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SOME ASPECTS OF SULFITATION AS A MEANS OF NEUTRAL SULFITE BLACK LIQUOR RECOVERY

INTRODUCTION

The paper industry has for various reasons shown renewed interest in recovery of black liquors from the neutral sulfite process. In one method of recovery which has been suggested, concentrated liquor is fed into Kraft recovery furnaces to obtain a smelt consisting principally of a mixture of sodium carbonate and sodium sulfide. It is generally believed that the dissolved smelt cannot be sulfited directly, however, for large percentages of objectionable thiosulfates, polysulfites, and polysulfur compounds are formed. In this report, preliminary experiments are described in which the effect of causticity of the green liquor and temperature of the reaction were investigated as possible retardants to the formation of sodium thiosulfate during the sulfiting process.

EXPERIMENTAL

Run number 1 was carried out as an orientation experiment. A Kraft white liquor of about 15% sulfidity was prepared to simulate causticized green liquor. The chemical concentration of the liquor was approximately 100 g./l. 900 ml. of liquor were placed in a one Liter beaker. Sulfur dioxide was introduced at a constant rate through a rotometer and capillary tube into the liquor. The

liquor was agitated continuously with a "Lightnin" mixer. No attempt was made to control the temperature of the reaction. A summary of the data collected during the run is given in Table I. At 90 minutes a very strong odor of hydrogen sulfide was noted.

During run number 2 the reaction temperature was maintained between 20 and 24° C. 3,750 cc. of Kraft liquor of approximately the same composition as that of run number 1 was placed in a 4-liter beaker in a water bath. Sulfur dioxide was introduced through a capillary tube at the same rate per unit volume as the first run. The liquor was agitated continuously. Samples of 250-cc. each were syphoned from the reaction mixture at 15 minute intervals. Table II is a summary of the data from the run.

After 105 minutes the pH fell rapidly to 8.5, then decreased gradually to 7.65. The odor of hydrogen sulfide became noticeable as the pH made the rapid drop.

Run number 3 was made in a temperature range of 90 to 95° C. All other conditions were the same as used in run numbers 1 and 2. Table III is a summary of the data obtained. After 80 minutes, noticeable hydrogen sulfide was evolved. The solution turned from a straw-yellow color to a very dark green. Sample 8 (105 minutes) was almost white. In this liquid was suspended a finely divided brown or black precipitate. At 107 minutes, the odor of hydrogen sulfide disappeared. Samples 9 and 10 were light green in color.

Equivalent weights of sodium carbonate were substituted for sodium hydroxide in runs 4 and 5 to serve as baseline conditions for runs 2 and 3. The temperature of the reaction and rate of sulfur dioxide addition of runs 2 and 3

TABLE I

RUN NO. 1

Time, min.	Volume, cc.	Rotometer, Rg.	pH	Temperature, ° C.	Na_2S as Na_2O		Na_2SO_3 as Na_2O		$Na_2S_2O_3$ as Na_2O		NaOH as Na_2O	
					g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.
0	900	1.5	10.6	-	14.2	11.3	0.35	0.17	0.41	0.16	82.9	64.2
4	900	1.5	10.5	-	-	-	-	-	-	-	-	-
7	900	1.5	10.4	34	-	-	-	-	-	-	-	-
21	900	1.5	10.3	37	-	-	-	-	-	-	-	-
50	900	1.5	10.3	41	-	-	-	-	-	-	-	-
75	900	1.5	10.3	43	-	-	-	-	-	-	-	-
90	900	1.5	10.3	44	-	-	-	-	-	-	-	-
92	900	1.5	6.9	44	5.8	4.6	126.2	62.1	37.5	14.7	0.0	0.0

