#1395 THE INSTITUTE OF PAPER CHEMISTRY 1948-49
(Prehydrolysis of Wood-Kraft Odor Problem)
Project Reports

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PROJECT REPORT FORM

PROJECT NO. 1395
COOPERATOR Institute
REPORT NO. Four
DATE August 3, 1949
NOTE BOOK 860
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SIGNED John R. Peckham
John R. Peckham

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Files
Steele
Forman
Pulp Lab
Peckham

Pages 110
114-118
120-124

The work covered by this report was done at the request of the International Paper Company and was performed with wood chips supplied by them. These chips contained 51% moisture and were sorted and bagged as has been previously described. Representatives of the company were present during most of the operations and many of the conditions used were suggested by them. The majority of the techniques practiced in this work have been described in previous project reports.

Cook 35 was the initial cook in this series and embodies a prehydrolysis operation of 80 p.s.i. steam pressure for 38 minutes. The prehydrolysis and cooking conditions and product variables for this cook and all cooks subsequently described will be found in Table I. It was thought that there was little of the typical kraft odor noticeable at the time the cook was blown.

Cook 36 was a baseline cook and used the same cooking conditions as the previous cook, but no prehydrolysis. The odor of this cook when blown was distinctly of a kraft nature. The pulp was not saved.

Cook 37 duplicated Cook 35 except for the prehydrolysis schedule, which was 120 p.s.i. steam pressure for 15 minutes. Top relief was constant throughout the cooking schedule. The relief was passed through a water-cooled glass condenser and was caught in a pliofilm bag tied firmly to the outlet of the condenser. The bag was replaced twice during the cook, the relief intervals being divided as follows:

1. from 100° C. to 173.5° C.
2. first half of time at maximum temperature
3. last half of time at maximum temperature

TABLE I

PULPING CONDITIONS AND PRODUCT VARIABLES

Cook	35	36	37	38	39
Prehydrolysis conditions:					
Steam pressure, p.s.i.	80		120		
1. Time to attain pressure, min.	1		2		
2. Time at pressure, min.	38		15		
3. Time to relieve to inject, min.			3		
4. Injecting time, min.	6		7		
Kraft cooking					
Time to maximum pressure, min.	60	60	60	60	60
Total time to max. temperature, min.*	105		87		
Maximum temperature, °C.	173.5	173.5	173.5	173.5	173.5
Time at maximum temperature, min.	60	60	60	60	60
Blow down time to 80 p.s.i., min.	15	15	15	15	15
Total time, cover to blow, min.	180	135	162	135	135
Active alkali as NaOH, %	22.0	22.0	22.0	22.0	23.0
Sulfidity, %	33.3	33.3	33.3	33.0	33.3
Water ratio, (ovendry), cc./g.	3.5**	4.5	3.5**	4.5	4.5
Permanganate number	22.6		23.0		26.0
Unscreened yield, %	40.27		38.72		45.92
Screened yield, %	37.71		37.19		43.34
Screenings, %	6.35		3.94		5.62
Prehydrolysis condensate data					
Volume of top relief, cc.	910		1230		
pH of top relief	4.2		4.32		
Volume of bottom relief, cc.	10,780		5,470		
pH of bottom relief	4.1		4.35		
Volume of top relief condensate from cook, cc.					
Black liquor analysis					
pH	12.5		12.6		12.7
Total alkali as Na_2O, g./l.	38.1		45.6		35.1
Active alkali as Na_2O, g./l.	8.4		11.0		12.1

* Includes 1, 2, 3, and 4 under prehydrolysis
** Does not include water from prehydrolysis

The samples were taken in this manner in order to trap the noncondensable gases for odor evaluation.

Cook 38 was made in the same manner as Cook 36, a nonprehydrolysis cook, and no pulp was saved. Top relief samples were taken as described for Cook 37 and were used to compare the odor of the gases from the two cooks.

The above mentioned comparison was made in a room having a high rate of air exchange by reason of an efficient exhaust fan. The samples were arranged around a long table and were coded by letter. Several Institute staff members were asked to smell each of the samples and to rate them as to the relative offensiveness of the odor. Without exception, Sample 1 from Cook 37 was declared least objectionable, and Sample 3 from Cook 38 the most offensive. When judged as a group, the three samples from Cook 38 were unanimously chosen as most objectionable.

Cook 39 was the baseline cook and, although more alkali was used than was necessary for the prehydrolysis cooks, the permanganate number was somewhat high. The cook was, however, accepted as the baseline effort and was evaluated.

The physical characteristics of the cooks which were of interest are shown in Table II and Figures 1 through 3. Comparison of the strength characteristics of the three pulps at similar freeness levels is made in Figures 4 through 6.

DISCUSSION OF RESULTS

International Paper Company's representatives, Mr. Gilbert and Mr. Harris, were present during the work herein described and suggested many of the conditions. They did not, however, comment officially on the odor attendant to the several cooks. Any comments in regard to this phase of the study are a reflection of the opinion of the writer only.

TABLE II

PHYSICAL CHARACTERISTICS OF SOUTHERN PINE KRAFT PULPS FOR INTERNATIONAL PAPER COMPANY

Cook		35	37	39
Prehydrolysis pressure, p.s.i.		80	120	—
Prehydrolysis time, min.		38	15	—
Permanganate number		22.6	23.0	26.0
Schopper-Riegler freeness, cc.	0	880	870	880
	5	870	870	875
	15	830	855	860
	30	700	740	710
	50	385	425	320
	70	230	265	165
Basis weight (24x36--480), lb.	0	40.7	39.2	39.5
	5	38.4	38.7	38.2
	15	38.5	37.6	39.8
	30	39.3	38.0	38.5
	50	39.1	38.6	38.6
	70	38.6	38.4	38.5
Caliper, in.	0	0.0050	0.0047	0.0052
	5	0.0041	0.0041	0.0042
	15	0.0037	0.0036	0.0040
	30	0.0035	0.0034	0.0036
	50	0.0032	0.0032	0.0033
	70	0.0031	0.0030	0.0031
Apparent density	0	8.1	8.3	7.6
	5	9.4	9.4	8.7
	15	10.4	10.4	10.0
	30	11.2	11.2	10.7
	50	12.2	12.1	11.7
	70	12.5	12.8	12.4
Bursting strength, pt./100 lb.	0	48	50	65
	5	102	103	107
	15	152	152	150
	30	176	177	172
	50	182	181	177
	70	170	165	173
Tear factor	0	3.93	4.54	4.66
	5	4.71	4.63	3.85
	15	3.32	3.40	3.12
	30	2.75	2.87	2.62
	50	2.17	2.38	2.18
	70	1.97	2.11	1.77

* This column denotes beating time in minutes

The series of three cooks which were completely evaluated covered a baseline and two prehydrolysis cooks wherein divergent presteaming conditions were used.

The pulp from Cook 39 is considered baseline or a typical kraft pulp from southern pine. The permanganate number was higher than was recorded for the two prehydrolysis pulps. Cook 35 produced the prehydrolysed kraft pulp using a mild presteaming treatment, and Cook 36 identifies the pulp obtained after a more rigerous steaming treatment.

The data in Table I shows that less alkali was needed to pulp to a given permanganate number when prehydrolysis was employed. The time of actual contact with the liquor was the same for the prehydrolysis cooks as for the baseline cook.

The yield of pulp was considerably lower when prehydrolysis was used, and Cook 37, which employed the more drastic steaming operation, produced the lowest yield in the series.

The screenings were not extremely high in either of the prehydrolysis cooks, probably because the schedules had provided an adequate time to maximum temperature.

The odor of the blow gases from Cooks 35 and 37 were typical of the prehydrolysis cooks made previously. The odor from Cooks 36, 38, and 39 was like that of any normal kraft cook. The odor of the gases obtained during Cook 37 was less objectionable than those obtained from Cook 38.

The pulp from Cook 39 (baseline) was somewhat easier beating than the pulps from the prehydrolysis cooks, as shown in Figure 4. The pulp from Cook 35 (mild prehydrolysis) beat more readily than that from Cook 37 (drastic prehydrolysis).

The bursting strengths of the 3 pulps (Figure 5) were much the same with a little advantage for the prehydrolyzed pulps.

The tear curves, shown in Figure 6, display more similarity than has been hitherto experienced in this work. However, it can probably be safely stated that the tearing strengths of the prehydrolyzed pulps are superior to that of the baseline pulp. The pulp from Cook 37 had a slightly higher tear than that from Cook 35.

CONCLUSIONS

The data obtained from this series of cooks corroborates many of the findings reported previously. Prehydrolysis of the wood chips, followed by a kraft cook resulted in lower yields than when no prehydrolysis was practiced. The more drastic steaming operation lowered the yield more than did the milder conditions.

The odor attendant to the blowing of the prehydrolysis cooks was less objectionable than that of the unprehydrolyzed cooks. The noncondensable gases from Cook 37 (prehydrolyzed) were less objectionable to a number of observers than were similar gases from Cook 38 which was a typical kraft cook.

The beating cycles and strength characteristics of the several pulps were more nearly alike than was typical in previous experiments.

Prehydrolysis conditions of 80 p.s.i. steam pressure for 38 minutes probably degrades the pulp less than 120 p.s.i. steam for 15 minutes.

jrp/mm

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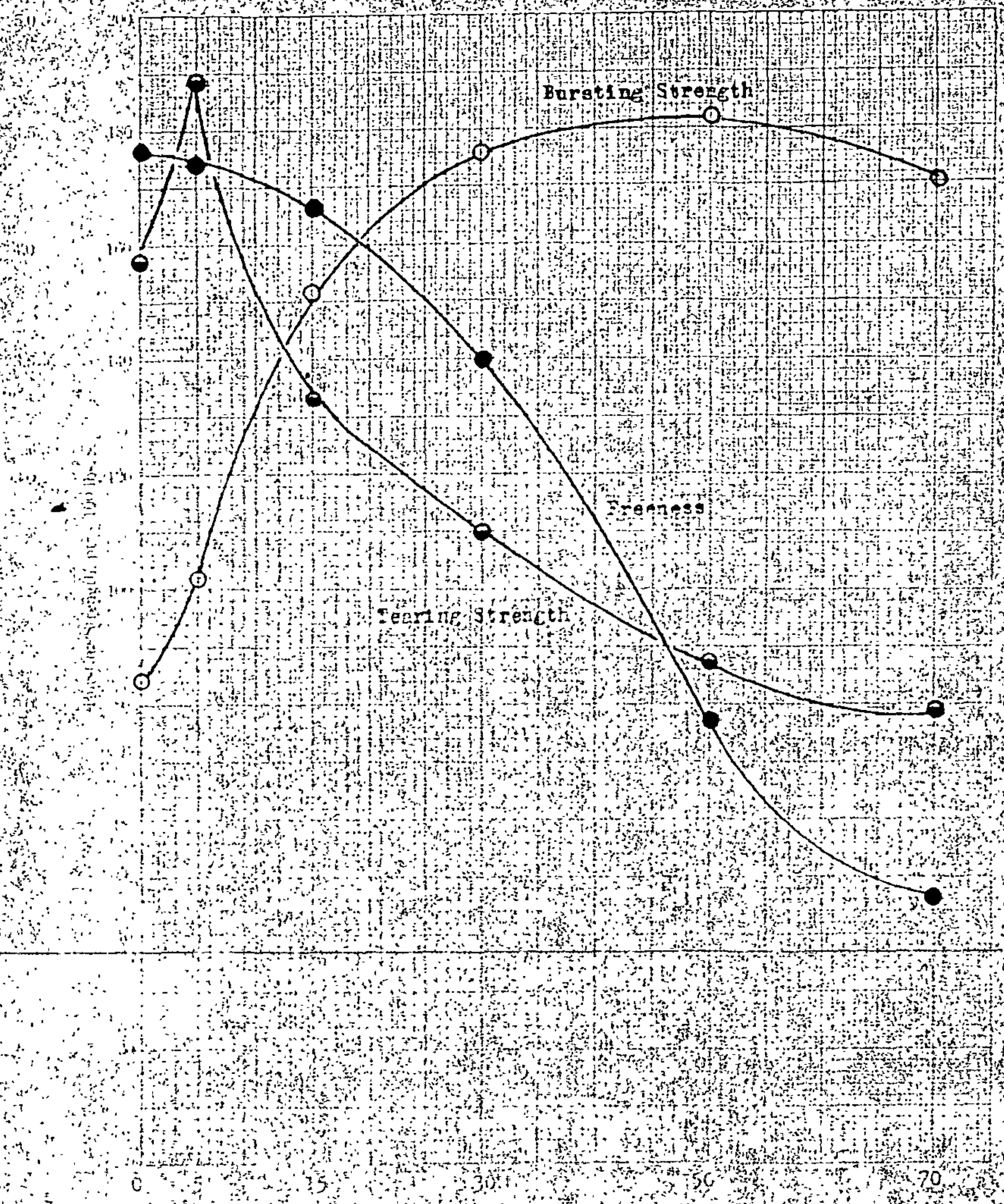
BEATING CURVES

Project 1395
File No.
Cook 35
Date
Type of Pulp

Figure 1



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BEATING CURVES

Project 1395

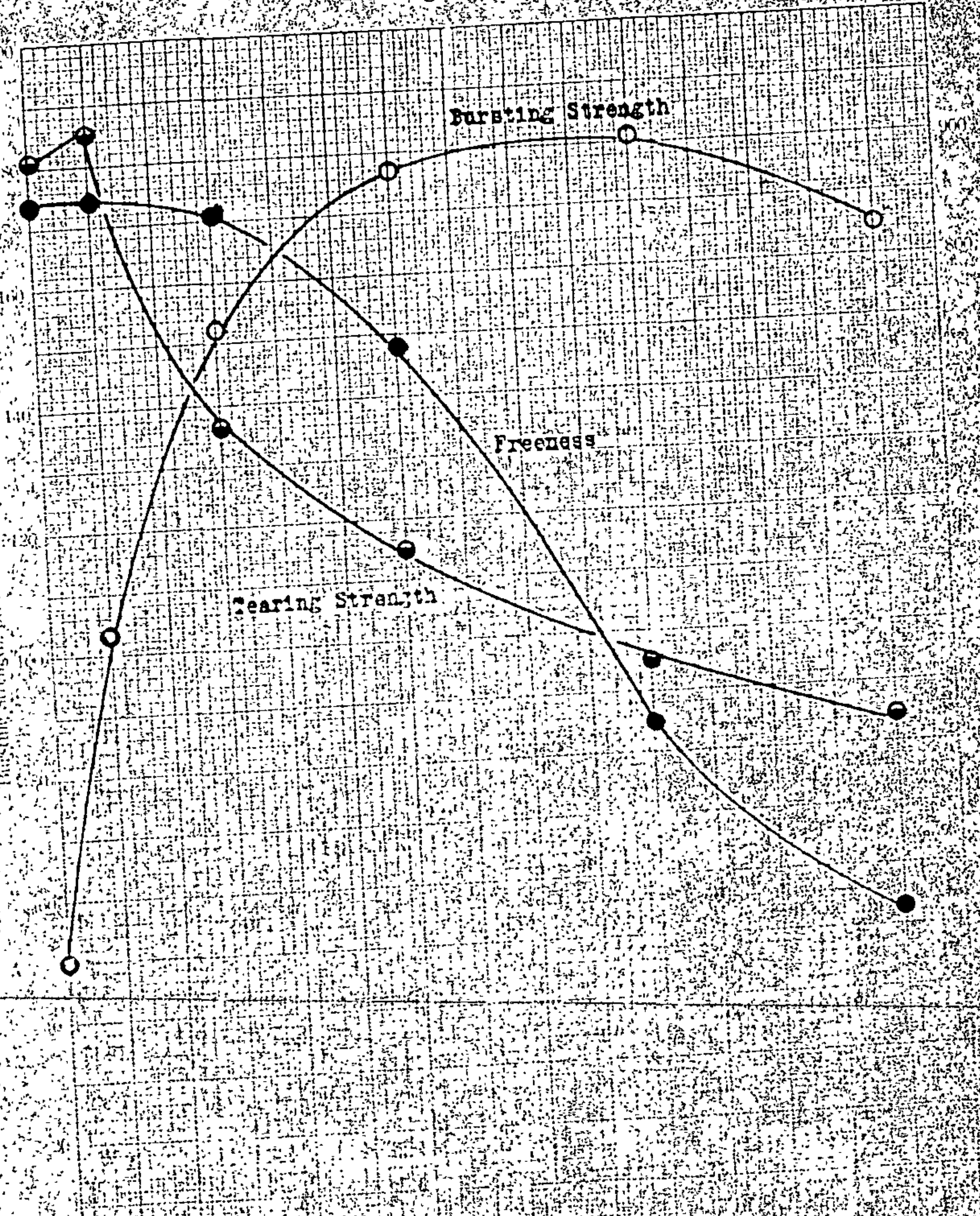
Date

Type of Pulp

File No.

