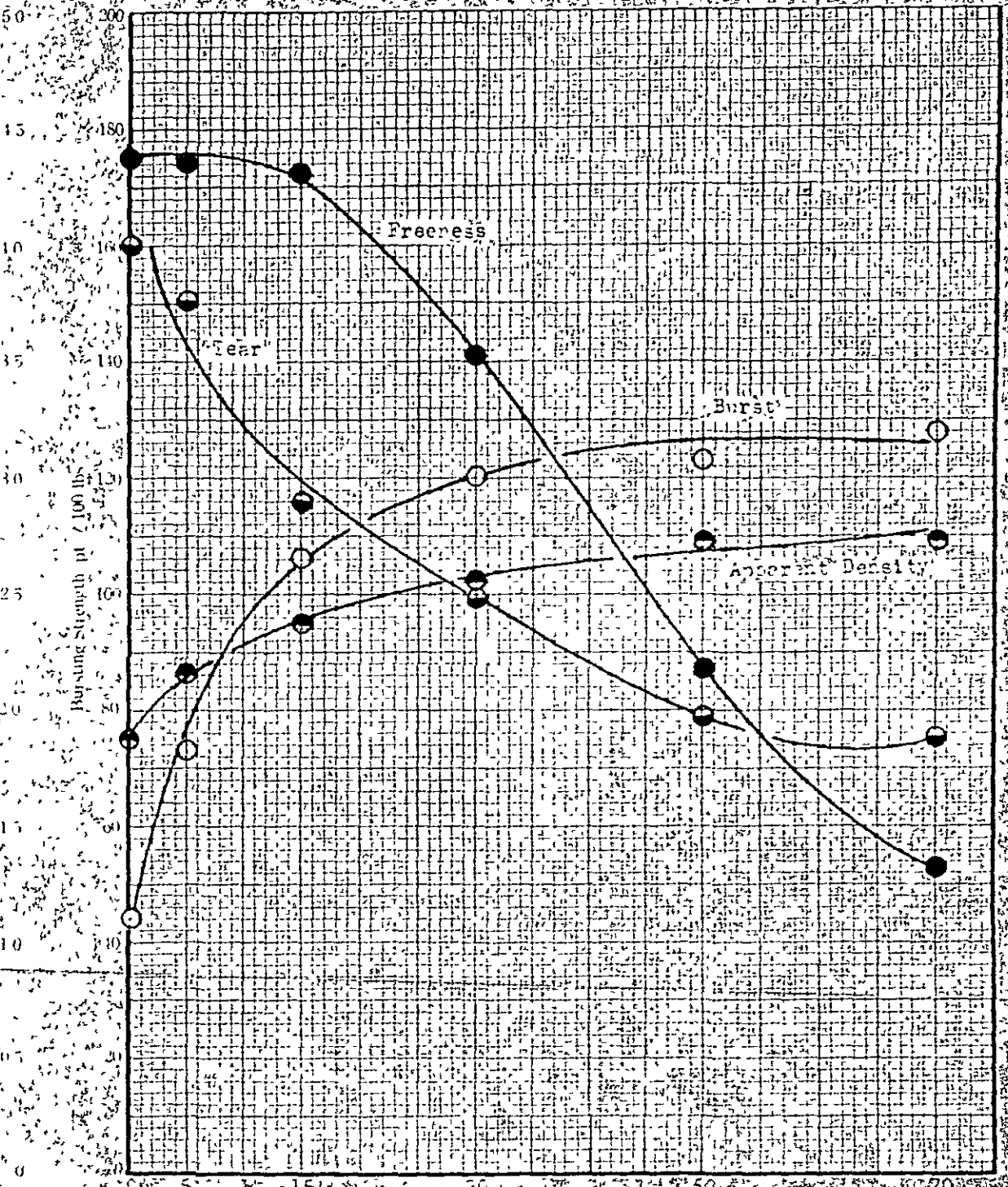
BEATING CURVES

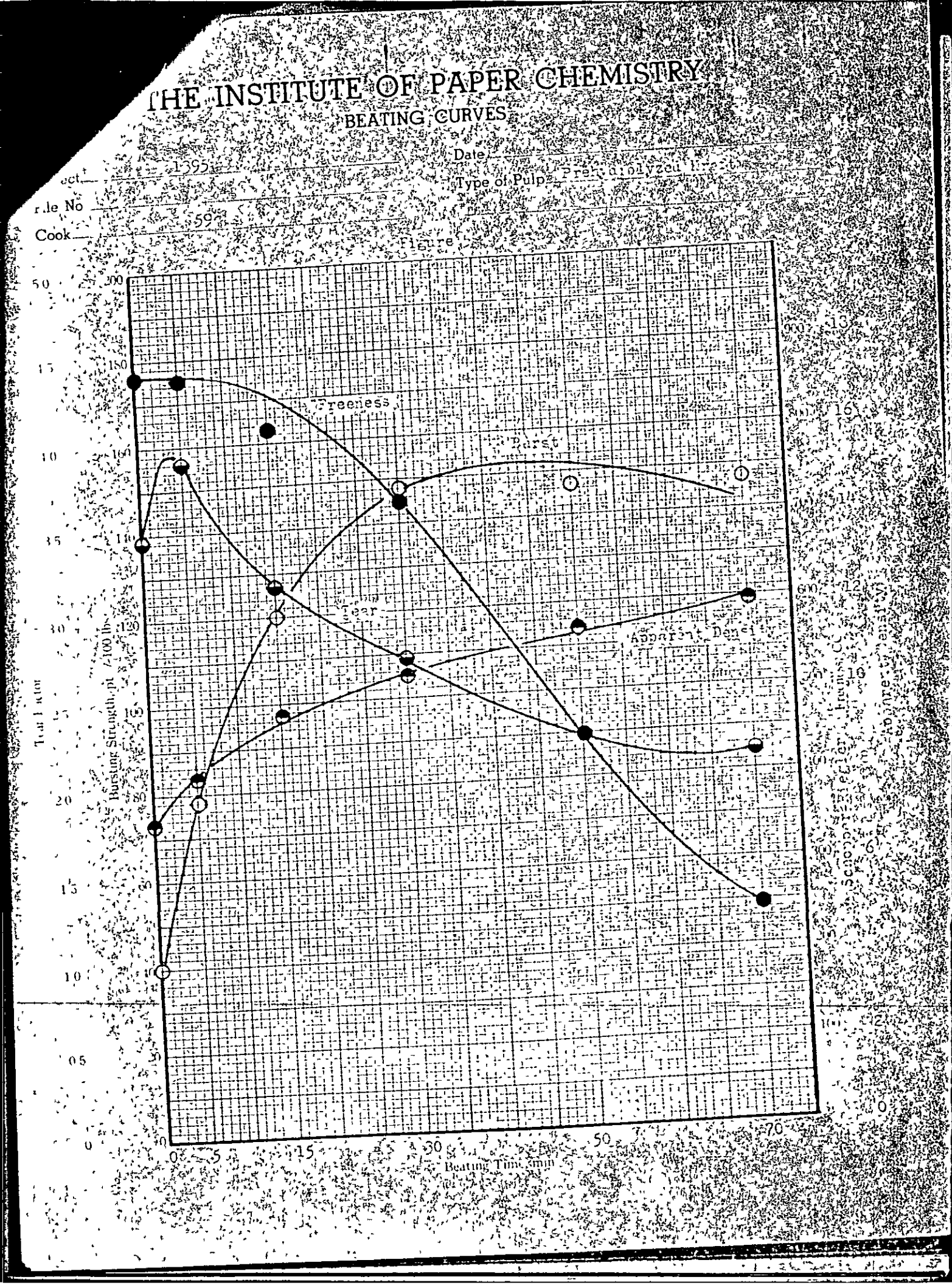
roject 1395 Date

File No Type of Pulp Prehydrolyzed kraft

Cook 58

Figure 4

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BEATING CURVES