TABLE II

Run No. 2

Sample No.	Time, min.	Volume, cc.	Rotometer Reading	pH	Temperature, ° C.	Na_2S as Na_2O		Na_2SO_3 as Na_2O		$Na_2S_2O_3$ as Na_2O		NaOH as Na_2O		Na_2CO_3 as Na_2O	
						g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.
1	0	3,750	6.25	13	20	13.3	10.6	0.6	0.3	1.2	0.5	83.6	64.8	1.3	0.8
2	15	3,500	5.82	13	21	12.9	10.2	20.9	10.3	4.2	1.6	-	-	-	-
3	30	3,250	5.42	13	23	12.3	9.8	37.6	18.5	5.4	2.1	-	-	-	-
4	45	3,000	5.00	13	23	11.8	9.4	53.3	26.2	8.5	3.3	-	-	-	-
5	60	2,750	4.58	13	24	10.4	8.2	72.7	35.8	11.3	4.4	-	-	-	-
6	75	2,500	4.16	13	22	10.6	8.4	88.2	43.4	14.8	5.8	-	-	-	-
7	90	2,250	3.75	13	22	9.7	7.7	102.6	50.5	18.4	7.2	-	-	-	-
8	105	2,000	3.33	13	23	6.8	5.4	121.2	59.6	25.3	9.9	-	-	-	-
9	115	1,750	-	7.65	23	6.0	4.8	111.3	54.8	38.4	15.1	0.0	0.0	5.3	3.1

TABLE III

Run No. 3

Sample No.	Time, min.	Volume, cc.	Rotometer Reading	pH	Temperature, ° C.	Na_2S as Na_2O g./l.		Na_2SO_3 as Na_2O g./l.		$Na_2S_2O_3$ as Na_2O g./l.		NaOH as Na_2O g./l.	
1	0	3,750	6.25	13.00	95	12.8	10.2	0.4	0.2	0.8	0.3	89.6	69.4
2	15	3,500	5.82	12.80	95	-	-	-	-	-	-	-	-
3	30	3,250	5.42	12.90	95	-	-	-	-	-	-	-	-
4	45	3,000	5.00	12.80	93	-	-	-	-	-	-	-	-
5	60	2,250	4.58	12.70	94	-	-	-	-	-	-	-	-
6	75	7,500	4.16	12.70	94	31.8	25.3	118.2	58.1	7.6	3.0	20.6	16.0
7	90	2,250	3.75	12.80	95	28.4	22.6	161.3	79.3	13.8	5.4	12.6	9.8
8	105	2,000	3.33	8.00	95	20.6	16.4	159.3	78.3	51.7	20.3	0.0	0.0
9	110	1,750	2.91	7.52	95	8.4	6.7	195.3	96.0	62.6	24.5	0.0	0.0
10	120	1,500	-	6.92	95	-	-	-	-	-	-	-	-

were duplicated in runs 4 and 5 respectively. Tables IV and V contain a summary of the data collected.

In run 6 an uncausticized green liquor was sulfited at 135° C. in a laboratory stationary digester. Sulfur dioxide was admitted to the digester through the auxiliary liquor injection system at 44 psi gauge (the vapor pressure at room temperature). The pressure in the digester itself was maintained at 34 psi gauge. Liquor samples were removed from the digester through a condenser at 15 minute intervals. Table VI contains a summary of the data.

SUMMARY OF RESULTS AND CONCLUSIONS

At the time of the writing of this report, six experimental runs have been made to investigate chemical reaction of sulfur dioxide with solutions of sodium sulfide and sodium hydroxide or sodium carbonate. Three different temperatures were used. A critical study of the results is difficult for attempts to minimize the work led to analysis of only selected samples, and of these, certain errors are known to exist and will be discussed.

1. The material listed as sodium thiosulfate represents the total of all reducing agents in solution. These would include the higher polysulfites. It is not known to what extent, if any, they are detrimental to pulp quality.

2. The scheme of analysis used is designed specifically for alkaline solutions and is consequently subject to error as the pH of the liquors becomes lower. This is especially true of the analysis for sulfide. For example, in Run 4, sample 12, 14.7 g./l of sodium sulfide is indicated, but yet the solution