Cook 37

Figure 2



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BEATING CURVES

Project 1395

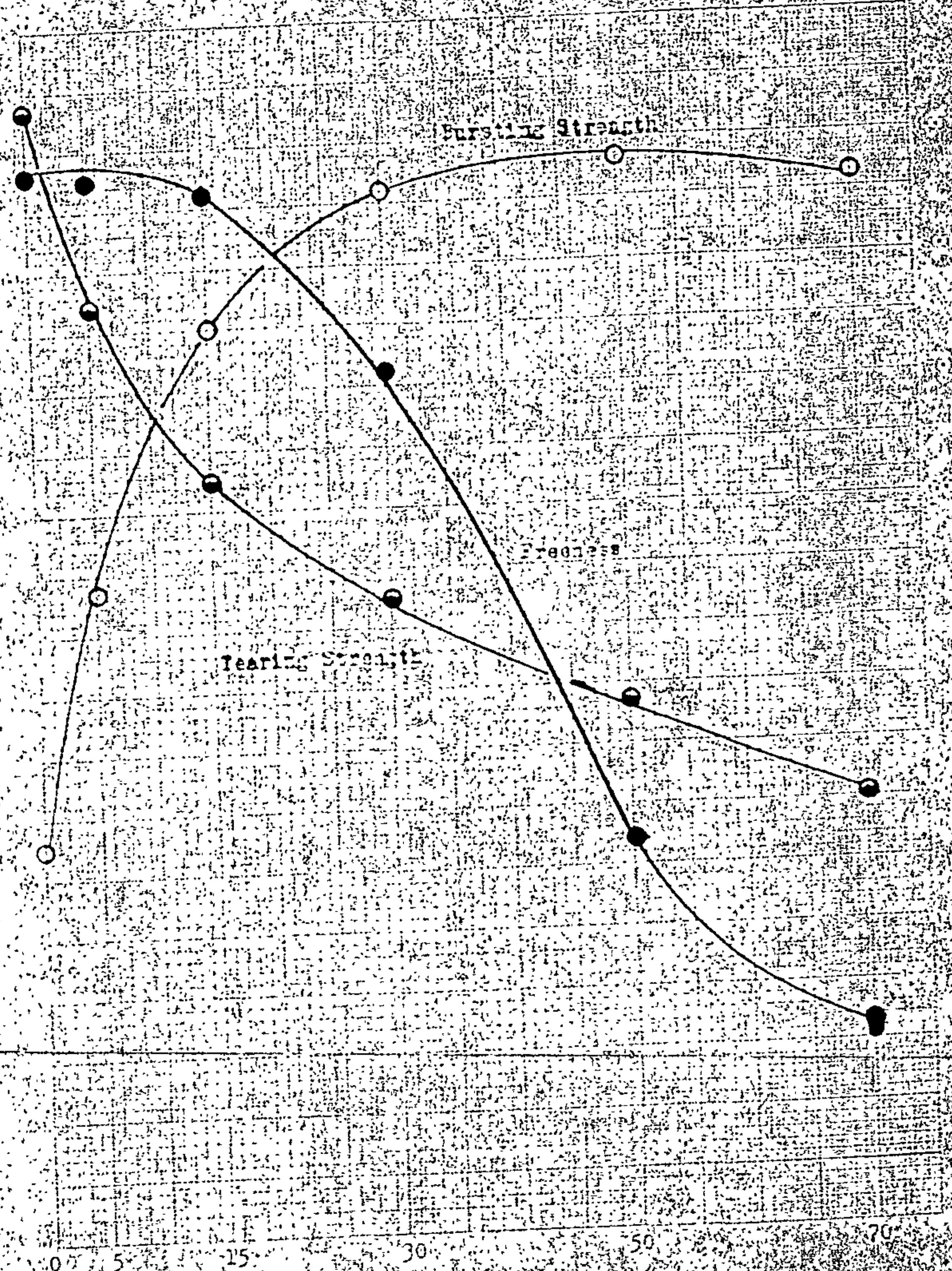
File No.

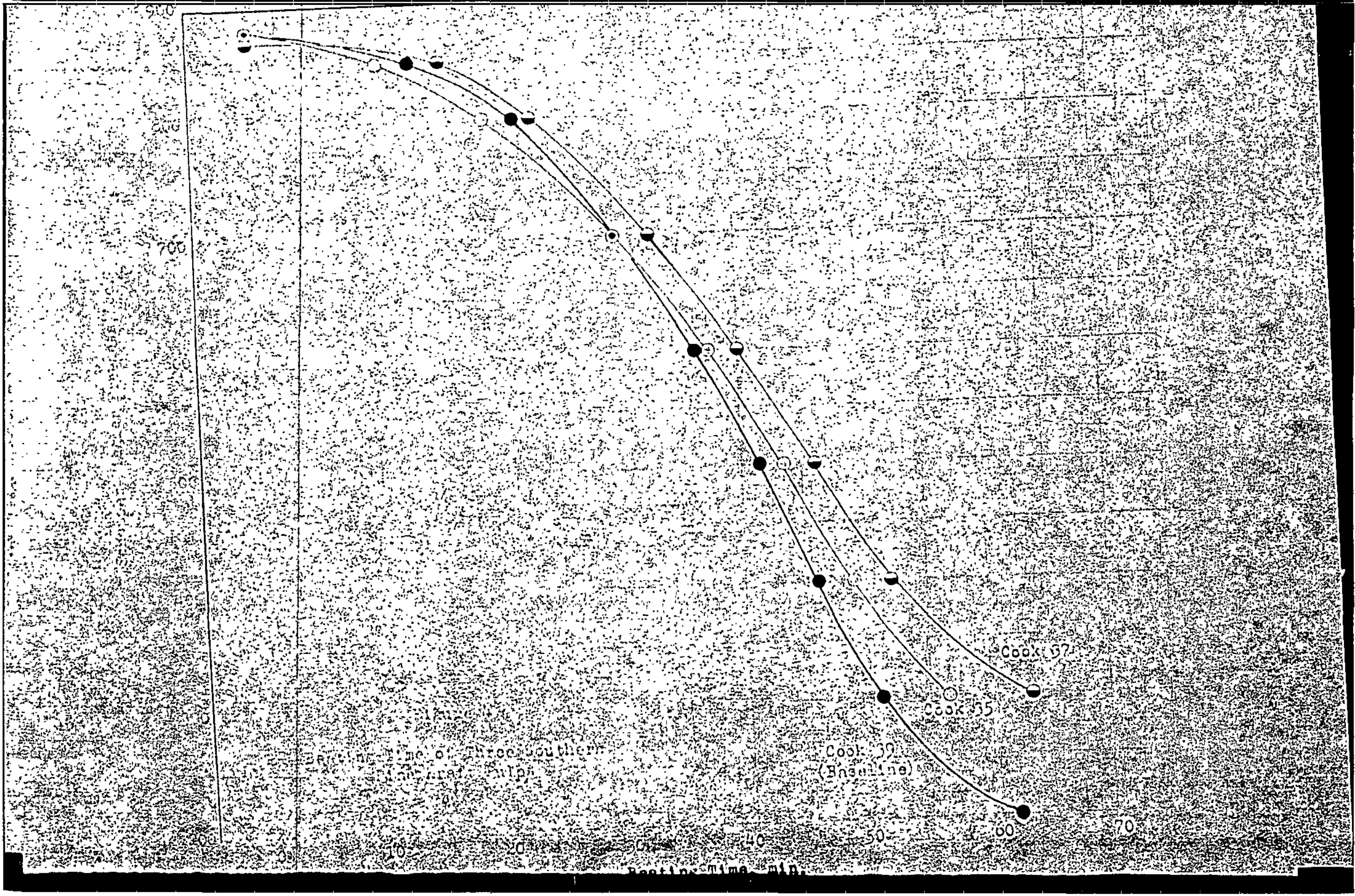
Cook 39

Date

Type of Pulp

Figure 3





Beating Time of Three Southern Kraft Pulps

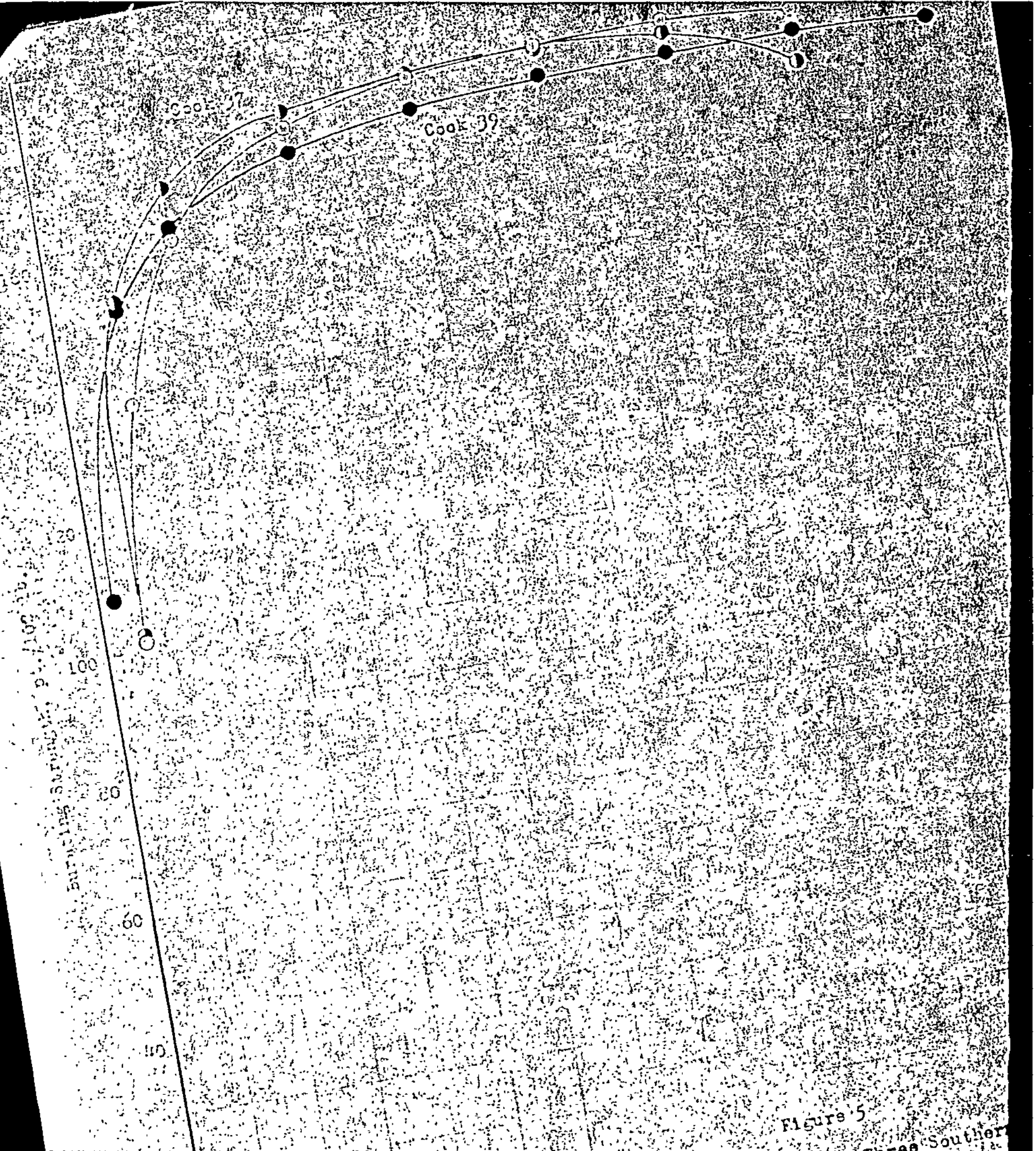
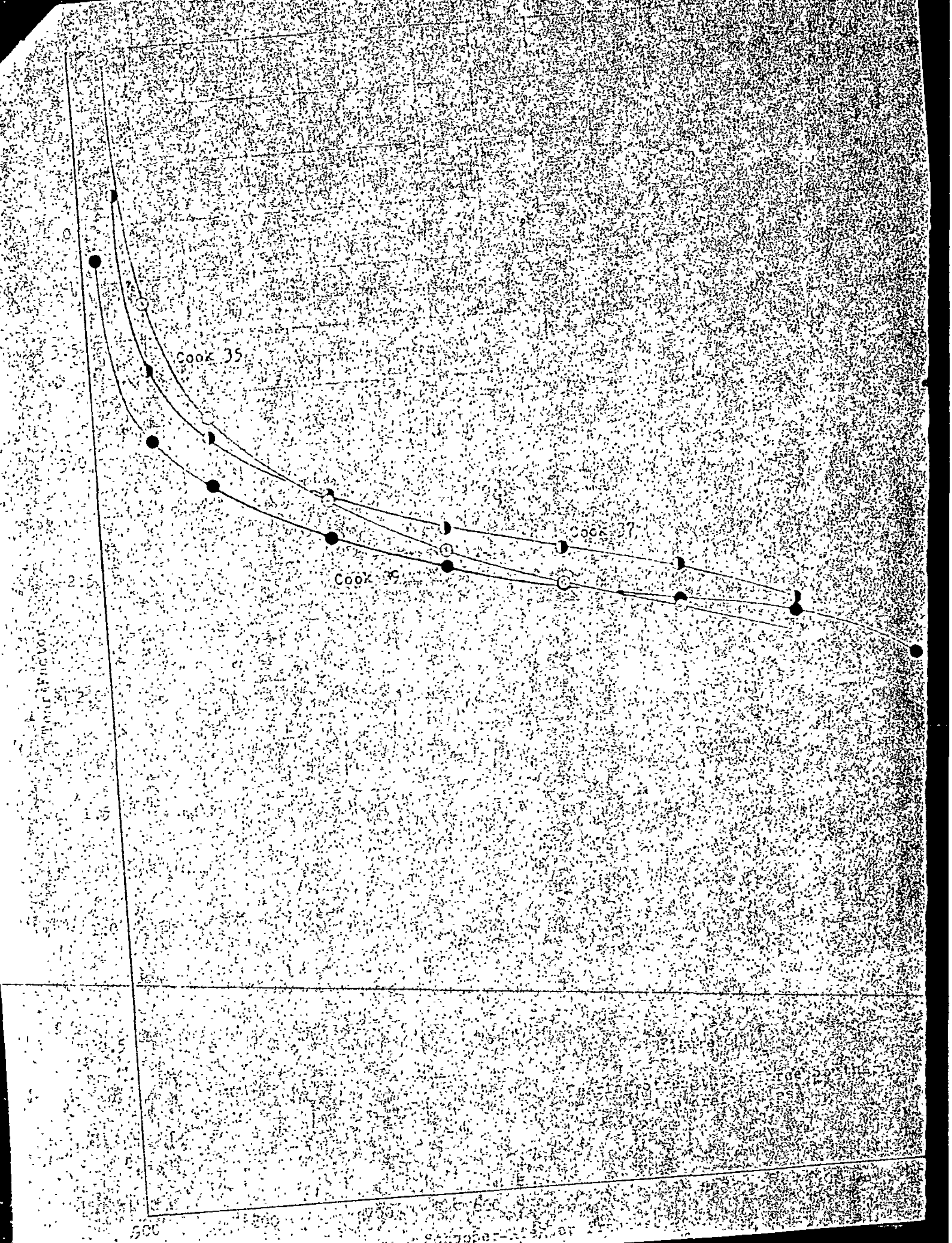


Figure 5

Bursting Strength of Three Souther
Pine Kraft Pulps


Cook 35
Cook 37
Cook 39
3.5
3.0
2.5
2.0
1.5
1.0
.5
factor
500
700
600
Schopper-Riegler

1949

PROJECT REPORT FORM

PROJECT NO. 1395
COOPERATOR Institute
REPORT NO. 3
DATE July 26, 1949
NOTE BOOK 860
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Pages: 89-109
111-113
126-127
134
140

PREHYDROLYSIS OF WOOD

Project Reports One and Two dealt primarily with preliminary experiments designed to demonstrate the efficacy of prehydrolysis of chips as a means of alleviating the odor normally associated with pulping by the kraft process. A laboratory stationary digester and a laboratory Asplund mill were investigated as vessels in which to demonstrate the process. Several miscellaneous experiments in which prehydrolysis played no part were also described.