Date
Type of Pulp
Figure
Freeness
Burst
Tear
Apparent Densi
Tear Factor
Bursting Strength, pt./100 lb.
Beating Time, min.

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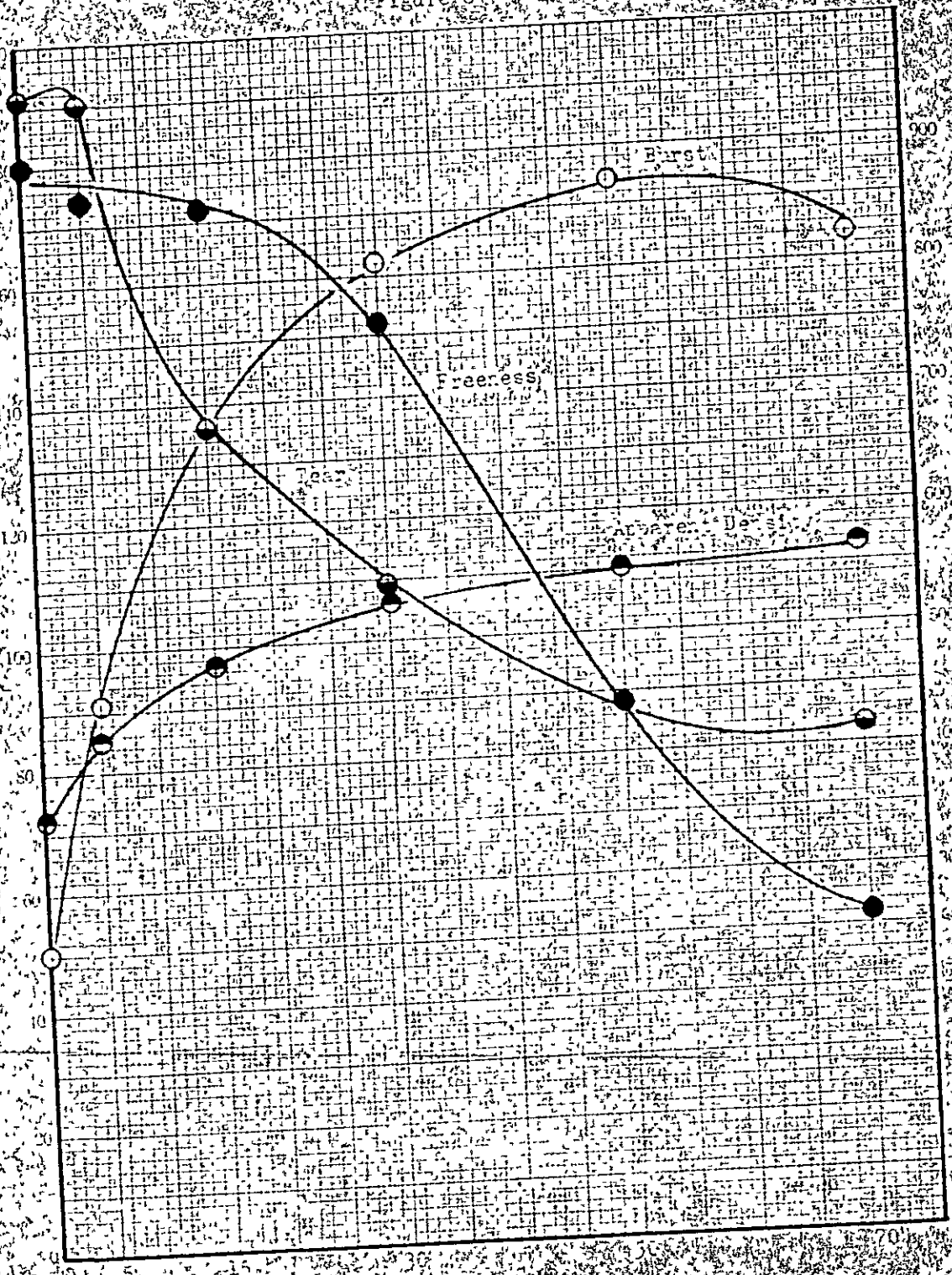
BEATING CURVES