TABLE IV

Run No. 4

Sample No.	Time, min.	Volume, cc.	Rotometer, Reading	pH	Temperature, ° C.	Na_2S as Na_2O		Na_2SO_3 as Na_2O		$Na_2S_2O_3$ as Na_2O		Na_2CO_3 as Na_2O	
						g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.
1	0	3,750	6.25	10.9	22	13.5	10.7	-	-	-	-	112.1	-
2	15	3,500	5.82	9.92	23	-	-	-	-	-	-	-	-
3	30	3,250	5.42	9.40	22	-	-	-	-	-	-	-	-
4	45	3,000	5.00	8.68	22	3.3	2.6	34.2	16.8	28.3	11.1	62.7	36.7
5	60	2,750	4.88	7.62	22	-	-	-	-	-	-	-	-
6	75	2,500	4.16	6.82	22	4.8	3.8	67.7	33.3	33.5	13.1	42.5	24.9
77	90	2,250	3.75	6.67	20	-	-	-	-	-	-	-	-
8	105	2,000	3.33	6.52	20	1.7	1.4	106.3	52.3	33.6	13.2	14.2	8.3
9	115	1,750	2.91	6.40	20	-	-	-	-	-	-	-	-
10	130	1,500	2.50	6.12	20	7.8	6.2	128.8	63.4	33.6	13.2	0.0	0.
11	145	1,250	2.16	5.90	20	-	-	-	-	-	-	-	-
12	160	1,000	1.75	5.60	20	14.7	11.7	158.9	78.2	33.2	13.0	0.0	0.

TABLE V

Run No. 5

Sample No.	Time, min.	Volume, cc.	Rotometer Reading	pH	Temperature, ° C.	Na_2S as Na_2O g./l.		Na_2SO_3 as Na_2O g./l.		$Na_2S_2O_3$ as Na_2O g./l.		Na_2CO_3 as Na_2O g./l.	
1	0	3,750	6.25	10.42	95	13.5	10.7	0.0	0.0	0.6	0.2	116.1	67.8
2	15	3,500	5.82	9.80	94	-	-	-	-	-	-	-	-
3	30	3,250	5.42	9.34	95	-	-	-	-	-	-	-	-
4	45	3,000	5.00	9.00	95	7.1	5.6	49.5	24.3	16.4	6.4	73.8	43.2
5	60	2,750	4.58	8.72	94	-	-	-	-	-	-	-	-
6	75	2,500	4.16	8.70	96	3.8	3.0	112.5	55.4	17.4	6.8	35.1	20.5
7	90	2,250	3.75	8.49	96	-	-	-	-	-	-	-	-
8	105	2,000	3.33	7.68	96	9.2	7.3	205.8	101.3	18.6	7.3	3.7	2.2
9	120	1,750	2.91	6.65	95	-	-	-	-	-	-	-	-
10	135	1,500	2.50	6.00	95	-	-	-	-	-	-	-	-
11	150	1,250	2.16	5.58	95	8.1	6.4	538.8	264.7	29.9	11.7	0.0	0.0

TABLE VI

Run No. 6

Sample No.	Time, Min.	pH	Na_2S as Na_2O		Na_2SO_3		$Na_2S_2O_3$ as Na_2O		Na_2CO_3 as Na_2O	
			g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.	g./l.
0	0	10.72	3.7	2.9	0.8	0.4	0.6	0.2	106.5	62.3
1	15	10.6	-	-	-	-	-	-	-	-
2	30	10.5	-	-	-	-	-	-	-	-
3	45	10.4	-	-	-	-	-	-	-	-
4	60	10.2	-	-	-	-	-	-	-	-
5	75	10.1	-	-	-	-	-	-	-	-
6	90	10.0	1.8	1.4	7.4	3.6	4.4	1.7	96.2	56.2
7	105	9.9	-	-	-	-	-	-	-	-
8	120	9.8	-	-	-	-	-	-	-	-
9	135	9.6	-	-	-	-	-	-	-	-
10	150	9.5	-	-	-	-	-	-	-	-
11	165	9.4	-	-	-	-	-	-	-	-
12	180	9.2	0.7	0.6	34.3	16.8	7.3	2.9	59.7	34.9
13	195	9.1	-	-	-	-	-	-	-	-
14	210	9.1	-	-	-	-	-	-	-	-
15	225	9.0	-	-	-	-	-	-	-	-
16	240	9.0	-	-	-	-	-	-	-	-
17	255	9.0	-	-	-	-	-	-	-	-
18	270	8.9	4.7	3.7	42.5	20.9	8.8	3.4	48.4	28.3
19	285	8.9	-	-	-	-	-	-	-	-
20	300	8.7	-	-	-	-	-	-	-	-
21	315	8.7	-	-	-	-	-	-	-	-
22	330	8.6	-	-	-	-	-	-	-	-
23	345	8.6	3.8	3.0	63.3	31.2	11.8	4.6	26.4	15.4

has a pH of 5.6 and therefore cannot contain sodium sulfide, nor was there an odor of Hydrogen sulfide which might be expected if the sulfide was present at low pH.