This report will cover a series of cooks made in an effort to determine optimum prehydrolysis conditions as they affect (1) pulp quality, (2) pulp yield, and (3) screenings ratio.

The basis for this work is contained in a memorandum from Forman to Peckham dated 2/28/49.

The equipment used has been previously described.

Cook 25 was made in No. 3 iron digester. The conditions for the cook are shown in Table I. This digester had not been used for some time due to operational difficulties. It had recently been overhauled and repiped, so it was put into service. The conditions used in the cook produced a pulp considerably harder than desired. Cook 26 was made, also in Digester No. 3 with an increase in active alkali. Only a small amount of this cook was screened when it became apparent that the chips had been incompletely pulped.

TABLE I

PULPING DATA AND PRODUCT VARIABLES

Digester No.	3	3	4	4	4	4	4	4	4	4		
Experiment No.	25	26	27	28	29	30	31	32	33	34	41	46
Prehydrolysis	none	none	none		none							
Steam pressure, psi.				120		80	100	100	120	120	80	120
(a) Time to attain pressure, min.				2		1	3	3	2	2	1	3
(b) Time at pressure, min.				15		38	15	25	15	15	10	15
(c) Time to relieve to inject, min.				2		0	2	2	2	3	0	2
(d) Injecting time, min.				5		6	5	5	8	8	4	8
Kraft Cooking												
Time to max. temp., min.	60	60	60	20	60	20	20	20	20	40	20	60
*Total time to max. temp., min.				44		65	45	55	47	68	35	88
Temperature, °C.	172	172	172	172	172	172	172	172	172	172	172	172
Time at max. temp., min.	75	75	75	75	75	75	75	75	75	75	75	55
Blowdown time, min.	15	15	15	15	15	15	15	15	15	15	15	15
Total time-cover to blow, min.	150	150	150	134	150	155	135	145	137	158	115	158
Active alkali, as NaOH, %	22.0	24.0	22.0	22.5	23.0	22.5	22.5	22.5	22.5	22.5	22.5	22.5
Sulfidity, %	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3
Water ratio, cc./g. o.d.	4.5	4.5	4.5	3.5	4.5	3.5	2.5	3.5	4.5	3.5	3.5	3.5
Permanganate no.	33.0	32.6	28.9	24.4	24.2	23.7	29.7	22.4	25.9	22.1	28.5	27.7
Unscreened yield, %	50.56		47.70	41.25	46.70	41.78	50.41	41.66	41.86	39.99	46.22	40.72
Screened yield, %	43.77		45.06	33.55	45.10	39.89	32.40	37.90	36.33	38.20	44.16	39.46
Screenings, %	13.42		5.54	18.68	3.42	4.52	35.72	9.02	13.20	4.48	4.45	3.09
Black liquor analysis:												
pH	12.5	12.6	12.6	12.2	12.7	12.4	11.0	11.5	11.4			
Total alkali, as Na_2O, g./l.	28.6	30.5	33.6	41.2	38.4	38.8	43.1	42.2	46.9			
Active alkali, as Na_2O, g./l.	4.3	7.0	9.1	9.2	11.0	9.1	8.9	9.4	10.0			

* Includes a, b, c, d in Prehydrolysis.

TABLE I (concluded)

Experiment No.	25	26	27	28	29	30	31	32	33	34	41	46
Prehydrolysis Condensate Data:												
Volume of top relief, cc.				790		1820	2192	1640	925	1250	950	940
pH of top relief				3.95		4.12	4.4	4.0	4.0	3.55	6.2	4.5
Volume of bottom relief, cc.				8705		8820	7860	14,525	6790	6040	3520	7230
pH of bottom relief				5.6		4.1	5.0	4.4	4.0	3.75	5.95	4.45

The work at this point was transferred to #4 stainless steel digester and Cook 25 was repeated as Cook 27. The desired permanganate number of 25 was not reached, so the cook was repeated as Cook 29, utilizing a small increase in active alkali. This pulp from this cook was considered satisfactory as a baseline.

Cook 28 had prehydrolysis conditions of 120 p.s.i. steam pressure, attained in 2 minutes and held for 15 minutes. Top and bottom relief were continuous throughout the steaming period. At the end of the 15 minutes, the steam was shut off and relief continued for an additional 2 minutes to an internal pressure of 80 p.s.i. At this point the liquor for the cook, which had been made up in advance and in a volume which provided considerable overage to fill the various injection lines, was injected. The water ratio, disregarding the water from the steaming operation, was 3.5 to 1, or one part less water than used in the baseline. It was assumed that the water from the prehydrolysis would compensate for this cut. The injection consumed an additional 5 minutes. The temperature was brought to maximum in 20 minutes after the completion of the chemical addition, and maintained there for 75 minutes. After a 15-minute blowdown, the cook was blown and thereafter washed, screened on .010" cut flat screen, and the yield was determined. All prehydrolysis operations hereinafter described were performed in the same manner except for time and pressure changes as noted. All prehydrolysis data are included in Table I.

Cook 30 had a prehydrolysis schedule of 80 p.s.i. steam pressure attained in one minute and held for 38 minutes. Other conditions were the same as for Cook 28. No steaming relief was necessary to permit injection since the pressure was already at the desired point.

Cook 31 also duplicated Cook 28, in prehydrolysis as well as cooking. The variable in this case was the water ratio, which was lowered from 3.5 to 2.5 to 1. Although this step was designed to obtain a higher chemical concentration in the cook and improve the degree of pulping, the results were exactly the reverse.

Cook 32 utilized a prehydrolysis of 100 p.s.i. steam applied for 25 minutes. After 2 minutes relief and 5 minutes injection time, the cooking followed the conditions of Cook 28.

Cook 33 was an attempt to improve the pulping conditions after a prehydrolysis of 120 p.s.i. Since cutting the water ratio (Cook 31) was unsuccessful, this cook was made with the same water ratio as the baseline cook. No improvement in cooking uniformity was noted.

Cooks 34 and 46 investigated the effects of increasing the time to maximum temperature, after prehydrolysis at 120 p.s.i. for 15 minutes. Cook 34 used 40 minutes and Cook 46 used 60 minutes to attain maximum temperature after injection of the liquor.

Cook 41 investigated the possibility of prehydrolysis at 80 p.s.i. for a short time (in this case 10 minutes). The permanganate number was high.

The pulps of interest—Cooks 28, 29, 30, and 32—were beater evaluated according to Institute Methods 403 and 411, using 6500 g. bedplate loading.

DISCUSSION OF RESULTS

After the work was transferred to No. 4 digester, Cook 29 was established as a baseline. The permanganate number was 24.2 and the yield and screenings ratio seemed typical of a southern pine kraft pulp of that degree of cooking. All of the prehydrolysis cooks which attained the desired permanganate number, displayed about 5% less yield on the unscreened basis than did Cook 29, the baseline cook. Another factor of note in the yield data was the high screenings ratio found in the prehydrolysis pulps. The trend was definitely higher as the maximum prehydrolysis steam pressure was increased, as can be seen from the yield data for Cooks 28, 30, and 32 in Table I. Increasing the time to maximum temperature (Cooks 28-34, and 46—Table I) was effective as a means of reducing screenings when 120 p.s.i. steam pressure was used in prehydrolysis. However, the over-all cooking time was lengthened appreciably by this procedure, and the permanganate numbers of Cooks 34 and 46 were so divergent that it would be unsafe to draw conclusions from these pulps.

In the laboratory work it is quite difficult to reproduce the water ratio of prehydrolysis cooks from experiment to experiment. In the work to date it has been assumed that the chips pick up their ovendry weight in moisture, but it is quite likely that many factors affect the validity of this assumption. The importance of chemical concentration in kraft pulping is sufficiently well known that it need not be dealt with here.

The strength data for Cooks 28-29, 30, and 32 are shown in Table II and Figures 1 through 4. Evaluation of Cooks 31, 33, 34, 41, and 46 were not attempted since the pulps were not entirely satisfactory. Comparisons of certain data are plotted against freeness in Figures 5 through 7.

The burst-tear relationships of the several cooks followed the trends which were discovered earlier, i.e., prehydrolysis pulps were higher in tear and lower in burst than the baseline pulp. The beating cycles were also typical of the previous results, where prehydrolysis pulps had been found to beat harder than a similar kraft pulp made without prehydrolysis.

A comparison of prehydrolysis pulps made at three maximum steam pressure levels shows that the pulp from Cook 30 (80 p.s.i. steam for 38 minutes) was outstanding. The burst was equal to that of the baseline pulp, and the tear was also very good. In ease of beating it was only slightly more resistant than the baseline pulp.

CONCLUSIONS

The work covered by this report bore out the findings of previous experiments in regard to yield and strength characteristics. All prehydrolysis cooks showed considerable loss in yield and high screening rejects. High tear, low burst, and resistance to beating were also typical of pulps where prehydrolysis was employed.

TABLE II

PHYSICAL CHARACTERISTICS

		Cook 28	Cook 29	Cook 30	Cook 32
Schopper-Riegler freeness, cc.	0	880	890	870	890
	5	870	880	860	880
	15	845	860	835	855
	30	725	720	740	750
	50	480	365	410	460
	70	305	185	255	260
Basis weight (24 x 36--500), lb.	0	37.6	38.4	40.7	40.3
	5	39.3	39.5	38.1	37.4
	15	38.6	38.9	39.5	38.9
	30	38.3	38.7	38.8	38.2
	50	39.6	38.0	38.8	38.2
	70	39.0	38.5	38.1	38.3
Caliper, in.	0	0.0048	0.0053	0.0055	0.0050
	5	0.0043	0.0048	0.0044	0.0041
	15	0.0040	0.0041	0.0040	0.0039
	30	0.0036	0.0038	0.0037	0.0037
	50	0.0035	0.0035	0.0035	0.0035
	70	0.0033	0.0033	0.0032	0.0034
Apparent density	0	7.8	7.2	7.4	8.1
	5	9.1	8.2	8.7	9.1
	15	9.6	9.5	9.9	10.0
	30	10.6	10.2	10.5	10.3
	50	11.3	10.9	11.1	10.9
	70	11.8	11.7	11.9	11.3
Bursting strength, pt./100 lb.	0	50	57	41	39
	5	101	98	92	89
	15	140	142	148	141
	30	164	174	179	158
	50	168	183	183	166
	70	158	171	167	167
Tear factor	0	3.40	4.01	4.03	3.67
	5	5.17	4.23	5.35	5.45
	15	3.89	3.24	3.65	3.70
	30	3.21	2.84	3.20	3.28
	50	2.63	2.26	2.60	2.45
	70	2.36	1.77	2.13	2.38