Project 1395 Date

File No Type of Pulp Sulfite Unbleached Kraft

Cook

Figure 6



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BEATING CURVES

Project 1395 Date

File No. Type of Pulp Kraft

Cook 60-A Composite--2 cooks

Figure 7

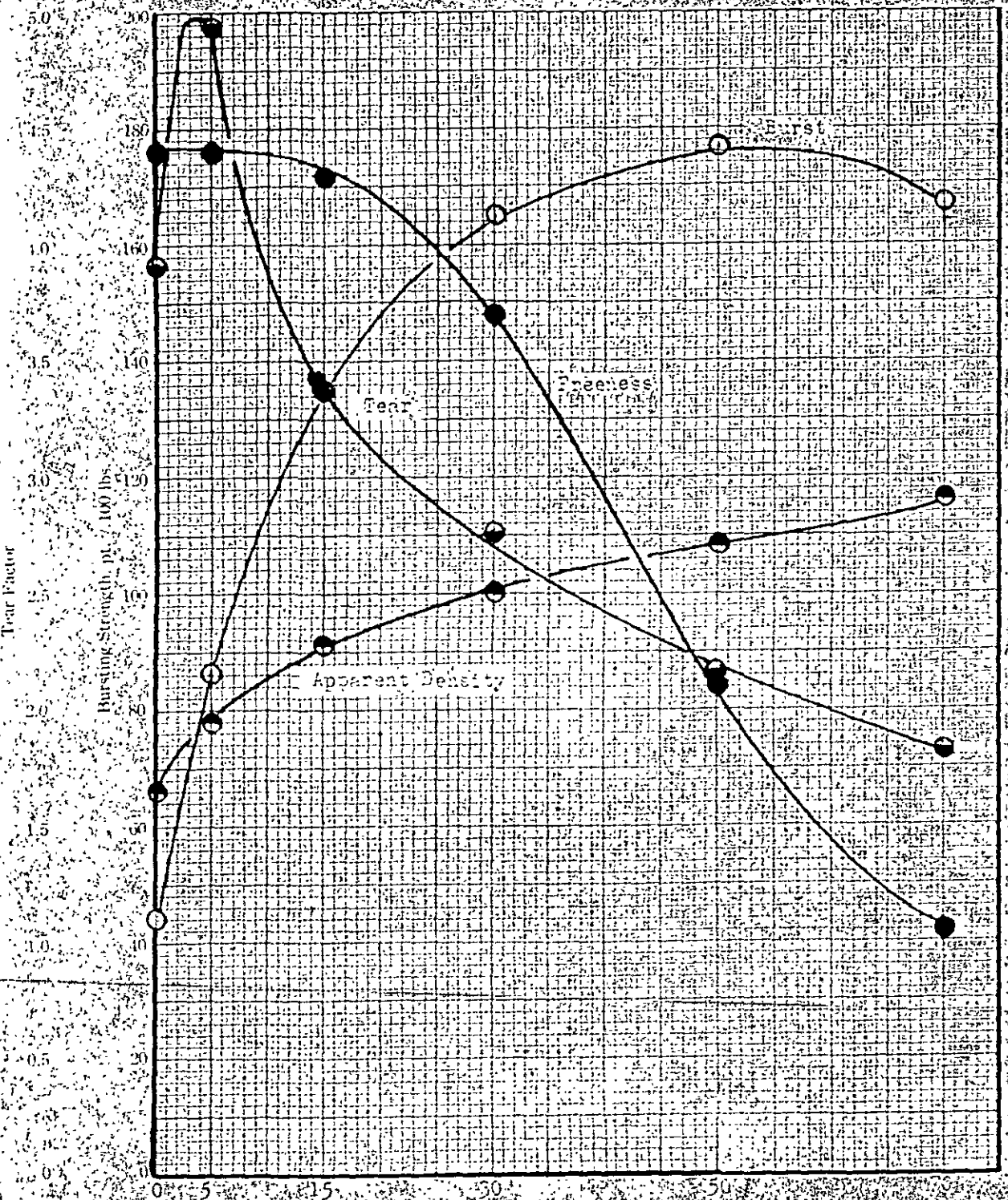

TABLE III

CHEMICAL ANALYSIS OF KRAFT PULPS

Pulp cook	Prehydrolysis	Permanganate Number	Unscreened Yield %	Screening %	Alpha cellulose %	Lignin %	Pentosans %
28	--	24.4	41.2	18.68	87.6	4.5	3.3
29	--	24.2	46.7	3.42	80.2	5.0	7.8
53	110/60	22.1	35.8	8.31	89.0	3.9	2.4
55	120/15	23.8	38.8	5.38	86.9	5.0	4.2
56	120/15	30.4	39.2	1.25	85.6	6.7	4.1
56*	--	--	--	--	83.1	8.8	3.7
57	120/15	54.5+	45.8	1.60	76.2	17.1	3.6
58	120/0	--	42.4	0.65	81.5	11.6	3.3*
59	110/0	22.3	39.0	1.64	86.3	4.2	4.7
60	100/15	24.4	43.7	0.58	83.8	4.7	4.8
60A	--	24.9	47.2	1.53	82.5	5.8	6.6

* Defibered screening

\+ Single determination

DISCUSSION OF RESULTS

The basic idea behind Cook 40 was not explored sufficiently well in this single effort to justify any conclusions. It was not felt that any appreciable diminution of odor was perceptible as a result of the pretreatment used in this cook. However, better control of the pretreatment conditions might have given different results.