By examining the data and curves plotted, an insight of the nature of the reaction may be gained.

1. In sulfitation, sodium sulfite is formed directly from the alkaline compound sodium hudroxide or sodium carbonate. This may best be proven by plotting the alkaline reagent concentration against the sulfite concentration and, as may be seen in Figure 1, essentially straight lines are formed. Thus the reaction may be expressed as:

1) $2\,NaOH + H_2SO_3 \rightleftharpoons Na_2SO_3 + 2\,H_2O$

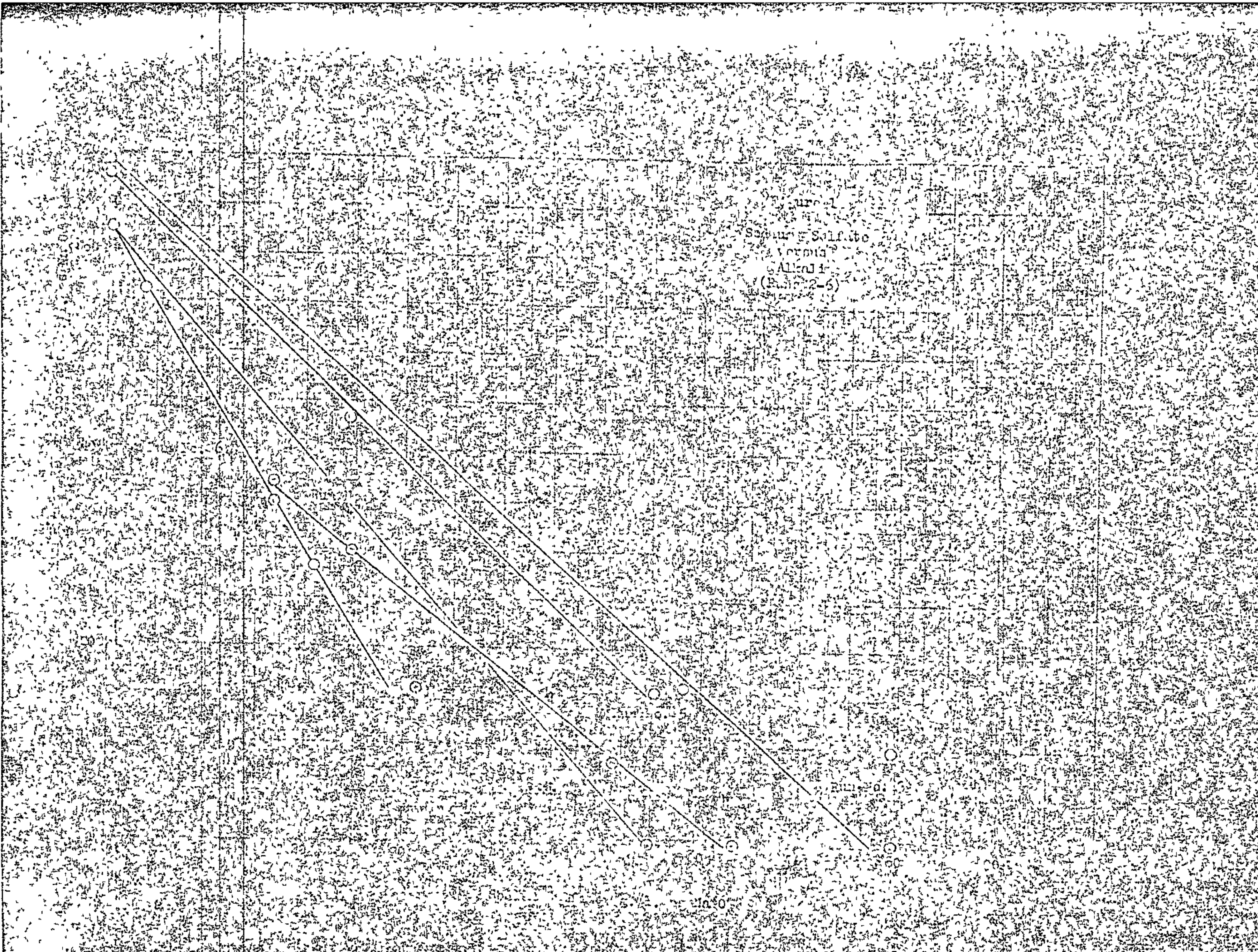
-or-

2) $Na_2CO_3 + H_2SO_3 \rightleftharpoons Na_2SO_3 + H_2CO_3$

2. If the polysulfites were formed directly from sodium sulfide the total of sodium sulfide and sodium thiosulfate expressed as Na_2O should remain constant. However, in three experimental runs for which the data appear to be essentially correct, this total increases,--in run 1 from 11.5 to 19.3, run 2 from 11.1 to 19.9, and run 3 from 10.5 to 31.2 g./l. Na_2O. This indicates that some of the alkaline reagent (sodium hydroxide) is involved in formation of the thiosulfate. The equation for the reaction might be expressed as:

3) $2\,Na_2S + 2\,NaOH + 4\,H_2SO_3 \rightleftharpoons 3\,Na_2S_2O_3 + 5H_2O$

4) $2\,Na_2S + Na_2CO_3 + 4\,H_2SO_3 \rightleftharpoons 3\,Na_2S_2O_3 + 4\,H_2O + CO_2$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Thermodynamic calculations based upon the equations listed above indicated that the equilibria becomes more favorable as the temperature of reaction is increased.