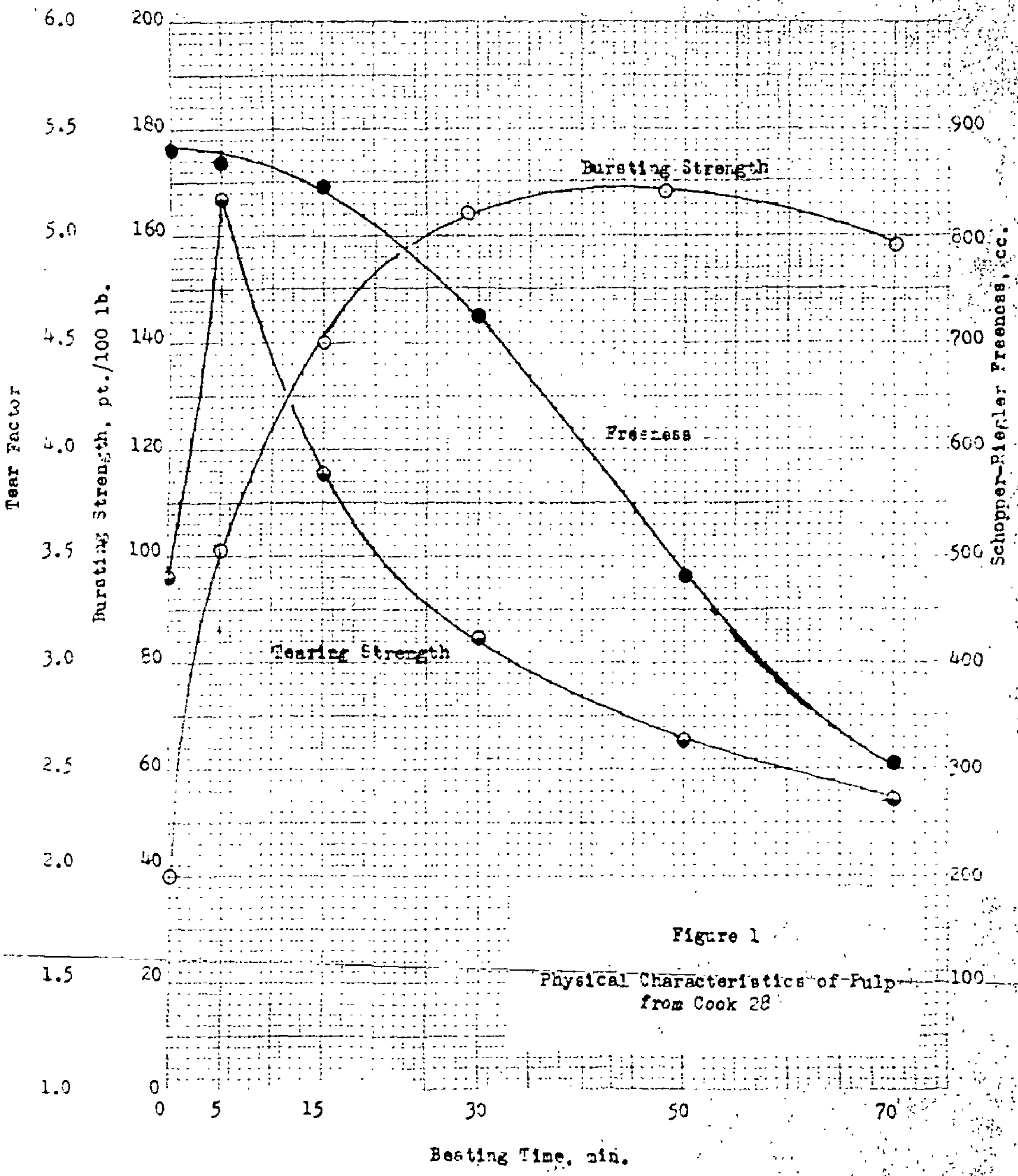

Figure 1

Physical Characteristics of Pulp from Cook 28

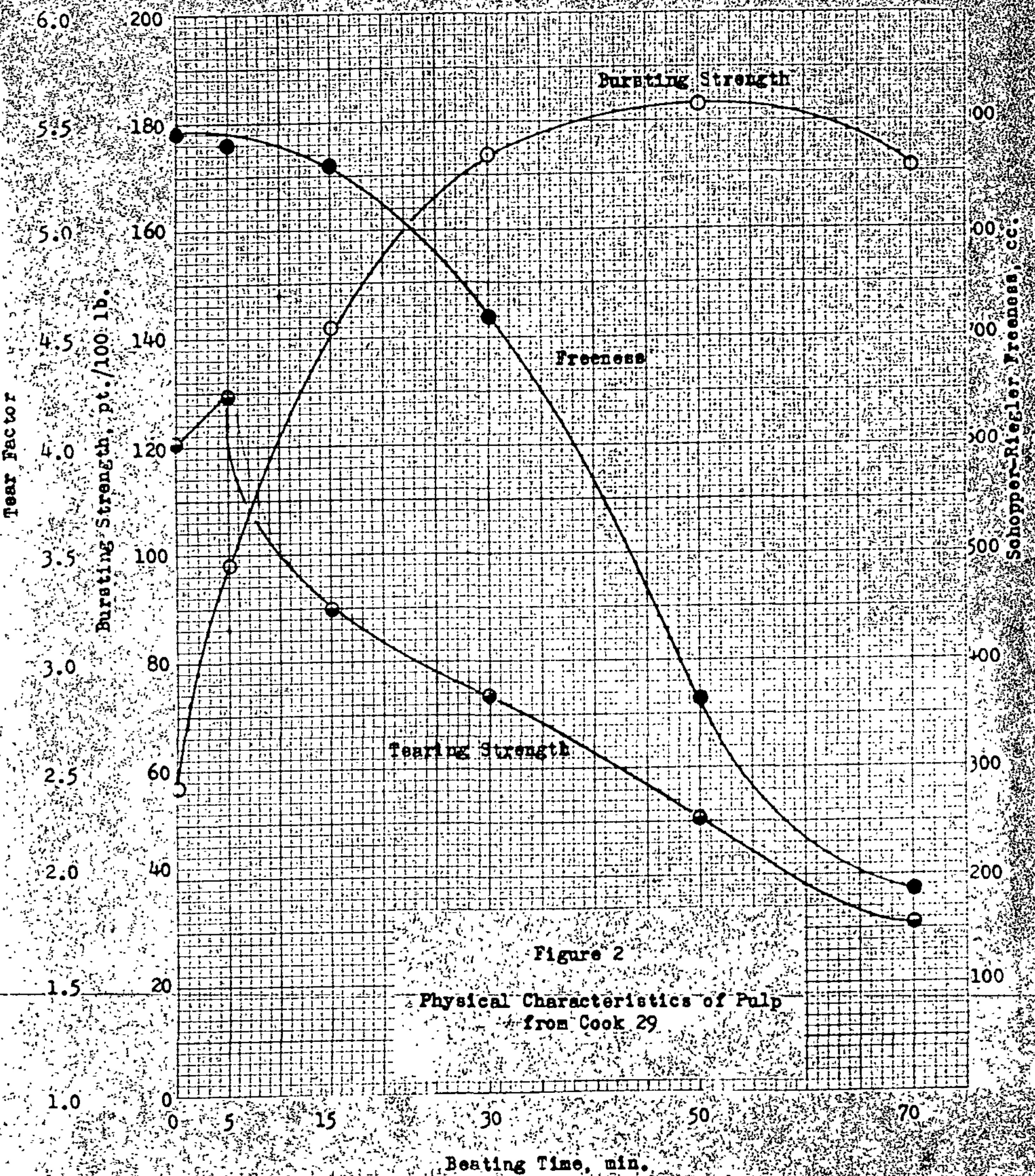

Figure 2

Physical Characteristics of Pulp from Cook 29

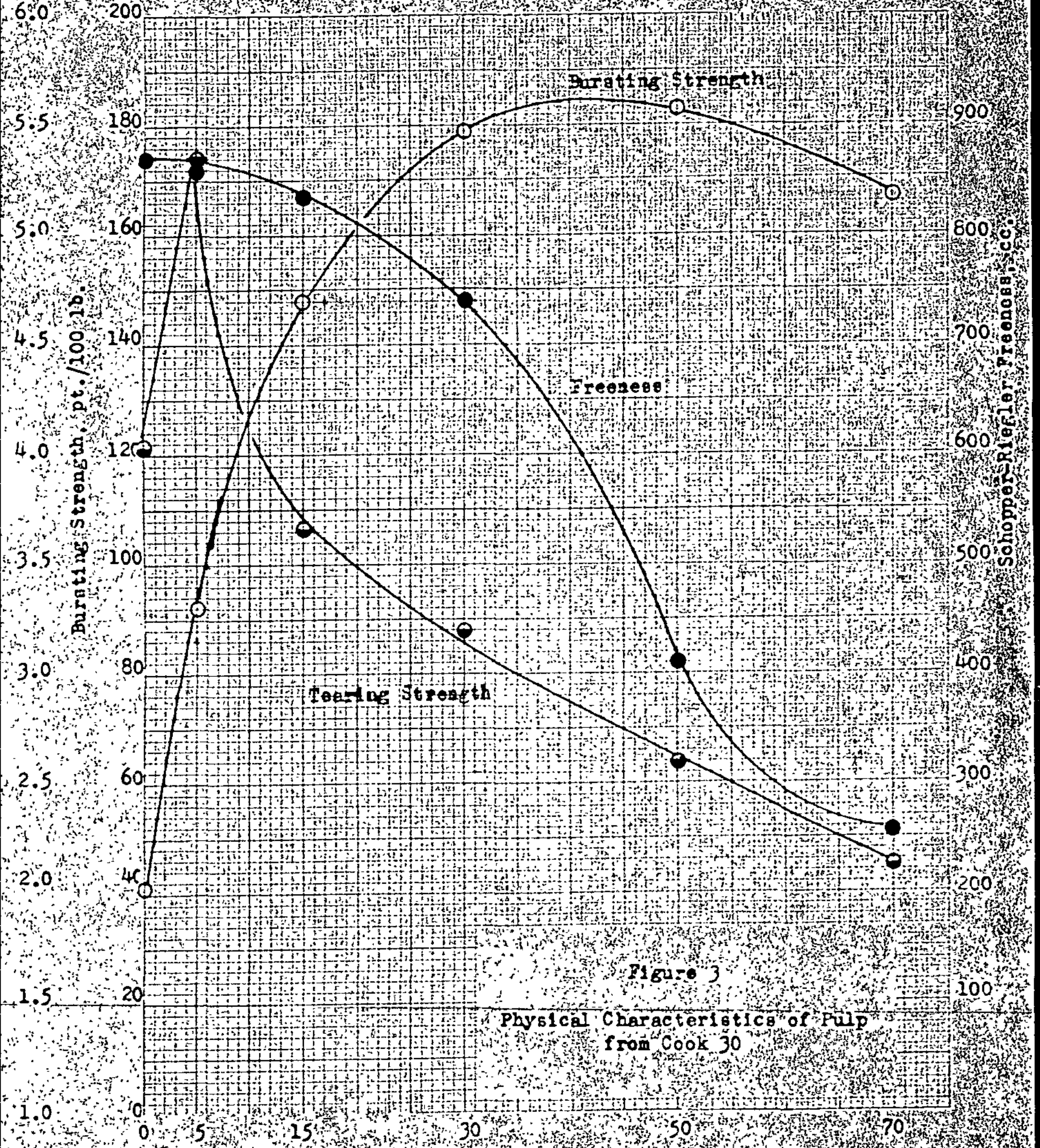

Figure 3

Physical Characteristics of Pulp
from Cook 30

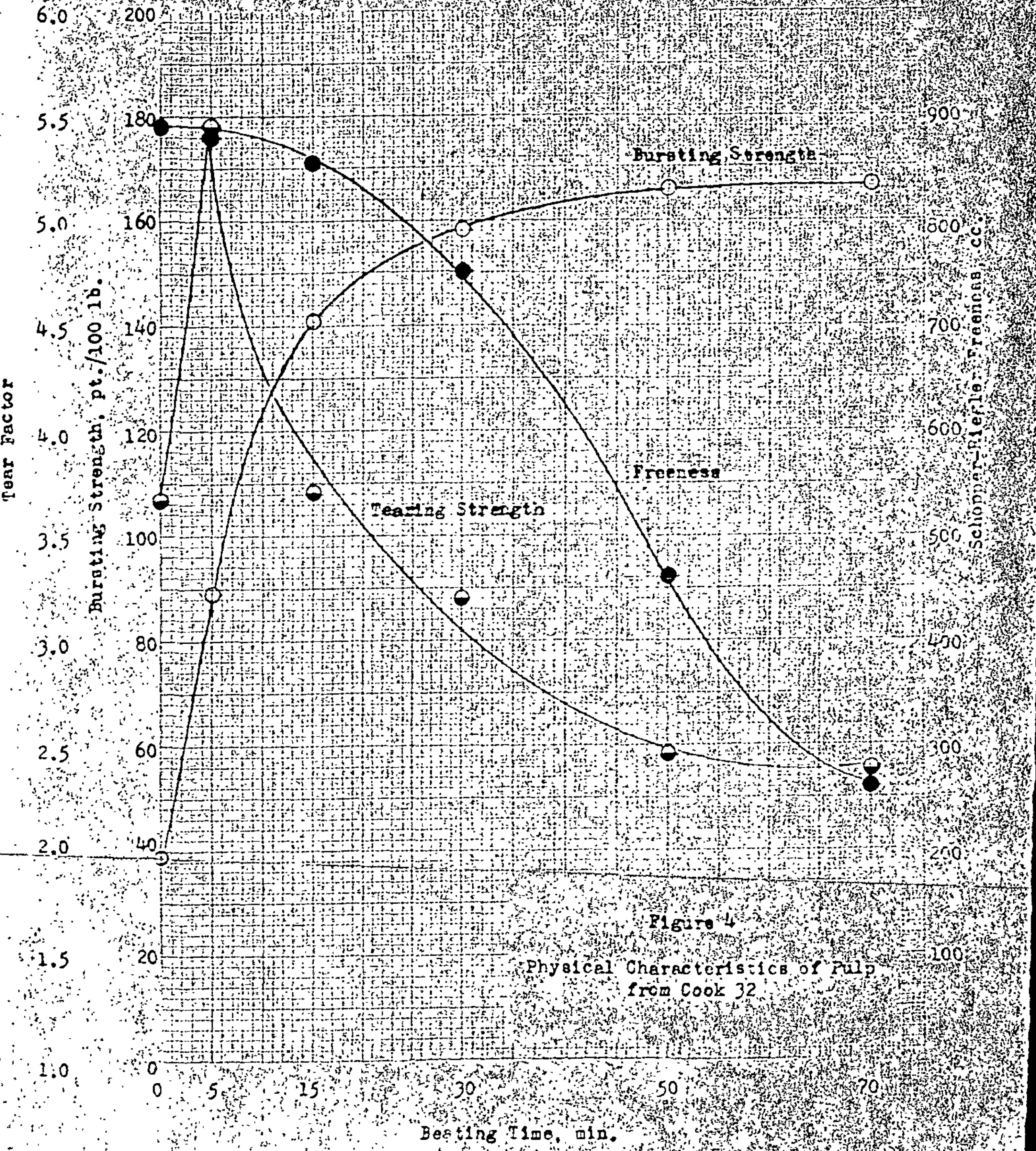

Figure 4

Physical Characteristics of Pulp from Cook 32

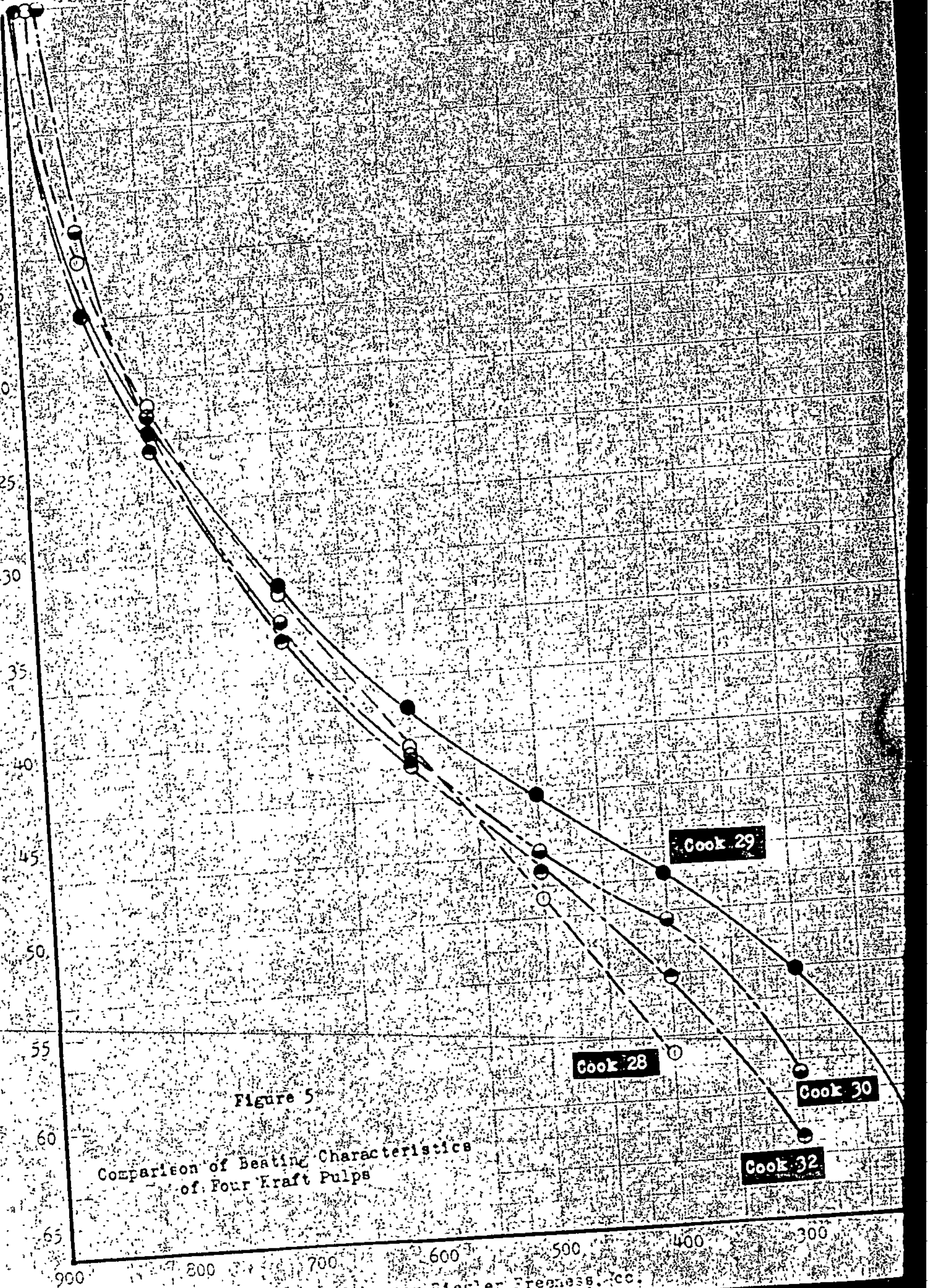

Figure 5

Comparison of Beating Characteristics of Four Kraft Pulps

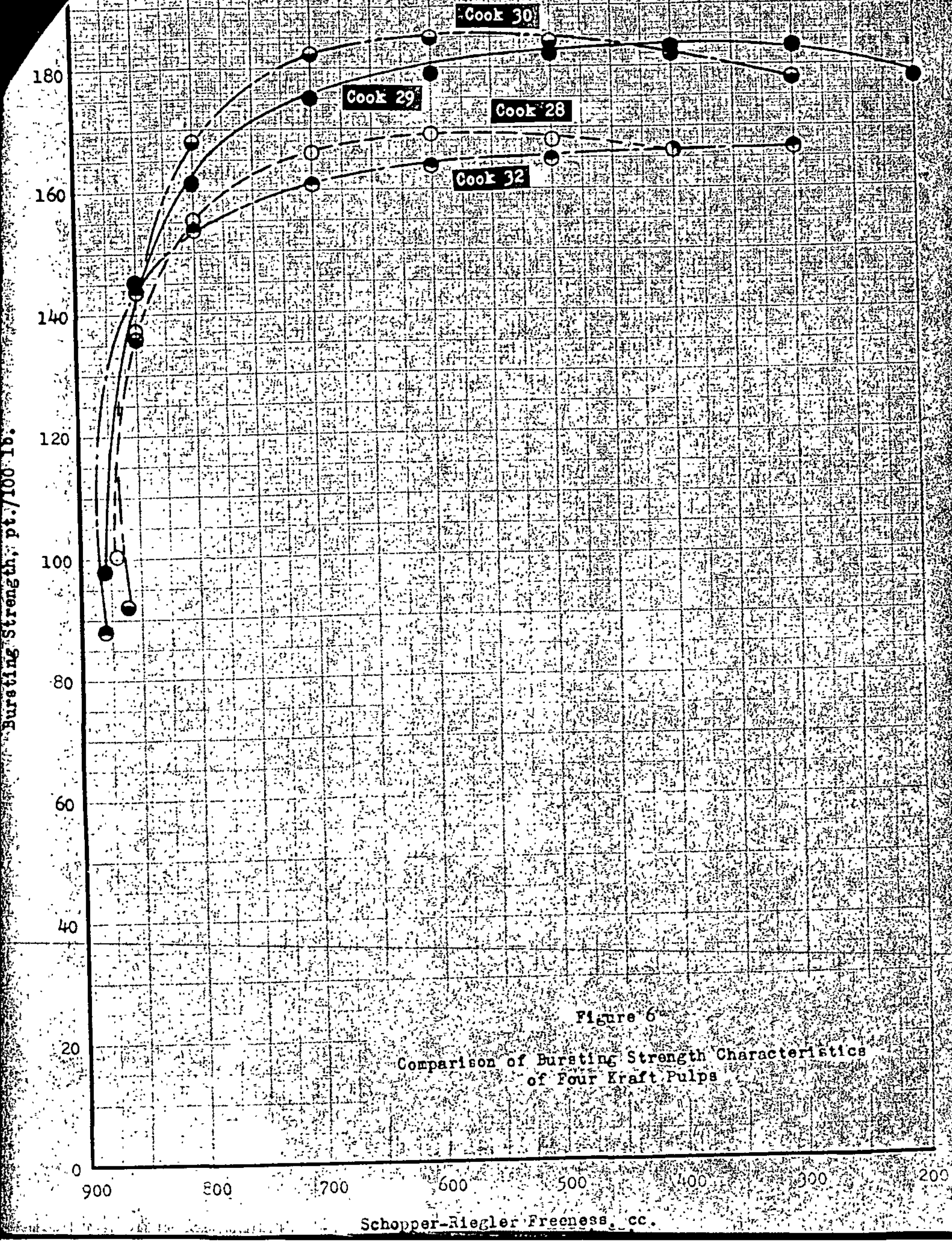

Figure 6

Comparison of Bursting Strength Characteristics of Four Kraft Pulps

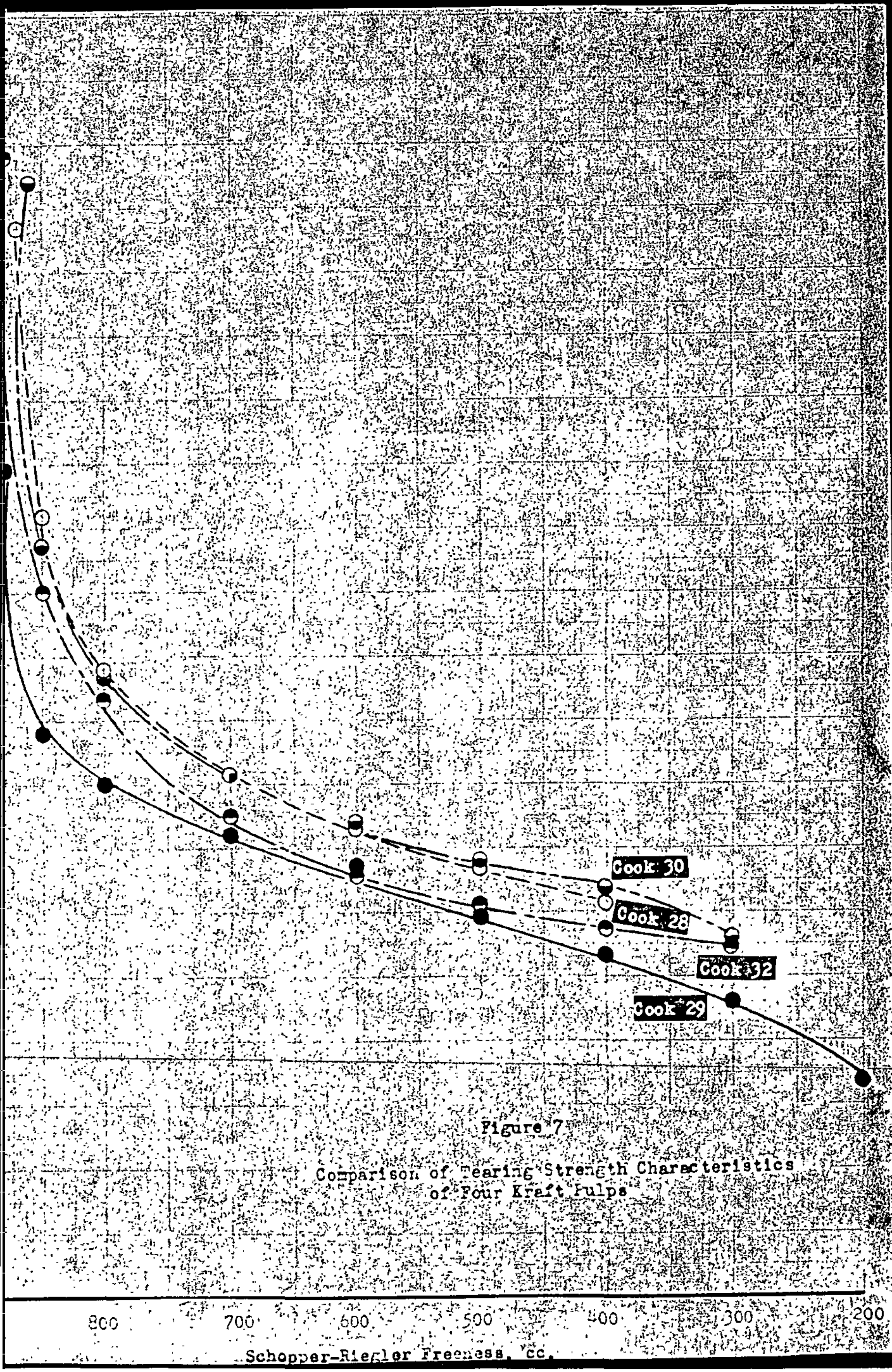

Figure 7

Comparison of Tearing Strength Characteristics of Four Kraft Pulps

A presteaming of 38 minutes at 80 p.s.i. followed by a kraft cook produced a pulp with the typical low yield, but the screenings ratio was not high. The strength of the pulp was very good, displaying burst the equal of the baseline effort and a higher tear. It was only slightly more resistant to beating than the baseline. The other two prehydrolysis conditions did not produce as satisfactory pulps, and the percentage of screenings increased with the increase in maximum steam pressure in the prehydrolysis.

Increasing the time to maximum temperature in the pulping operation was successful as a means of reducing the screening ratio in cooks where a prehydrolysis of 120 p.s.i. steam pressure was used.

Insufficient work was done to investigate optimum steaming time when 80 p.s.i. steam pressure was used for prehydrolysis.

The reproducibility of any laboratory prehydrolysis cook is adversely affected by the difficulty in ascertaining the amount of water deposited on the chips by the presteaming operation. This would presumably not be a difficulty in commercial operation.

jp/mmm

PROJECT REPORT FORM

PROJECT NO. ✓ 1395
COOPERATOR Peol
REPORT NO. Five
DATE July 1, 1949
NOTE BOOK 860
PAGE 138 thru 144
SIGNED Charles Peckham
Charles Peckham

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Mr. J. Peckham

The object of this experiment was to better understand the effects of presteaming on subsequent impregnation by kraft cooking liquors.

SAMPLES AND PREPARATION

Cubes of wood (southern pine) 1-inch on a side were furnished by the pulping laboratory. They were cut from a green log which had a moisture content of approximately 55% (based on green weight). These cubes were divided into eight groups of eight, weighed to the nearest gram and measured to the nearest millimeter (radial, tangential and longitudinal dimensions). The cubes were then returned to the pulping laboratory and given special steaming treatments. The treatments given the cubes were:

<u>Treatment 1</u>

The cubes were placed in a 10-lb. capacity vertical, stationary autoclave and steamed at 120 p.s.i. for 10 minutes.

<u>Treatment 2</u>

This treatment was the same as Treatment 1 except the steaming was for 30 minutes at 80 p.s.i.

<u>Treatment 3</u>

This treatment was the same as Treatment 1, except that the cubes were submerged in water.

<u>Treatment 4</u>

Twelve liters of water were placed in the autoclave and the pH was adjusted to 11.4 with Na_2CO_3. The cubes were placed in a wire basket and suspended approximately 1-inch over the solution. The cubes were simultaneously steamed at 100 p.s.i. and washed with the Na_2CO_3 solution for 15 minutes. The Na_2CO_3 solution was continually pumped out of the autoclave and then back over the cubes.

Treatment 5

The conditions were the same as Treatment 4, except that the pH of the solution was 9.9 and the steam was at 110 p.s.i. for 10 minutes.

Treatment 6

The conditions were the same as for Treatment 4, except that the steam was raised to 120 p.s.i. for 10 minutes.

Treatment 7

The cubes were dried in a drying oven (105° C.) until they were of constant weight (ovendry). (Performed in the wood technology laboratory.)

Treatment 8

This was a control and the cubes were not treated in any way.

After the cubes had been treated they were again weighed and measured.

WHITE LIQUOR IMPREGNATION PROCEDURE:

The cubes were placed in separate 200 cc. crystalizing dishes, 130 cc. of the white liquer was added and the cubes were submerged with glass weights. The dishes were placed in a homemade pressure chamber and subjected to 80 p.s.i. of air for 30 minutes. The pressure chamber consists of a 4-inch diameter pipe which was closed on one end. The open end was sealed by means of an iron cover, held on by bolts, and sealed with a rubber washer. The cover had a valve stem and a pressure gage.