Cook 51 was not tested in any manner except that a portion was screened and a permanganate number determination was made. A sample of the black liquor was used in work on odor analysis.

Cook 53 embodied a long prehydrolysis and was made to investigate the effect of such a treatment on penetration of the cooking liquor. The digester was brought to maximum temperature 20 minutes after injection of cooking liquor was completed. This cook can perhaps best be compared with Cook 28, which differed from Cook 53 only in that the maximum steaming pressure was 120 p.s.i. and it was held at this pressure for 15 minutes. Some improvement in screening rejects was noted, 8.3% against 18.7%. The permanganate number was somewhat lower than that of Cook 28, 22.1 for Cook 53 and 24.4 for Cook 28. This would indicate the probability that the wood charge after the 60-minute steaming was less than remained after 20 minutes steaming, with the result that although the same amounts of alkali were used, the alkali to wood ratio was higher for Cook 53 than for Cook 28. The chemical analysis of the two pulps are compared below.

Pulp	Prehydrolysis	$KMnO_4$ No.	Unscreened Yield, %	Screenings %	Alpha Cellulose %	Lignin %	Pentosans %
28	120/15	24.4	41.2	18.68	87.6	4.5	3.3
53	110/60	22.1	35.8	8.31	89.0	3.9	2.4

Some of the differences noted could probably be partly explained by the difference in permanganate number. However, the greatly reduced pentosans of Cook 53 are probably caused directly by the difference in steaming techniques.

Cooks 55 and 59 represent an effort to evolve a prehydrolysis schedule of sufficient drasticity to produce the desired improvement in odor, combined with cooking conditions that will produce a pulp having a yield comparable to that of a non-prehydrolysis cook. Ideally, such a set of conditions would also produce a pulp of low screenings content. To that end a cooking schedule utilizing 75 minutes to maximum temperature was used in Cooks 55 to 58, and a 60-minute rise in Cook 59. The conditions and product variables of Cook 29 are considered baseline for non-prehydrolysis pulp for this series of experiments. Cook 28 was the typical prehydrolysis experiment which was chosen as the point from which this investigation proceeded.

Cooks 55 through 57 investigated a decrease in cooking chemical as a means of increasing the yield of prehydrolysis kraft pulp to a point where it would be comparable to that of Cook 29.

The yield data are as follows:

Cook	28	29	55	56	57
Active alkali as NaOH, %	22.5	23.0	22.5	21.0	18.0
Permanganate Number	24.4	24.2	23.8	30.4	54.5
Unscreened yield, %	41.2	46.7	38.8	39.2	45.8
Screenings, %	18.68	3.42	5.34	1.25	1.60*

These data would tend to indicate that within the range of normal cooking conditions, the yield of pulp is controlled primarily by drasticity of the prehydrolysis step. The similarity in prehydrolysis and variation in cooking conditions are reflected in the analytical data shown below.

Cook	28	29	55	56	57
Permanganate Number	24.4	24.2	23.8	30.4	54.5
Alpha cellulose, %	87.6	80.2	86.9	85.6	76.2
Lignin, %	4.5	5.0	5.0	6.7	17.1
Pentosans, %	3.3	7.8	4.2	4.1	3.6

The degree of pentosan removal appears to be quite similar in the prehydrolysis cooks, while the lignin content increased with increasing permanganate number. The pulp of Cook 56, with a permanganate number of 30.4, had a higher alpha cellulose content than that of Cook 29 with a permanganate number of 24.2.

The strength characteristics of the above mentioned five pulps are compared in Figures 8 through 10, these data being taken from graphs made on the individual pulps.

* This pulp was Bauer-refined before screening.