In Figure 2, sodium sulfite is plotted against the thiosulfate content. It is immediately evident that the ratio of sulfite to thiosulfate is more favorable as the temperature of reaction is increased. It is also interesting to note that in the carbonate runs, (numbers 4-6), the thiosulfate reached a maximum value, dependent upon temperature, although a greater proportion of the sulfite was formed beyond this point. The reverse seems to be true when sodium hydroxide is employed.

The rate of reaction during run No. 6 was, in comparison with the other experimental work, much slower, for the data indicates that even after a period of nearly six hours, the sulfiting was not completed. It is believed that the method of introduction of the sulfur dioxide into the digester did not provide enough contact between the gas and liquor. When further work is done at elevated temperatures, it will be advantageous to pack the pressure vessel with coke or other acid-resisting material and introduce the gas into the stream of cascading liquor at that point.

To summarize, it may be cohcluded that in sulfitation, sodium sulfite is formed by the direct combination of the alkali compound with sulfur dioxide. The thiosulfates, or polysulfites, at least in the range of high pH, are believed to result from interaction of both sodium sulfide and the alkaline material with sulfur dioxide. The equilibrium conditions are such that higher temperatures retard the formation of the objectionable polysulfites. There is also an indication that a more favorable ration of sulfite to thiosulfate may result when sodium carbonate rather than sodium hydroxide is employed in the liquor.