Following the pressure treatment, the cubes were removed from the pressure chamber, the white liquor was drained off and the cubes were blotted free of the excess white liquor. The cubes were then reweighed, measured and split in half. Each half was stained with phenopthalein and the depth of penetration of the white liquor was measured.

RESULTS

The presteaming treatments discolored the cubes making them a dark greyish brown and small blisters of pitch formed over the openings of the resin canals. There was a small amount of swelling because of the steaming treatments, but not enough to be of any importance. The presteaming treatments raised the moisture content of the cubes except in Treatment 1 (120 p.s.i. steaming for 10 minutes) in which case the moisture content dropped (see Chart I).

The amount of white liquor picked up by the cubes seemed to depend upon the moisture content of the cubes. For instance, the ovendried cubes picked up 6 times as much white liquor as the control. The control, with a moisture content of 117% picked up approximately twice as much liquor as the cubes with the moisture content of 134%. (Percentages are based on the ovendry weight of the cubes.)

The depth of penetration of the white liquor varied inversely with the moisture content of the cubes treated. The depth of penetration ranged from 6 to 13 millimeters or from 50 to 100%.

CHART I

KRAFT WHITE LIQUOR PENETRATION STUDY

Pretreatment	Moisture Content of Green Cubes, %	Moisture Content of Steam-treated Cubes, %	White Liquor Picked Up By Cubes, %	Depth of Penetration of the White Liquor (with the grain)								Total Alkali as Na_2O of White Liquor After Treatment: g./l.
				Springwood				Summerwood				
				Range		Average		Range		Average		
				%	mm.	%	mm.	%	mm.	%	mm.	
Treatment 1	117	89	37	54-69	7-9	62	8	23-38	3-5	31	4	21.2
Treatment 2	117	120	21	69-85	9-11	77	10	23-38	3-5	31	4	18.9
Treatment 3	117	134	11	46-54	6-7	50	6.5	23-38	3-5	31	4	21.6
Treatment 4	123	126	21	46-62	6-8	54	7	23-38	3-5	31	4	omitted
Treatment 5	85	120	20	46-62	6-8	54	7	23-38	3-5	31	4	omitted
Treatment 6	85	113	13	46-62	6-8	54	7	23-38	3-5	31	4	omitted
Treatment 7	117	0 ovendried	107	100	13	100	13	100	13	100	13	24.9
Treatment 8	117	117 no treatment	17	78-92	10-12	85	11	23-38	3-5	31	4	21.4

Note (1) The moisture percentages were based on the ovendry weights of the cubes

(2) The total alkali as Na_2O grams/liter of the untreated white liquor was 35.1

The white liquor, before being used in a treatment, had a total alkali as Na_2O of 35.1 grams per liter. The white liquor used in the control test had an alkali content as Na_2O of 21.4 grams per liter. The liquor from the steam-treated cubes was approximately the same as for the control. The total alkali for the white liquor from the Na_2CO_3 treatments showed a big discrepancy and were not recorded.

CONCLUSIONS

The white kraft cooking liquor appeared to penetrate deeper into the springwood than the summerwood. The presteaming and the Na_2CO_3 treatments of the cubes appear to reduce the penetration of the white liquor; however, this might be due to the high moisture content of the cubes. This point is brought out by the fact that the cubes that were submerged in the water (Treatment 3) had less penetration of the white liquor than those subjected to the other treatments. The penetration of the white liquor for all the Na_2CO_3-treated cubes was approximately the same. This indicates that the pH of the Na_2CO_3 solution had little to no effect on the penetration.

cp/mc

PROJECT REPORT FORM

PROJECT NO. 1395
COOPERATOR Pool
REPORT NO. Five
DATE July 1, 1949
NOTE BOOK 860
PAGE 138 thru ~~##~~ 144
SIGNED Charles Peckham
Charles Peckham

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cp/mc

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				Springwood				Summerwood				
				Range		Average		Range		Average		
				%	mm.	%	mm.	%	mm.	%	mm.	
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Note (1) The moisture percentages were based on the ovendry weights of the cubes

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APR 1949

PROJECT REPORT FORM

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COOPERATOR Institute
REPORT NO. 2
DATE April 20, 1949
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PAGE TO
SIGNED John R. Peckham
John Peckham

Pages 27-28
34-41
45-47
50-51
57-63
70
74-88

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Project Report One dealt with preliminary experiments which were intended to show (1) that prehydrolysis of chips prior to kraft pulping would reduce the objectionable mercaptan odor, (2) the effect on pulp strength of the prehydrolysis stage, and (3) the practicability of treating the chips with an alkali to reduce the corrosion caused by the low pH of the hydrolysis liquor.