Figure 6

Comparison of Beating Characteristics of Treated Pulps

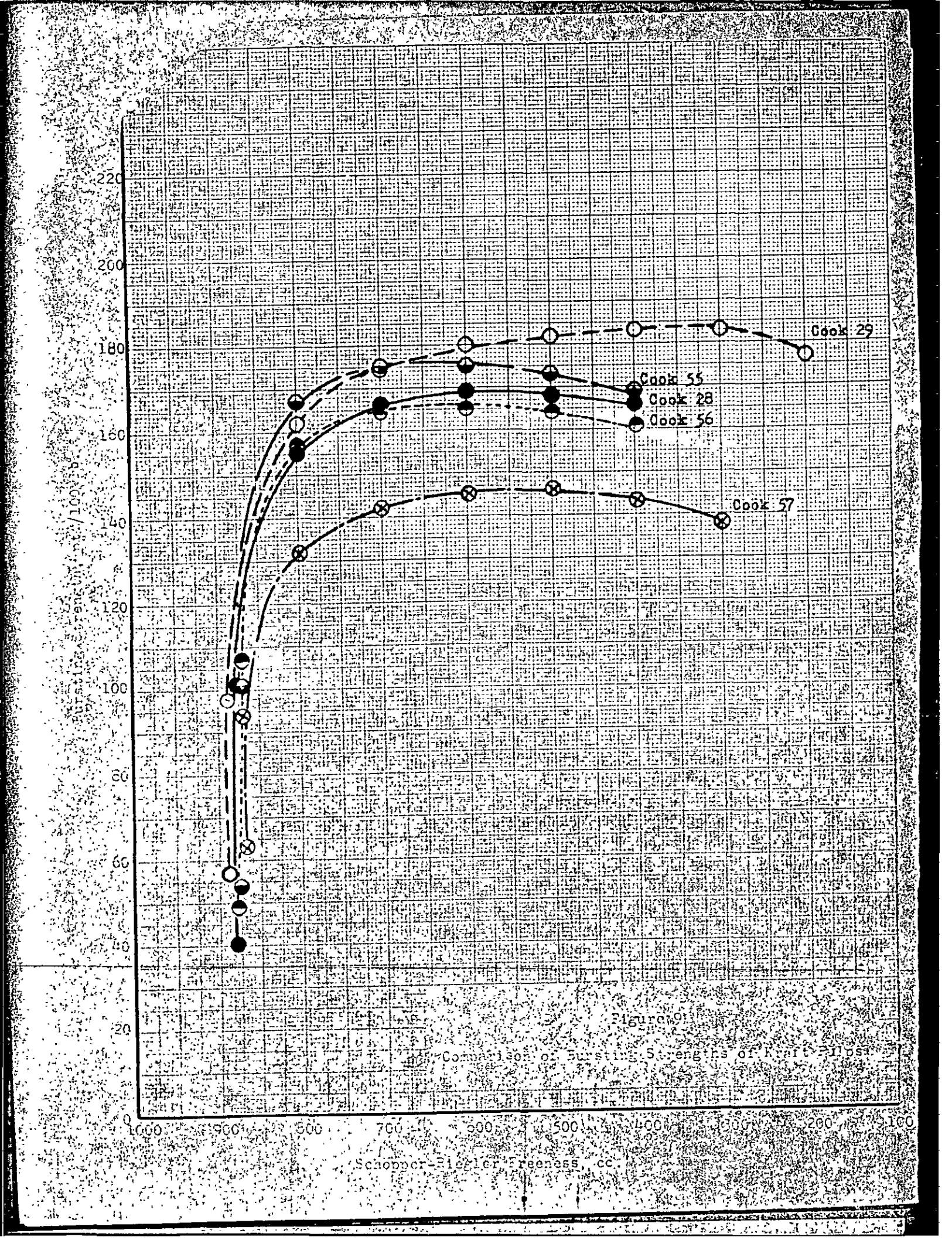

Figure 6

Comparison of Bursting Strengths of Kraft Pulps

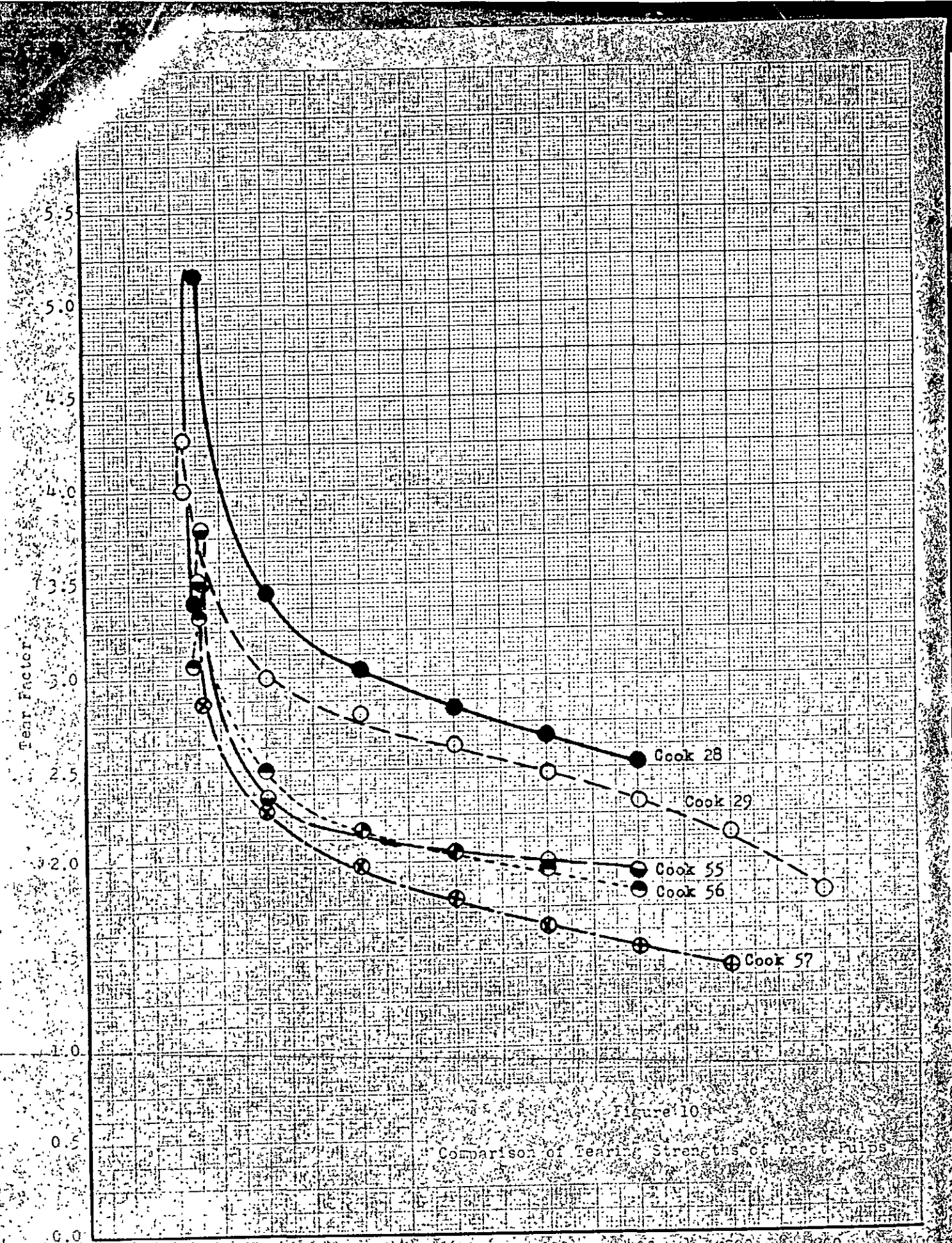

Figure 10

Comparison of Tearing Strengths of Kraft Pulps

Figure 8 indicates that the very raw prehydrolysis experiment, Cook 57, was next to the regular kraft cook (Cook 29) in ease of beating, with the other prehydrolysis kraft pulps showing similarity in their resistance to refining.

A comparison of tearing strength of the several pulps is made in Figure 9. These data show that the regular kraft pulp reaches maximum bursting strength late in the beating cycle, while the prehydrolysis pulps pass through a maximum at about 600 cc. S. R. freeness. At 700 cc. S. R. freeness the bursting strength of Cook 55 is similar to that of the regular kraft pulp, but it then declines whereas that of Cook 29 increases in the lower freeness levels. The bursting strength values of Cooks 28 and 56 are quite similar.

The tearing strength advantage generally exhibited by prehydrolysis pulps over regular kraft pulps is not demonstrated in Figure 10. The strength values for Cooks 55, 56, and 57 are all appreciably lower than those determined for Cook 29. Cook 57 has the lowest tear in this series.

The prehydrolysis conditions used in Cook 58 were thought to have some merit in that the chips would not be at an elevated temperature for a long period of time. The yield was not satisfactory, even though the pulp was too raw to screen without a preliminary defibering step.