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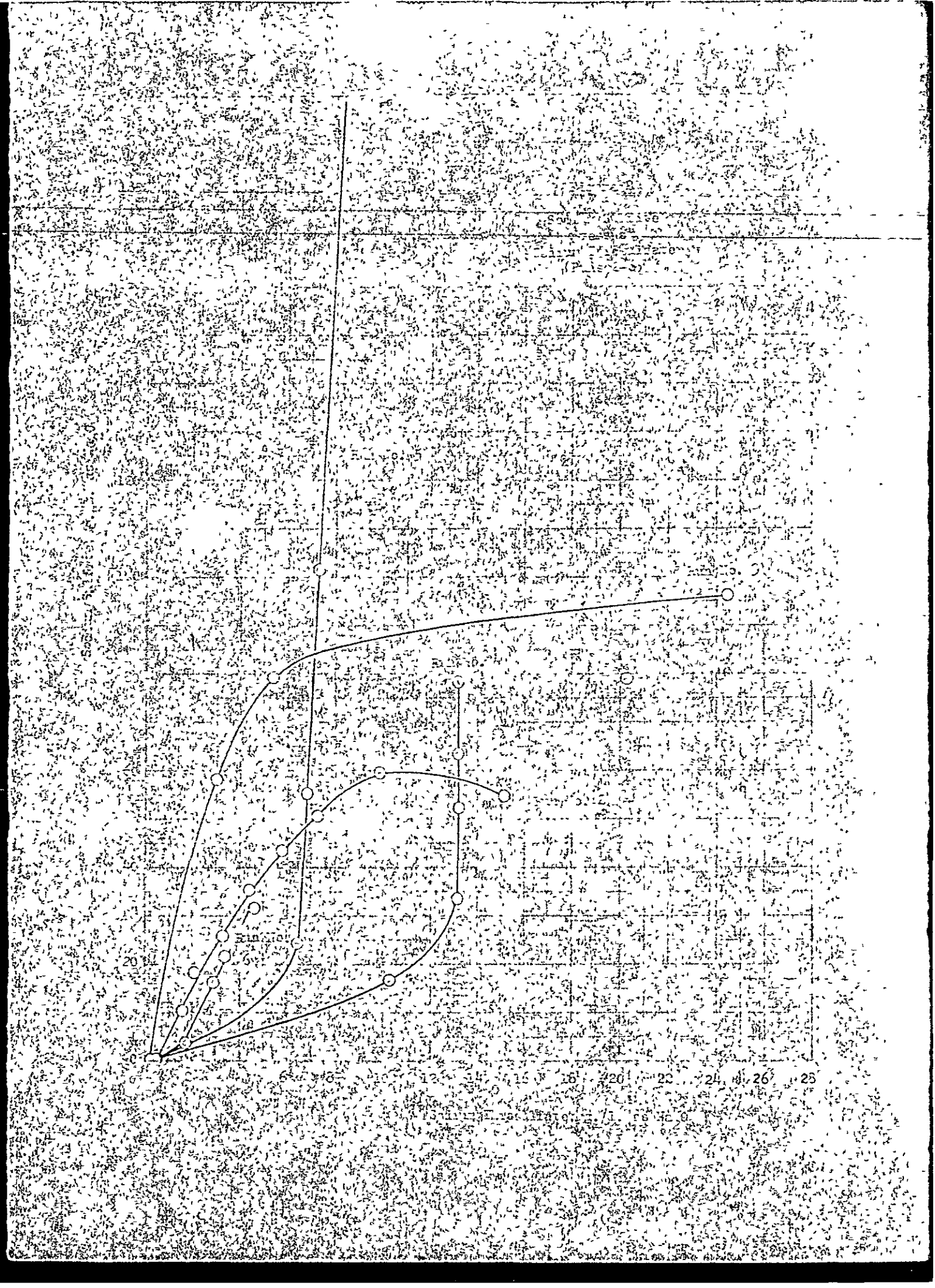

PROJECT REPORT FORM

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BLEACHING OF SEMICHEMICAL PULPS

"Is it possible to delignify only the surfaces of the fibers, thereby improving the nature of the bonded areas from a strength standpoint?" was the question asked by Dr. Forman in a memorandum dated March 28, 1950 to Mr. Kottwitz with regard to semichemical pulps.

As a start toward answering this question, six "bleaches" have been performed on an unbarked commercial aspen neutral sulfite semichemical pulp. Each of the six "bleaches" were performed with relatively small quantities of different chemicals, the object being not to make a white pulp or--for that matter--not even a pulp with improved color, but to find out if these chemical treatments have a tendency to increase or decrease the strength properties and to what degree, as indicated by Valley beater evaluation. No attempt was made to find out the optimum conditions for the use of each chemical, but it was hoped that the results might indicate what path to follow, should further study be desired.

CHEMICAL TREATMENTS

The main reacting agents for the six chemical treatments that were given to the aspen neutral sulfite pulp were:

1. Calcium hypochlorite
2. Sodium chlorite
3. Potassium permanganate
4. Chlorine gas, followed by sodium hydroxide
5. Sodium peroxide
6. Zinc hydrosulfite

The following is the procedure used in each case:

(1) Calcium hypochlorite

500 grams (ovendry basis) of the dry lap pulp was added to 10 liters of water and this was disintegrated in the Williams disintegrator. The stock was then diluted to such an amount that after calcium hypochlorite bleaching solution was added the consistency would be 3.0%. The stock was then placed in a 10 gallon size crock in a water bath and bleaching proceeded as follows:

Elapsed Time Minutes	
0	Temperature of stock 35° C., pH 6.9, 2.0% bleach added on pulp weight basis as available chlorine.
5	Chlorine exhausted as indicated by starch iodide paper
7	2.0% additional bleach added as available chlorine.
12	pH 9.0
17	Chlorine exhausted. Pulp was dumped in muslin-covered wash box, washed with cold water, then dewatered, pressed, and shredded. Moisture samples for purpose of yield determination were taken. Brightness sheets were made and sample was taken for lignin determination.