This report will cover several miscellaneous experiments, some of which have no relation to the prehydrolysis work.

The laboratory Asplund mill was suggested as an instrument for experiments in the reduction of the kraft odor because of the small chip charge and short reaction time. Several experiments were made wherein chips were cooked in the preheater and defibrator of the mill, the chemical being applied partly by presoaking and partly by addition to the defibrator. These data are shown in Table I. One experiment was made to determine whether the methyl alcohol formed by hydrolysis of the wood, would form mercaptans if not voided from the digester. Five cc. of methyl alcohol was added to a liter of kraft white liquor and held at 120 p.s.i. pressure for 28 minutes. No mercaptan odor was apparent.

TABLE I

ASPLUND MILL EXPERIMENTS

Experiment	A1	A2	A3	A4*	A5**
Preheating time, min.	15	15	15	15	15
Preheating pressure, p.s.i.	120	120	100	120	120
Defibering time, min	10	10	10	10	10
Defibering pressure, p.s.i.	120	120	100	120	120
Odor observation	No kraft	Slight kraft	Little kraft	Some Na_2S	No kraft

* No chips, treated 1000 cc. kraft liquor

** No chips, treated 1000 cc. kraft liquor plus 5 cc. methyl alcohol

Constant conditions:

Loblolly pine chips	
Active alkali as NaOH, %	25.8
Sulfidity, %	31.5
Water in defibrator, cc.	875
Kraft liquor in defibrator, cc.	125

The use of the Asplund mill was abandoned when it became apparent that the volumes were too small to allow an accurate judgment of odor.

Cook 7 was made with the pine chips described on page 3 of Project Report One as the raw material. The basis for this cook, the conditions of which are shown in Table II, was to explore the theory that the mercaptans formed by the kraft cooking would be present in a gaseous form and could possibly be absorbed or voided in some manner. A high water ratio was used and the digester was relieved continuously from the cover relief line throughout the cook. The kraft odor was strong when the cook was blown. Cook 15 was a continuation of this line of attack. However, in this case the top relief, which was continuous, was condensed in cooled sodium peroxide solution. The relief products reduced the peroxide to the extent of 160.9 g. The cook had a very noticeable kraft odor when blown.

Cook 16 was made to investigate the role of the oxygen present in the chip charge in the production of the mercaptan odor. A charge of chips was placed in the digester and the cover was bolted on. A cylinder of nitrogen was attached to the digester and the pressure was brought up to 65 p.s.i. by means of the gas, then relieved down to 5 p.s.i. pressure. This operation was repeated three times. The pressure was then brought up to 65 p.s.i. and left that way overnight. The next morning the pressure had dropped to 10 p.s.i. It was raised to 65 p.s.i. and lowered to 5 p.s.i. twice. The same

TABLE II

KRAFT PULPING EXPERIMENTS

Cook	7	9	10	11	12	13	14	15
Digester	3	3	3	3	4	3	3	3
Wood Species	Loblolly pine	Loblolly pine	Loblolly pine	Loblolly pine	Loblolly pine	Loblolly pine	Loblolly pine	Loblolly pine
Chip pretreatment	none	none	none	none[b]	none	6% kraft	none	none
Prehydrolysis conditions:	none			none	none		none	none
Prehydrolysing pressure, p.s.i.		120	120			120		
Prehydrolysing time, min.		15	12[a]			20		
Top relief while steaming, min.		15	13.5			15		
Bottom relief while steaming, min.		10	13.5			20		
Pressure when liquor was added, p.s.i.		0	70			20		
Cooking conditions:								
Active alkali as NaOH, %	25.8	25.8	25.8	28.5	30.0	21.9	25.8	25.8
Sulfidity, %	33.3	33.3	33.3	33.3	—	33.3	33.3	33.3
Maximum temperature, °C.	172	172	172	172	172	176	176	172
Water ratio (disregarding water from prehydrolysis), cc./g. (O.D.)	5.5	4.5	4.0	4.97	4.5	4.5	4.5	4.5
Time to maximum temperature, min.	60	60	60	60	60	30	60	60
Time at maximum temperature, min.	75	75	75	75	240	60	60	75
Cooking time, exclusive of prehydrolysis, min.	150	150	150	150	315	105	135	150
Odor observation	Strong kraft	Some kraft	Definite kraft	Some kraft	Soda	Some kraft	Definite kraft	Strong kraft
Permanganate number	21.3	14.3	22.3					
Unscreened yield, %	46.24	37.39	40.90					
Screened yield, %	45.93	37.26	40.26					
Screenings, %	0.66	0.34	1.56					

Note: a. Four separate steamings with relief to 20 p.s.i. between each steaming
b. Overnight soak in cooking liquor

TABLE II CONTINUED

KRAFT PULPING EXPERIMENTS

Cook	16	17	18	19	20	21	22	23	[illegible]
Digester	4	3	3	3	4	4	4	4	[illegible]
Wood specie	Loblolly pine	Loblolly pine	Slash pine	Slash pine	Slash pine	Mixed Hardwood	Loblolly pine	Jack pine	Lobl[illegible] pine
Chip pretreatment	none[a]	none	none	none	none	none	none	none	none[c]
Prehydrolysis Conditions:	none				none				none
Prehydrolysing pressure, p.s.i.		110	110[b]	110		120	110	110	
Prehydrolysing time, min.		10	10[b]	10		10	210	10	
Top relief while steaming, min.		—	—				210		
Bottom relief while steaming, min.							210		
Pressure when liquor was added, p.s.i.		80	0	70		70	0	70	
Cooking conditions:									
Active alkali as NaOH, %	25.8	25.8	25.8	25.8	25.8	25.8	20.6	25.8	19.36
Sulfidity, %	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	26.0
Maximum temperature, °C.	172	172	176	176	176	176	176	176	178
Water ratio (disregarding water from prehydrolysis), cc./g. (O.D.)	4.5	3.5	3.5	3.5	4.5	3.5	3.5	3.5	4.5
Time to maximum temperature, min.	60	30	30	30	60	30	60	30	90
Time at maximum temperature, min.	75	60	68	68	68	45	68	60	60
Cooking time, exclusive of prehydrolysis, min.	150	105	113	113	143	90	143	105	165
Odor observation	Strong kraft	No kraft	Little kraft	Little kraft	Strong kraft	Unpleasant burnt odor	Some kraft burnt odor	No kraft	Some kraft, strong perfume
Permanganate number	17.1			19.5			36.2		
Unscreened yield, %	44.09			38.72			37.07		
Screened yield, %	43.40			37.56			9.44		
Screenings, %	1.57			2.99			74.52		

a. Air in digester replaced with nitrogen
b. Two steamings of 5 min. each with relief to 20 p.s.i. between
c. Five cc. of "ammomask" added to the cooking liquor

procedure was used the evening of the second day and the morning of the third day. The chemicals were injected into the digester while the nitrogen pressure inside the digester was at 25 p.s.i. Nitrogen pressure was also used to inject the liquor. When the liquor was all in, the digester pressure was reduced to 5 p.s.i. and cooking proceeded. Cooking conditions are shown in Table II. At 100° C. the pressure was again reduced to 5 p.s.i. When blown the cook had a strong kraft odor. The pulp was washed, screened, and yield was determined. The pulp was beater evaluated.

Several miscellaneous cooks were run as follows: Cook 10 employed four separate steamings of three minutes duration at 120 p.s.i. each, with relief to 20 p.s.i. between steamings, in the prehydrolysis stage. The top relief from each steaming was sampled and tested for the presence of methyl alcohol. The test showed a sharp gradation of methanol content, with the first relief being relatively rich in the material and the fourth showing only a trace. The pH of samples of bottom relief condensate at 5 minutes elapsed steaming time and at the end of the hydrolysis were 10.4 and 4.1, respectively. The cooking conditions are described in Table II. The cooking chemicals were injected into the digester by the use of air pressure when the digester pressure reached 70 p.s.i. after the last steaming. A kraft odor was apparent on blowing, but it was not strong.

Cook 11 had the same cooking schedule as Cook 10, but contained more chemical. The chemical and water charge were added the day preceding the cook, and no prehydrolysis was attempted. The kraft odor was very evident. No pulp was saved.

Cook 12 was a soda cook on pine chips, to acquaint the staff with the odor attendant to this type of cooking process. The pulp from this cook was discarded.

Cook 13 was similar to Cook 8 reported in Project Report One. However, more alkali was used in the pretreatment, the presteaming was carried out for five minutes longer and a higher temperature and somewhat shorter time at maximum temperature were employed. The cooking chemicals were injected into the digester while at 70 p.s.i. pressure from the presteaming. The pulp was not saved. The odor was distinctly kraft in character but not very strong.

Cook 14 was a typical kraft cook made to refresh the memory of the observers as to the odor normally attendant to the operation.

Cook 17 was made with no relief at any point from the time the cover was bolted on until the cook was blown. Prehydrolysis was at 110 p.s.i. for 10 minutes, and 10 minutes from 110 p.s.i. to 80 p.s.i. The liquor was injected and cooking proceeded as shown in Table II. This cook was designed to further prove the point that after the methoxyl groups were changed to methanol they would not form mercaptans if left in the digester. The odor of this cook was considered to be almost entirely free of mercaptans. Cook 19 was practically the same as Cook 17 except that the pulp was screened and yield was determined.

Cook 18 was a prehydrolysis cook wherein two steamings of 5 minutes at 110 p.s.i. pressure were utilized, each time relieving to zero pressure by top and bottom relief. The cooking liquor was applied by removing the cover. This cook also had little of the true kraft smell.

Cook 20 was another demonstration cook without prehydrolysis. No pulp was saved. The odor was typically kraft in nature.

Cook 21 was a prehydrolysis cook on mixed hardwoods, taken from a supply on hand for use in Project 1393. The procedures were the same as for Cooks 17 and 19. The odor here was very unpleasant, having what seemed to be a mixture of kraft and burnt sugar smells.

Cook 22 was made in an effort to determine the amount of alkali which could be saved by removing the condensate from the prehydrolysis stage. The procedure suggested was constant relief from top and bottom of the digester during steaming, such steaming and relief to be continued until the pH of the condensate showed it to be neutral. A battery of glass condensers was used to take care of the top relief, and a large, stainless steel, multiple tube condenser with an auxiliary glass condenser was used for the bottom relief. Steaming was carried out at 110 p.s.i. pressure over a period which totaled 3-1/2 hours. At the end of this time the pH of the condensate showed it to be still acetic. The condensate removed was separated into three samples as follows:

1. Top relief condensate for first hour of the steaming
2. Top relief for the remainder of the steaming, and
3. The bottom relief condensate

Sample 1 had a volume of 20.58 liters, a pH of 3.8, and a total acidic equivalent of 0.14 g./l. of NaOH. Sample 2 had a volume of 25.7 liters, a pH of 5.3, and a total acidic equivalent of 0.02 g./l. of NaOH. Sample 3 had a volume of 18.12 liters, a Ph of 3.3, and a total acidic equivalent of 1.4 g./l. of NaOH;

After relief to atmospheric pressure the digester was opened and the chips were found to be considerably softened and quite dark. The chemical and water were then added and the chips were cooked. The alkali ratio was reduced from 25.8% NaOH normally used to 20.6% and a typical kraft cooking schedule was followed. The chips were poorly pulped so only enough was screened to provide material for permanganate number determination.

Cook 23 was made to demonstrate the efficacy of the prehydrolysis treatment in reducing the odor of a kraft cook on jack pine. There was little kraft odor. The pulp was discarded.

Cook 24 was an experiment wherein a perfume base was used to attempt to mask the kraft odor. The cooking conditions employed were those recommended for a project wherein western hemlock was pulped by the kraft process, and embodied a high temperature, low chemical ratio cook. Ten cc. of "Ammomask" were added to the digester when charging the liquor. When blown, the kraft odor had overtones of the perfume, and the mixture was faintly reminiscent of the odor of skunk. The pulp before screening was highly perfumed, but this condition did not exist after the screening operation. The pulp was very raw and was discarded.

DISCUSSION OF RESULTS

The Asplund mill was found to be unsatisfactory as a vessel for cooking chips by the kraft process to evaluate different means of reducing the kraft odor. The primary disadvantage was the small volume, which made it difficult to evaluate the odor.

It could not be demonstrated that copious relief during the cooking process alleviated the odor the cook when it was blown. Cooks 7 and 15 were judged to be little different in odor from straight kraft cooks.

Apparently the air present in the chips and in the interstices between chips has little to do with the formation of mercaptans. Cook 16, in which the air was replaced by nitrogen, had the typical kraft odor when blown. Also, the pulp was very similar in strength characteristics to Cook 5, reported in Project Report One. The physical characteristics of this pulp are shown in Table III.

TABLE III

PHYSICAL CHARACTERISTICS OF COOK 16

Schopper-Riegler freeness, cc.	0*	870
	5	865
	15	845
	30	665
	50	330
	70	210
Basis weight (24 x 36—500), lb.	0	39.3
	5	37.2
	15	38.4
	30	38.7
	50	36.9
	70	38.2
Caliper, in.	0	.0052
	5	.0041
	15	.0038
	30	.0036
	50	.0032
	70	.0031
Apparent density	0	7.6
	5	9.1
	15	10.1
	30	10.8
	50	11.5
	70	12.3
Bursting strength, pt./100 lb.	0	54
	5	108
	15	148
	30	167
	50	168
	70	155
Tear factor	0	4.33
	5	3.63
	15	2.94
	30	2.38
	50	1.95
	70	1.88

* This column denotes beating time in minutes.

Cook 11, which was a conventional kraft cook without prehydrolysis did not show any advantage in odor characteristics due to presoaking the chips in the cooking liquor for several hours. While the odor was not particularly strong, it was definitely of a kraft nature.

Cooks 10 and 18 made with multiple steamings with relief between steamings, did not seem to have any advantage over cooks wherein the prehydrolysis was carried out using a single uninterrupted steam treatment. The odor was still faintly that of a typical kraft cook.

Prehydrolysis treatment without any relief before adding the cooking chemicals seemed to be the best treatment as far as alleviation of odor was concerned. Cook 17 was thought to be practically free of mercaptan odor.

The prehydrolysis treatment apparently was as successful on jack pine as on southern pine. Cook 23, when pulped in this manner had no appreciable kraft odor.

Hardwoods, however, probably pose a different problem. In the experiment carried out in this phase of the work, Cook 21, a prehydrolysis kraft cook on mixed hardwoods, gave a very obnoxious odor. While it was probable that the mercaptan odor was either absent or masked by the other odors, a very unpleasant smell which was likened to burnt sugar was predominant. This may be due in some part to the lack of the pine oils and turpentine odors which may mask a similar smell in a cook on pine.

A soda cook on southern pine (Cook 12) indicated that 1) the odor of a prehydrolysis plus kraft cook, while differing from a conventional kraft cook, did not have the same smell as a soda cook on the same species of wood, and 2) even when no mercaptans are present, a cook made with a strong alkali as the cooking agent will have a typical, unpleasant odor.

Cook 24, wherein a perfume base was added to the chemicals, did not entirely discount this means of improving the odor of a kraft cook. Some observers were quite positive that a definite improvement was shown. The particular base used, "Ammomask," a product of Dodge and Olcott, Inc., has a very tenacious odor which existed long after the kraft smell disappeared.

From the results of Cook 23, it seems unlikely that any appreciable saving in alkali could be made where the wood acids freed by the hydrolysis treatment completely removed from the digester before treatment. After hydrolyzing for 3-1/2 hours and the removal of 64.4 liters of condensate, the total NaOH equivalent of the acids removed was only 28.76 g. on the basis of a digester charge of 5633 g. (ovendry basis) of chips and a chemical ratio of 25.8% NaOH, this amounts to 1.98% of the chemical used, or 0.51% chemical on the basis of the wood.