The prehydrolysis step used in Cook 59 apparently was not instrumental in bringing the yield of pulp to a desirable level. Although the physical characteristics of the pulp were somewhat superior

to those of Cooks 57 and 58, they were not outstanding.

Cook 60 investigated the effect of an alkaline prehydrolysis wherein the pH of the reaction was maintained in a range above 7.0 by the presence of ammonia gas in the chips. The cook was made on a sample of chips which had previously been pulped in connection with another project. The yield and strength data for comparison with Cook 60 were thus available. Although the digester was relieved copiously during and after prehydrolysis, and in spite of the fact that the pH of the top relief condensate was below 7.0 during the last 10 minutes of steaming, the blow gases smelled strongly of ammonia. Analysis revealed 1.0 g./l. of NH_3 in the black liquor.

The yield of pulp from Cook 60 was substantially less than that determined on duplicate cooks of the material made earlier without pretreatment (43.7 as compared to 47.2). The permanganate number was 0.5 lower and the screenings rejects were about 1/3 of the weight of those from the baseline cooks.

A comparison of the physical characteristics of the pulp from Cook 60 with the average values for duplicate cooks on the same material is made in Figures 11-13. It will be noted that the pulps reacted very similarly to the beating processing.

The results of the chemical tests made on the two pulps (Table III) show that the effect of the prehydrolysis step was to increase the alpha cellulose and decrease lignin and pentosan content.