(2) Sodium Chlorite

500 grams of pulp was made up exactly as was the pulp for the previously described calcium hypochlorite bleach and it was diluted to such an amount that after adding a sodium chlorite solution (that was made up to 30 g./l. of sodium chlorite), the consistency would be 3.0%. Glacial acetic

acid was used to lower pH. Following is the schedule used:

Elapsed Time Minutes	
0	Temperature, 37°C., pH reduced from 8.0 to 5.1 with 2 ml. acetic acid, then 221 ml. of sodium chlorite solution added (which tested 45.2 g./l. of available chlorine). This equals 2.0% available chlorine or 10.0 grams on airdry pulp weight basis.
4	2 ml. more of acetic acid added. pH 4.7
8	2.0% more available chlorine added.
64	Dumped. pH 4.8. Residual available chlorine was 19.2 grams so only 0.8 grams of available chlorine was consumed. The pulp was then treated the same as was the pulp of the calcium hypochlorite treatment after dumping.

(3) Potassium permanganate

Pulp was prepared in the same manner as was that for hypochlorite treatment. Consistency during reaction was 3.0%.

The following is the schedule for the permanganate treatment:

Elapsed Time Minutes	
0	Temperature 35° C. pH reduced to 2.9 with sulfuric acid and then 1035 ml. of .4824 normal potassium permanganate was added with good stirring. This was equal to 15.8 grams of potassium permanganate or 3.16% on ovendry pulp weight basis.

3 The potassium permanganate was apparently exhausted as no purple color remained. Therefore pulp was dumped in wash box and washed with cold water.

The pulp was dark due to manganese dioxide on the fibers, so it was diluted to 3.0% consistency with cold water and 15 grams of sodium bisulfite was added in order to dissolve out the manganese dioxide.

After this treatment the pulp was washed with cold water in muslin wash box and treated the same as the pulp of the calcium hypochlorite treatment after it was dumped.

(4) Chlorine Gas Followed by Sodium Hydroxide

590 grams of pulp was disintegrated in the same manner as was the pulp of the calcium hypochlorite treatment.

This was then placed in the pulp laboratory chlorinator and was diluted with water to 2.21% consistency. The pulp was then chlorinated as follows:

Elapsed Time Minutes	
0	Chlorine gas added at rate of 1.27 grams per minute; temperature of stock 27° C.
7.88	Chlorine gas addition completed. 10.0 grams total chlorine was added in the 7.88 minutes.
12	No residual chlorine gas left in stock so circulation was stopped.

After this chlorination, the pulp was not removed from the chlorinator but was given the following treatment with sodium hydroxide:

Elapsed Time Minutes	
0	5.0 grams sodium hydroxide added to stock in chlorinator, circulator running.
9	pH 4.6
14	5.0 grams sodium hydroxide added. Pulp became darker
16	pH 10.2
44	pH 9.9
74	pH 9.8. Temperature 26° C. Dumped; pulp was then washed with water at 30° C., dewatered, pressed, shredded, and handled same as pulp of calcium hypochlorite treatment.

(5) Sodium Peroxide

500 grams (ovendry basis) of the dry lap pulp was prepared in the same manner as was pulp for calcium hypochlorite treatment and it was diluted to such an amount that the consistency would be 5.0% after addition of a solution containing 5.0 grams of sodium peroxide.

Before the addition of the sodium peroxide, 0.05% magnesium sulfate on pulp weight basis was added to the stock. During the reaction, the pH was controlled with 40° Baumé sodium silicate solution. Following is the schedule:

Elapsed Time Minutes:	
0	pH adjusted to 9.4 with the sodium silicate after 0.25

Minutes

grams of magnesium sulfate was added. Temperature of stock, 43° C. 5.0 grams or 1.0% of sodium peroxide was then added to stock.