Cooks 7, 9, 10, and 19 were the only cooks pertinent to the prehydrolysis study which were evaluated for yield and permanganate number. From these date (see Table III) it appears that at a permanganate number in the range of 20±3, a loss of about 5 to 7% of screened pulp would be expected were prehydrolysis utilized.

CONCLUSIONS

The following might be concluded from the foregoing data:

1. Constant relief of gases from the digester during cooking did not alleviate the kraft odor.

2. Replacement of the air in the digester by nitrogen did not produce any noticeable diminution of the mercaptan odor when followed by a kraft cook.

3. Presoaking the chips in the cooking liquor for several hours prior to pulping was apparently not successful as a means of alleviating the mercaptan odor.

4. Addition of a perfume base or some other masking material to the cooking chemicals in a kraft cook showed some merit.

5. Variations in prehydrolysis procedures seemed to indicate that the best results in odor alleviation are obtained by an unbroken steaming interval with no relief at any point, the cooking liquor being injected against the residual steam pressure.

6. Little saving in chemical consumption would be realized by elimination of the wood acids released by hydrolysis with high pressure steam.

7. Prehydrolysis is effective as a means of reducing the mercaptan odor in the kraft pulping of jack pine.

8. Hydrolysis may possibly reduce the mercaptan odor when used as a pretreatment in the kraft pulping of hardwoods, but the effect is minimized by the burnt sugar odor caused by the steaming. Perhaps the latter odor could be partially eliminated by variations in the steaming procedure.

9. To date prehydrolysis in kraft pulping has shown some diminution in mercaptan odor, but enough residual odor is present to be objectionable.

10. Prehydrolysis treatment caused a marked decrease in yield of pulp.

jp/mc

PROJECT REPORT FORM

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Dr. Brauns
Dr. Forman

PROJECT NO. 1395
COOPERATOR Institute
~~REPORT NO.~~ Final
DATE April 16, 1949 (Typed 4/22/49)
NOTE BOOK 860
PAGE 14-15, 30, 54-56 TO
SIGNED F. E. Brauns
F. E. Brauns

FINAL REPORT ON THE WORK DONE ON THE KRAFT ODOR PROBLEM

In the cooking of wood, particularly hardwoods, a bad odor is produced which is caused by the formation of methyl mercaptan, CH_3SH, and probably other volatile organic sulfur compounds such as dimethyl sulfide, $(CH_3)_2S$, and, quite possibly, hydrogen sulfide. The liberation of hydrogen sulfide, of course, will depend on the final alkalinity of the black liquor. Because methyl mercaptan is a much weaker "acid" than hydrogen sulfide, it is much more readily released from the black liquor on heating or by the action of carbon dioxide in the air. Dimethyl sulfide has no "acid" properties at all and, therefore, is not combined by the alkali. On account of its low boiling point (38° C.) it is readily released into the air when the digester is blown or when the warm black liquor is exposed to the open air.

Since it had been established that volatile organic sulfur compounds are responsible for the bad odor of kraft cooks, the question arose as to what is the cause of the formation of these compounds, or from what do they originate. Methyl mercaptan and dimethyl sulfide, under the conditions of the kraft cooking process, can be formed only by the interaction of hydrogen sulfide or its salts with methyl groups in their nascent state. Such methyl groups can be formed only by a hydrolysis of methoxyl groups present in the wood. Coniferous woods contain as a rule about 4.5% methoxyl as determined by the Zeisel method;

desiduous woods are higher in methoxyl and run between 5.5 and 6.5% The greater part of the methoxyl in wood is combined with the lignin. If the methoxyl of the wood were entirely attached to the lignin, the methoxyl content of coniferous lignin should be around 18%--that of deciduous wood about 28%. The actual methoxyl content of coniferous lignin is found to be 14.8%--that of deciduous lignin about 20-21%. This shows that 8-10% of the methoxyl in conifers and almost 15% of the methoxyl in hardwoods are combined in the woods to components other than lignin.

For a long time it was the unproven belief that the lignin is responsible for the formation of the bad odor in the kraft cooking process. However, it was found in the lignin work at the Institute many years ago that isolated lignins--e.g., Willstätter (hydrochloric acid lignin) and Freudenberg lignin (cuoxam lignin)--, when heated with sodium hydrogen sulfide under the conditions used in the kraft cooking process, are dissolved, giving so-called "thiolignins" with the same methoxyl content as that of the original lignin, taking into account the entrance of the sulfur into the lignin molecule. In other words, no methoxyl groups were split off from the lignin. It is not surprising, therefore, that such a "lignin kraft cook" does not have the unpleasant bad odor of a wood kraft cook.

Although this observation had been made repeatedly during the lignin course work and in the preparation of thio hydrochloric acid spruce lignin, another series of experimental kraft cooks was carried out with different types of lignins in order to substantiate the earlier claims.

In general the cooks were carried out as follows: The lignin was mixed with about 10 times its weight of a kraft white liquor composed of 20 g. sodium hydroxide and 31 g. sodium sulfide nonahydrate in 200 cc. water and the mixture heated in an autoclave at 170-180° C. for a period of 2 hours. The bomb was then cooled and opened and tested immediately for its odor. There was no discoloration of lead acetate paper and no odor of a typical kraft cook from either the cold or the heated black liquor. In all cases the lignin was completely dissolved, giving a dark reddish brown solution from which, upon acidification, the thio lignins precipitated in the well-known manner.

The following lignin preparations were subjected to a kraft cook: hydrochloric acid (Willstaetter) spruce lignin, hydrochloric acid aspen lignin, native spruce lignin, and cuoxam (Freudenberg) spruce lignin. In all cases the lignin went into solution and no odor resembling a commercial kraft cook could be detected. These results confirmed the previous observations.

After it had been established that the bad odor of a kraft cook did not originate from the lignin, a kraft cook was carried out with slash pine holocellulose. Here, too, no kraft odor was formed.

benzene-alcohol and water 75°

Cooks with pre-extracted aspen wood with a "synthetic" and a commercial kraft cooking liquor gave normal pulps, but no odor of a typical kraft cook could be detected. Because it had been intimated that the mercaptan and other volatile sulfur compounds are the result of a reaction between methanol and the cooking liquor, a cook was carried out to which methanol was added before the cook, but here, too, not a trace of the odor of mercaptan was found. A cook of the resinous extracts obtained with alcohol or benzene-alcohol with a commercial kraft cooking liquor did not produce a kraft odor. On the other hand, when a small amount of pectin, which is known to possess methyl ester groups, was added to extracted aspen wood and a kraft cook was carried out a slight odor resembling a kraft cook could be detected.

feb/hw

PROJECT REPORT FORM

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Mr. Steele
Dr. Forman
Mr. Peckham
Pulping Laboratory

PROJECT NO. ✓ 1395
COOPERATOR The Institute
REPORT NO. One
DATE February 16, 1949
NOTE BOOK 860
PAGE 7-13, 16-26, 29, 31-34, 39, 51
SIGNED J. R. Peckham

Several approaches have been investigated in an attempt to alleviate the odor normally attendant to blowing a kraft cook. This report will deal with the work done to date and will include the writer's observations as to the odor, yield data from several cooks and some strength data.

The majority of the work has been based on the theory that if the methoxyl groups in the wood were hydrolyzed to methanol, the objectionable mercaptans would not be formed. Some work has been done in an attempt to determine the feasibility of treating the vapors as they are formed during the cook. One cook was made wherein the air in the digester and chips was replaced with nitrogen before cooking.

The first cooks were very exploratory and the wood used was chipped, unbarked southern pine, which happened to be available. No attempts were made to obtain yield or strength data on the pulps. Prehydrolyzing and cooking data are shown in Table I.

In Cook 1, the chips were prehydrolyzed in a digester equipped for direct steaming, then transferred to another digester for cooking. The steam was relieved rapidly at the end of the steaming period.

Since this cook gave an indication that prehydrolysis was beneficial with regard to odor, the next step was to determine whether the natural

TABLE I

PRELIMINARY EXPERIMENTS

Cook	1	2	3	4	A	B
Pretreatment						
Amount of chemical (O.D. wood basis), %	None	2.0 NaOH	2.0 H_2SO_4		2.0 Kraft(as NaOH)	2.0 Na_2CO_3
Prehydrolysis						
Digester No.	1	1	1		1	1
Pressure, p.s.i.	130-120	120	120		120	120
Time, min.	15-5	20	20		20	20
pH of condensate--5 min.		8.7	2.7		8.0	8.1
pH of condensate--end	4.0	5.6	2.5		4.7	5.0
Cooking Conditions						
Digester No.	2	3	3	2		
Active alkali as NaOH, %	28.4	28.4	28.4	28.4		
Sulfidity, %	33.3	33.3	33.3	33.3		
Maximum temperature, °C.	168	176.5	176.5	168		
Time to maximum temperature, min.	60	60	60	60		
Time at maximum temperature, min.	75	60	30	30		
Time of final relief, min.	15	15	15	15		
Total time, cover to blow, min.	150	135	105	105		
Appearance of pulp	Well pulped grayish tinge	Well pulped typical color		Raw		
Odor of blow	Faint kraft	some kraft	Strong kraft	Strong kraft		

Constant conditions:
Unbarked southern pine wood
Water ratio--cc./g. Ovendry 4.5

wood acids formed by the steaming operation could be neutralized to eliminate corrosion in iron digesters. Cook 2 was the first of these experiments and was performed in the same manner as Cook 1, except that the chips were impregnated with sodium hydroxide the day before the cook.

Cooks 3 and 4 were deviations from the trend of the cooking operations made to give bases of comparison. In Cook 3, the chips were impregnated with a weak sulfuric acid liquor the day before cooking, and Cook 4 was a regular kraft cook. In both, the kraft odor was strong.

Next, a series of pre-impregnation tests was performed wherein prehydrolysis only was carried out. The efficacy of the treatment was judged by the pH of the condensate at the end of the prehydrolysis and by the odor of the relieved steam. Kraft liquor and soda ash were the chemicals applied in the pretreatments and the results are shown in Table I.

At this point, a supply of typical wood for kraft pulping was desired, and six 4-ft. seasoned bolts of peeled loblolly pine were chipped to a nominal 3/4-inch length in the laboratory chipper. The chips were screened on a 4-mesh screen, hand sorted for large knots and slivers, and bagged in equal-size digester charges. Moisture samples taken at the time of bagging determined the ovendry content of each charge.

A series of prehydrolysis experiments was made on the new wood without following each with a cook. The conditions for these operations and the results in terms of pH of the condensate at the end of the steaming period are shown in Table II.

TABLE II

PREHYDROLYSIS EXPERIMENTS

Experiment	P1	P2	P3	P4
Chemical pretreatment	Soda	Kraft*	Kraft*	Na_2CO_3
Chemical ratio, %	2.0	4.0**	6.0**	2.0
Presoaking time, hr.	—	—	—	—
Prehydrolysis schedule	120 p.s.i. for 10 min. Relief to zero p.s.i. Steam to 120 p.s.i., immediate relief.	120 p s.i. for 20 min. Last 2 min. with bottom relief wide open.	Same as P2 except total time 22 min.	Same as P3
Condensate sampling:				
Time of first sample, min.	8-9	5-10	5-10	7-10
pH of first sample	5.4	8.0	10.7	6.35
Time of last sample, min.		20	20	20
pH of last sample		4.2	7.85	4.6
pH of distilled water diffusion of hydrolyzed chips	6.2	6.75	8.0	5.6
Odor of condensate	Piney, acrid No H_2S	Piney, acrid No H_2S	Piney, acrid No H_2S	Piney, acrid Faint H_2S

* Sulfidity 33.3%
** As NaOH

Cook 5 was made as a baseline cook without any pretreatment. Cooking conditions, product variables, and pertinent observations for Cook 5 and subsequent cooks are shown in Table III. Cook 6 utilized baseline conditions except for a pre-impregnation of the chips with NaOH, and prehydrolysis. Both pulps were washed, screened, and yield and permanganate number were determined.

Cook 8 was made in the same way as Cook 6, except that 5% active alkali as NaOH was applied to the chips as an impregnation with kraft liquor. In the cooking operation the active alkali was cut back 3.9% on the assumption that the chemical applied in the pre-impregnation stage had satisfied some of the chemical demand of the wood.

Cook 9 was similar to Cooks 6 and 8, except that there was no pretreatment of the chips. The top relief from the prehydrolysis was condensed and tested for the presence of methyl alcohol. Samples of the bottom relief condensate were also so tested. Only the top relief indicated the presence of the alcohol.

The above series of cooks was beater evaluated according to Institute Methods 403 and 411. Strength data are included in Table IV and are compared in Figures 1-3.

In Table V, an abridged analysis of the data in Tables III and IV and Figures 1, 2, and 3 may be seen.

In examining these data, it should be remembered that the degree of cooking was somewhat greater than would be used by many southern kraft mills. Also, further work should be done at constant permanganate number and also at constant yield, if that is possible, before many conclusions

TABLE III

PREHYDROLYSIS AND KRAFT COOKING

Cook	5	6	8	9
Pretreatment	None			None
NaOH as NaOH, %		2.0		
NaOH as kraft white liquor, %			5.0	
Reaction time, min.		30	30	
Prehydrolysis	None			
Steam pressure, p.s.i.		120	120	120
Total steaming time, min.		20	15	15
pH of condensate--5 min.		6.1	10.1	10.4
pH of condensate--end		3.7	8.8	4.2
Cooking				
Active alkali as NaOH, %	25.8	25.8	21.9	25.8
Sulfidity, %	33.3	33.3	33.3	33.3
Water ratio, cc./g. ovendry	4.5	4.5	4.5	4.5
Maximum temperature, °C.	172	172	172	172
Time to maximum temperature, min.	60	60	60	60
Time at maximum temperature, min.	75	75	75	75
Relief to blowing pressure, min.	15	15	15	15
Total time, cover to blow, min.	150	150	150	150
Permanganate number	17.6	18.0	21.2	14.3
Unscreened yield, %	44.7	41.6	44.0	37.4
Screened yield, %	44.6	41.4	43.9	37.3
Screenings, %	0.23	0.43	0.12	0.34
Odor	Strong kraft	Some kraft	Some kraft	Some kraft

TABLE IV

PHYSICAL CHARACTERISTICS OF PULPS DESCRIBED IN TABLE III

Cook		5	6	8	9
Schopper-Riegler freeness, cc.	0*	885	890	890	870
	5	890	865	880	880
	15	835	835	860	850
	30	545	625	660	690
	50	250	320	290	475
Basis weight (24x36—480), lb.	0	38.0	38.0	39.5	40.8
	5	37.9	37.7	37.4	38.6
	15	37.2	38.5	38.0	38.0
	30	37.3	38.4	38.1	38.9
	50	34.7	34.9	38.7	37.7
Caliper, in.	0	.0050	.0052	.0052	.0054
	5	.0044	.0043	.0043	.0044
	15	.0038	.0038	.0039	.0038
	30	.0034	.0035	.0036	.0036
	50	.0029	.0030	.0033	.0032
Apparent density	0	7.6	7.3	7.6	7.6
	5	8.6	8.8	8.7	8.8
	15	9.8	10.1	9.7	10.0
	30	11.0	11.0	10.6	10.8
	50	12.0	11.6	11.7	11.8
Bursting strength, pt./100 lb.	0	60	44	55	39
	5	101	91	103	87
	15	148	142	146	138
	30	153	163	165	156
	50	144	150	175	171
Tear factor	0	4.58	3.05	4.48	3.55
	5	3.40	4.03	3.56	5.00
	15	2.45	2.83	2.63	3.45
	30	1.90	2.45	2.15	3.03
	50	1.47	1.98	1.76	2.31