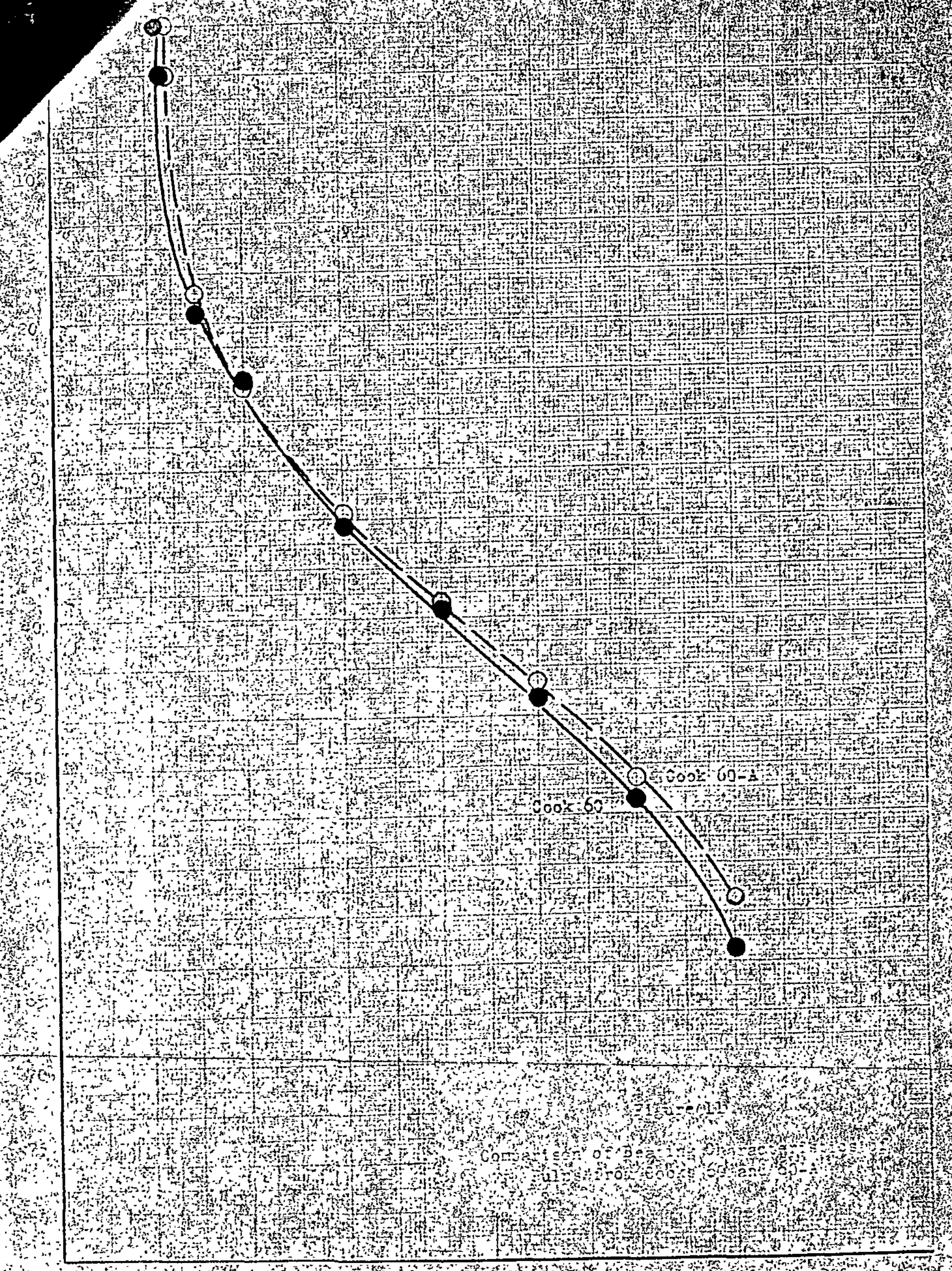

Figure 11

Comparison of Beating Characteristics of Pulps from Cooks 60 and 60-A

Figure
Comparison of Bursting Strength Characteristics
of Coating for Cooks 60 and 60-A

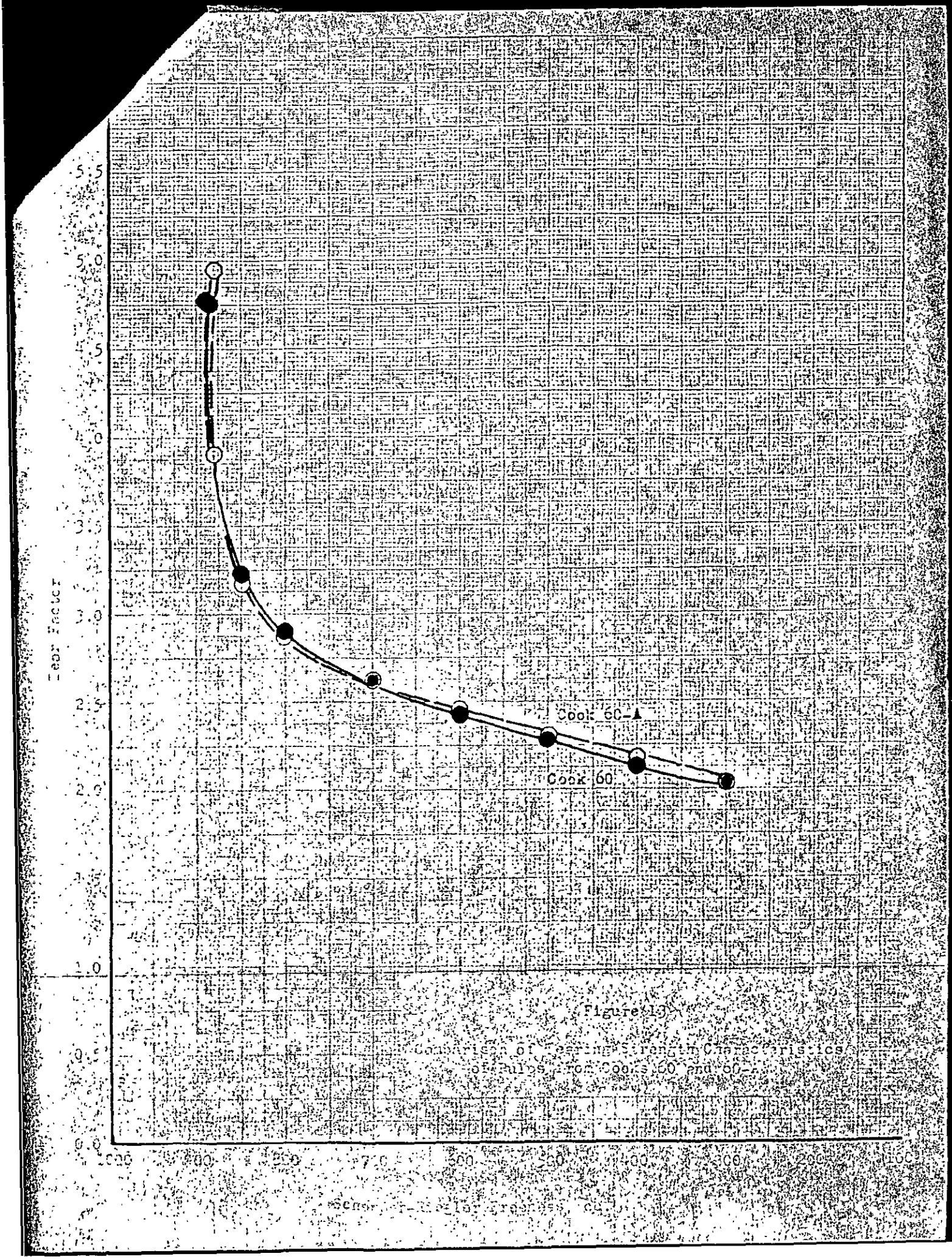

Figure 13

Comparison of Strength Characteristics of Balls from Cooks 60 and 60-A

CONCLUSIONS

From the experiments described in this report, the following conclusions are drawn:

1. The single experiment which utilized a lengthy hot water soak of the chips prior to pulping did not indicate that this pretreatment was effective in reducing the odor of the kraft cooking process.