* This column represents beating time in minutes

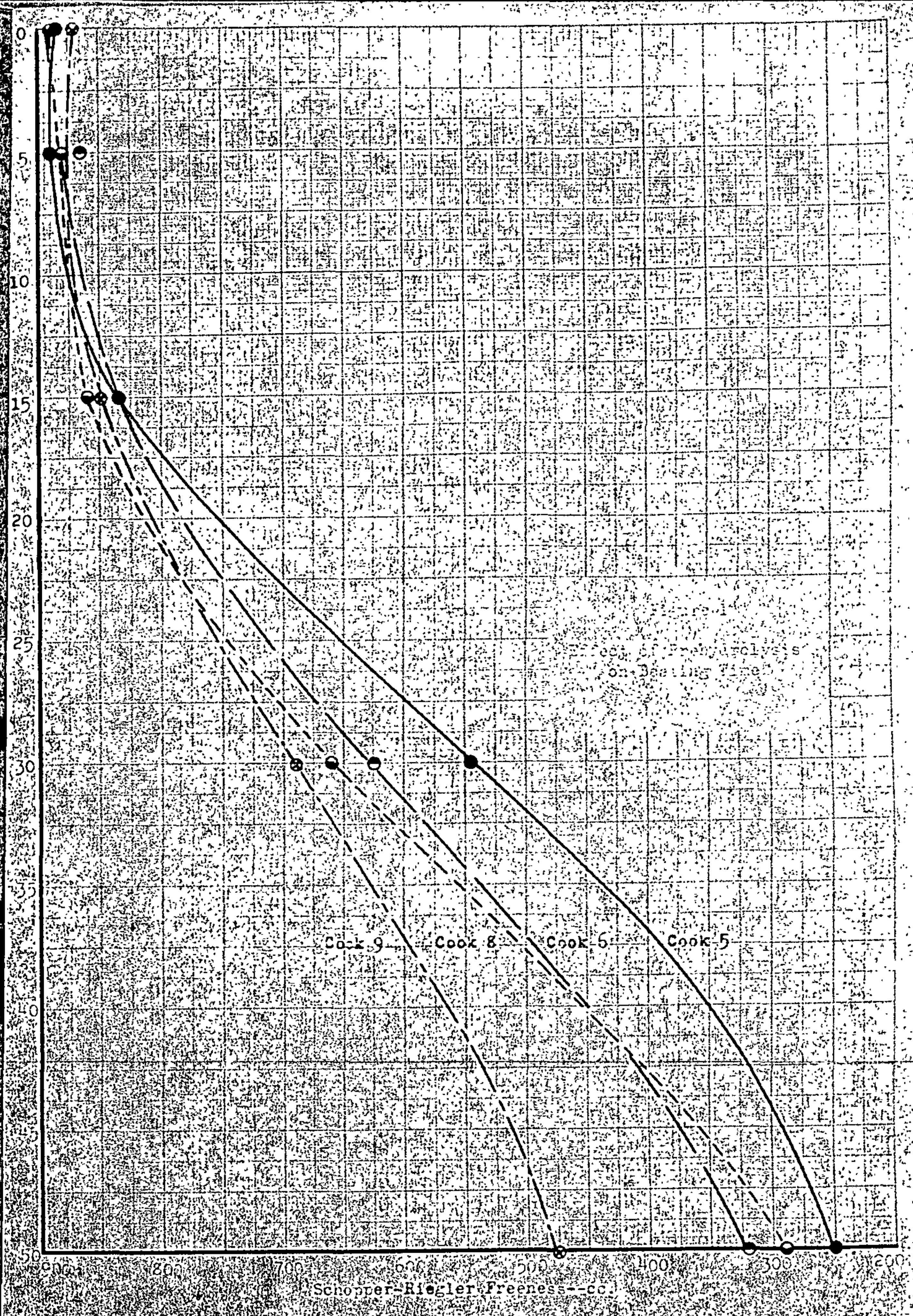


Figure [illegible]
Effect of Prehydrolysis
on Beating Time

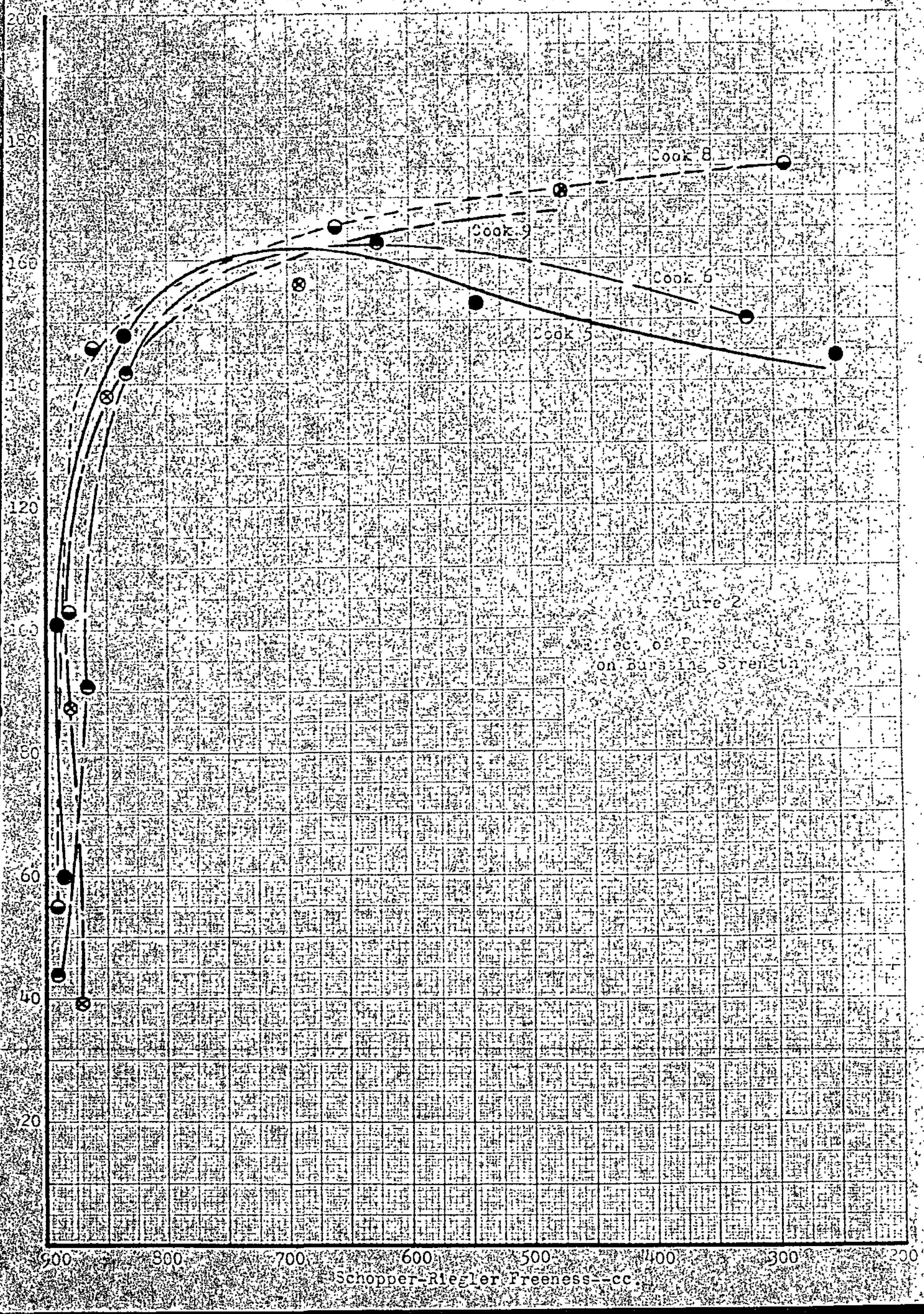
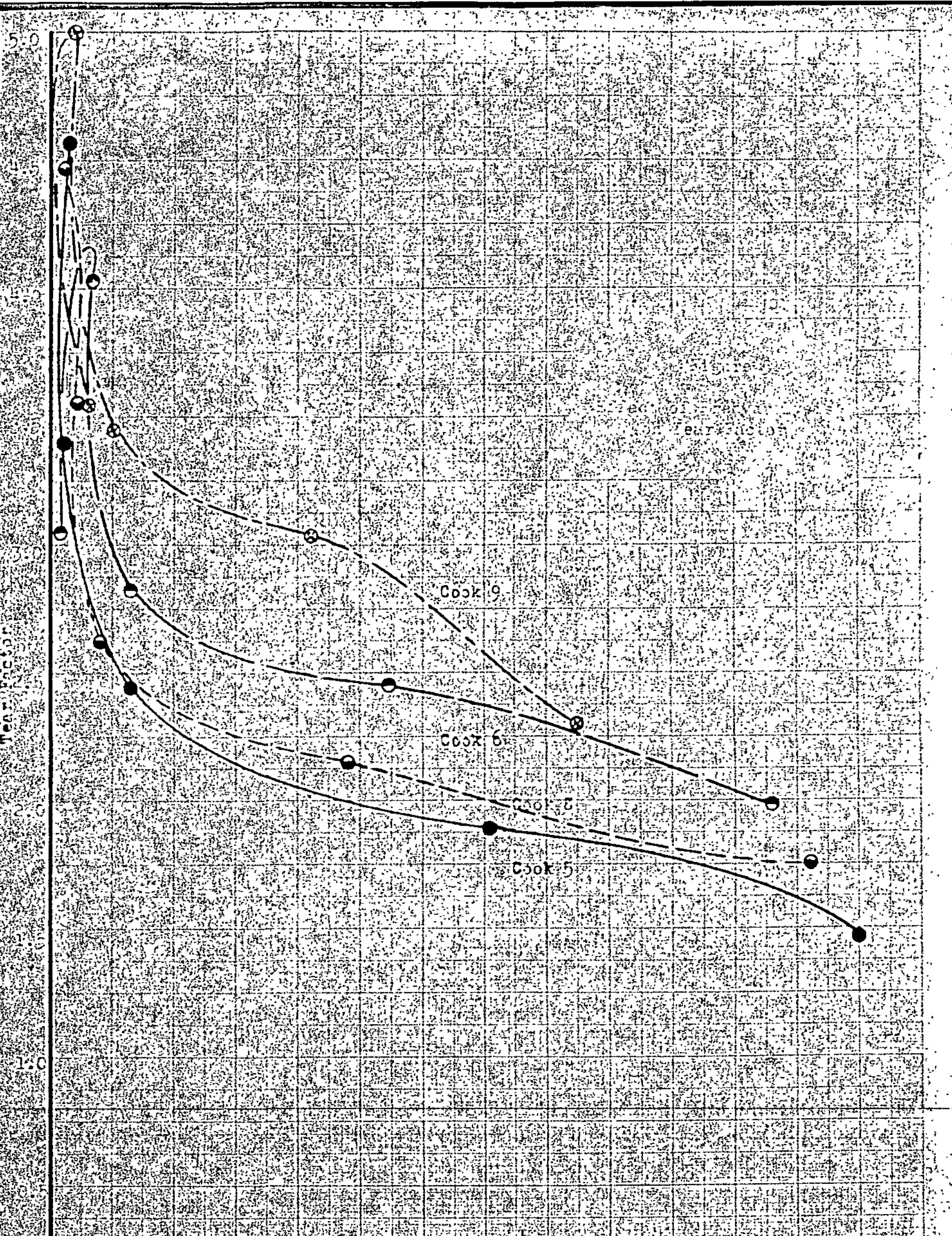


Figure 2

Effect of Prehydrolysis on Bursting Strength

5.0
4.5
3.0
2.0
1.0
0.5
Tear Factor
Cook 9
Cook 6
Cook 8
Cook 5
900
800
700
600
500
400
300
200
Schopper-Riegler Freeness--cc.

are drawn concerning pulp strength.

CONCLUSIONS

Because of the limited amount of data reported herein, no definite conclusions can be drawn. There are indications that prehydrolysis may decrease the intensity of the odor, reduce the yield, increase the power required for refining and improve the tearing strength of the pulp. If there is an improvement in bursting strength it is at lower freeness values than are normally attained on such pulps.

PROJECT REPORT FORM

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PROJECT NO.	1395
COOPERATOR	Institute
REPORT NO.	1
DATE	9-22-48
NOTE BOOK	860
PAGE	65-69 TO
SIGNED	William Shockley William Shockley

INTRODUCTION

This portion of project 1395 was concerned with the oxidation of the liquor in a kraft mill which would ordinarily go to the evaporators. Dr. Kress proposed to study the oxidation of this liquor by passing it down a column with a countercurrent of (1) air, and (2) air plus carbon dioxide.

EQUIPMENT

A Pyrex tube approximately 4 inches in diameter and 36 inches in length was packed with 6 x 6 mm. Raschig rings. Air was introduced at the bottom of the column through a sintered glass funnel, and the liquor flowed out through a trap designed to prevent any passage of air; at the top of the column scrubbers were provided to entrap any hydrogen sulfide gas emanating from the oxidized solution, and the sodium sulfide solution was introduced at the top of the column.

Ten liters of sodium sulfide solution were prepared by diluting a 35-gram/liter solution found in the Pulping Laboratory. The original grams/liter content was never accurately established due to the fact that suitable analytical techniques were not used at the beginning of the experiment. However, on titration with hydrochloric acid to the phenolphthalein and methyl orange endpoint, a value of 13.7 grams/liter was obtained.

The passage of air upward through the column was calculated to be approximately 50 ml./sec. or 3000 ml./min. This figure is strictly an estimate and no accurate measurement was made due to the fact that the experiment was regarded as being merely qualitative. The sodium sulfide flow was adjusted to approximately 2 liters/hour. The oxidized sodium sulfide solution was collected in a large bottle.

METHOD OF ANALYSIS

At first it was thought possible to analyze for sodium sulfide by a direct titration with hydrochloric acid to the phenolphthalein and methyl orange endpoint. However, after several analyses had been made, it became obvious that the method was not applicable on oxidized sodium sulfide solutions since the analyses indicated that more sodium sulfide was present after the oxidation--which is of course impossible. Therefore the evolution technique (Institute method 109, page 8) was employed. In this method hydrogen sulfide is evolved by the addition of sufficient hydrochloric acid to adjust the pH to 4.0 and absorbed in a solution of standardized iodine and titrated against sodium thiosulfate. The analyses obtained by this method appeared to be logical.

EXPERIMENTAL

With the sodium sulfide passing through the column at a rate of approximately 2 liters/hour, two experiments were carried out. In the first experiment air plus carbon dioxide was introduced in the bottom of the column in the ratio of 6 carbon dioxide to 1 air. Hydrogen sulfide was immediately given off and trapped at the cadmium sulfate scrubber, but otherwise this oxidation proceeded without difficulty. In the second experiment the sodium sulfide solution which had been exposed to the air plus carbon dioxide mixture was oxidized with air alone. On analysis by the evolution technique, the original material was found to have 13.3 grams/liter of sodium sulfide. The material which had been oxidized with the mixture of carbon dioxide plus air contained 9.8 grams/liter sodium sulfide and that material, when oxidized with air alone, was reduced to 6.0 grams/liter sodium sulfide. Qualitative observations during the oxidation indicated that even though the air oxidation was continued for 3 hours as against 1 hour for the carbon dioxide plus air experiment, the latter oxidation yielded approximately 8 times as much hydrogen sulfide as did the former.

Another experiment was performed by simply bubbling air through a fritted gas dispersion tube into a bottle of sodium sulfide solution. Hydrogen sulfide was observed emanating from the bottle. Unfortunately the analysis of this oxidized material was done by titration and the results could not be regarded as valid.

CONCLUSION

Apparently from this one spot experiment sodium sulfide solution can be oxidized by passage through a column of extended surface with a countercurrent of air. ~~Thus~~ It would not appear feasible to use flue gas in an oxidation of this type due to the production of huge quantities of hydrogen sulfide.

vs/fl