2. It is possible to combine a prehydrolysis step with a mild kraft cook to produce a pulp with a yield similar to that of a straight kraft cook. However, a prehydrolysis pulp of that yield is so raw that it might have to be defibered mechanically and the pulp is harsh and comparatively low in strength qualities. The blow gas odors from such a cook are not objectionable.

3. A stepwise prehydrolysis with a maximum steam pressure of 110 p.s.i. was apparently only slightly preferable to a quick rise to that pressure, as far as yield and strength results are concerned.

4. The use of ammonia gas in the digester during the steaming period will have the effect of keeping the prehydrolysis reaction in an alkaline medium. That this base is any more effective than sodium carbonate in its results was not demonstrated. In the single experiment described in this report the blow gas odors were extremely unpleasant, much more so, in fact, than those of a straight kraft cook.

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PROJECT REPORT FORM

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DATE March 10, 1950
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Dr. Browning

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In studying the development of odors during kraft pulping, the investigation of individual chemical compounds sealed in glass tubes with kraft white liquor and heated according to a typical cooking schedule has seemed to offer a technique which might be of value. In this way, it would be possible to investigate many compounds during a single cook.

This procedure was followed in a test of 15 compounds, which were prepared and heated on January 24, 1950. Unfortunately, all but 7 of the tubes broke during the heating period. With the experience gained, it is believed that the tubes can be sealed in future work in such a way that breakage will be minimized.

The compounds tested and the observation of odors after opening the tubes were as follows: A total of 6 observers contributed to the smelling tests.

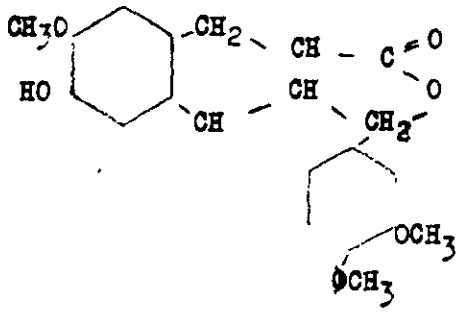
1. Acetophenone. $C_6H_5COCH_3$. The odor was described as penetrating, and aromatic. It was a strong odor, like "city gas works." There was no strong suggestion of a typical kraft odor. The original compound also has a strong penetrating odor, which was evidently somewhat modified.

2. Cinnamic Aldehyde. $C_6H_5CH{=}CH\ CHO$. The odor was very objectionable, skunk-like, or resembling burning rubber. The odor was slightly acrid and appeared to contain some hydrogen sulfide, but not much. Again, the

original compound has considerable odor, but in this case it is of quite different character.

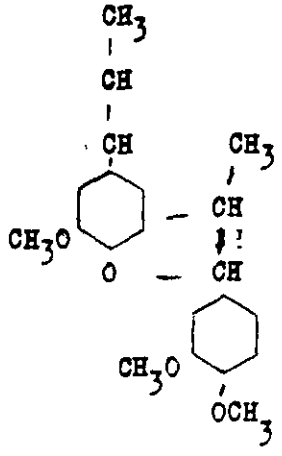
3. Cymene. $CH_3C_6H_4C_3H_7$. Only the original and pleasing aromatic odor was present.

4. Conidendrin (beta).



The strong odor of rotten egg was present. There was a pressure in the tube on opening.

5. Dehydrodiisoeugenol methyl ether. The odor seemed to be hydrogen sulfide, various observers reporting from strong to faint. Some observers reported the odor to be one of sulfide but not H_2S.



6. Formaldehyde. Rotten egg odor, H_2S.

7. Furfural. Obnoxious odor, closest to kraft pulping odor.

"Smells like an oil refining."

After the digestions, all the samples were strongly alkaline--pH above 10 as judged by alkacid paper. The alkaline cook strongly affected the glass tubes, which were left severely etched. There was probably some reduction in alkalinity caused by reaction with the glass.

Although the experiments in this series were not wholly successful, it is believed that sufficient promise has been shown to warrant some further work. It might be hoped that investigation of a series of model compounds would show that certain groups are capable of reacting with kraft liquor to yield noxious odors. The behavior of the constituents of wood might than be interpreted in a more fruitful manner.

In addition to hydrogen sulfide, mercaptans, sulfides and disulfides, which are usually considered the chief odoriferous constituents produced in kraft pulping, it may be worth considering the possible promise of other compounds such as the aldehydes and ketones. These are stated to have powerful and very objectionable odors. Thioacetone, in particular, is stated to have a more offensive odor at extremely great dilutions. The following scattered observations may be of interest for compounds of this type. 1. Thioformaldehyde (CH_2S) polymerizes very readily and cannot be obtained in pure form. 2. These aldehydes and ketones are formed by the action of H_2S on aldehydes and ketones. A catalyst is not essential, but the reaction proceeds more readily if acid or $ZnCl_2$ is present.

3. $Na_2S_2O_3$ may be used instead of H_2S in preparation of thio aldehyde and ketones. 4. Thioketones are hydrolyzed to ketones by heating with dilute alkali. 5. Thioaldehydes combine with H_2S: $CH_2S + H_2S \rightarrow CH_2{<}^{SH}_{SH}$

At least some of these compounds appear to be readily hydrolyzed by alkali and, hence, may be present in the gas phase (relief) but not in the liquor. In this respect, the glass tube experiments, and cooks in which there is no relief and the digester is cooled before opening might possibly give different results from tests in which a relief or condensate may be taken off.