3 pH 10.2

60 pH 10.1. Residual sodium peroxide was 2.37 grams or only 52.6% of sodium peroxide was consumed. The pulp was dumped at the 60 minute time, then it was handled in the same way as the pulp of the calcium hypochlorite treatment after it was dumped.

(6) Zinc Hydrosulfite

500 grams (ovendry basis) of the dry lap pulp was disintegrated and treated in the same way as the pulp of the calcium hypochlorite treatment, except that only enough water was added so that after addition of the zinc hydrosulfite solution, the consistency would be 4.0%.

Following is the schedule:

Elapsed Time

Minutes:

0 Temperature 32° C., pH 6.8. 2.0% of zinc hydrosulfite added to stock (10 grams).

3 pH 6.0

30 pH 6.0. Dumped, washed with cold water, and handled same as pulp of calcium hypochlorite treatment.

Permanganate numbers were run in duplicate on each of the six pulps plus duplicate runs on the "as received" semichemical pulp. The results, including lignin content, permanganate number, yield, brightness, and other data are given in Table I.

BEATER EVALUATIONS

Beater evaluations by Institute Method 403 were made using Valley beater No. 2 with a 5,500 gram bed plate load. Seven evaluations were run, one on each of the six chemically treated pulps plus one on the untreated pulp. Samples for British handsheets were taken at the 0, 5, 15, 30, and 50 minute interval.

The British handsheets were tested for basis weight (25 x 40—500), caliper, apparent density, bursting strength, tearing strength, and tensile strength. The results of these tests were plotted with apparent density on the abscissa against freeness, bursting strength, tearing strength, and tensile strength. From these plots, strength comparisons at apparent densities of 9.2 and 10.2 were made and these appear in Table I. (The original rough plots are attached to the file copy of this report.)

DISCUSSION

Refering to Table I, it may be found that the strength results and freenesses have been rated using the unbleached pulp as the baseline. The positive sign indicates that the value is higher than baseline; a negative sign that it is lower. The numerals indicate the standing; 1 is a higher rating than 2, whether the sign be positive or negative.

An examination of Table I shows that the calcium hypochlorite treatment weakened the pulp in bursting strength and tensile strength to a greater degree than any of the other treatments, but it increased the tearing strength a respectable amount.

The reducing chemical, zinc hydrosulfite, gave the pulp the greatest increase of any of the chemicals in both bursting strength and tearing strength. At 9.2 apparent density, it rated second to sodium peroxide in tensile strength although it was below the baseline tensile strength. At 10.2 apparent density, the hydrosulfite treated pulp was not the greatest nor was it the least in tensile strength when compared to the other five treated pulps.

It appears that as far as strength characteristics are concerned, the hypochlorite treatment as applied in this work definitely was the least encouraging while the zinc hydrosulfite treatment was the most encouraging.

A further examination of Table I shows that the sodium peroxide treated pulp rates next below zinc hydrosulfite in strength development or improvement, and that there is not much choice between the chlorine-sodium hydroxide combination and sodium chlorite.

CONCLUSIONS

Because no attempt was made to find the concentration of each of the six chemicals which would give the optimum in strength, it is not strictly proper to rate results as was done in this report. It is

possible that a 2.0% sodium peroxide treatment would give pulp which, upon evaluation, would give paper of better strength characteristics than the 2.0% zinc hydrosulfite treated pulp, or that 4.0% potassium permanganate would give better results than the 3.16% potassium permanganate which was used.

It is quite definite that calcium hypochlorite weakens neutral sulfite semichemical pulp and that it should be ruled out as far as this particular work is concerned.

Although this work is purely academic, potassium permanganate should probably be ruled out because of its relatively high cost and because it showed no appreciable improvement in the pulp as shown by the beater evaluation.

It is suggested that if further work be desired, the chemical concentrations of sodium chlorite, chlorine-sodium hydroxide, sodium peroxide and zinc hydrosulfite be found that impart optimum strength to pulp and then the optimum strength of each be compared with one another.

Perhaps neutral sulfite semichemical is one of the most difficult pulps to increase the strength by this method. Would semi-chemical kraft be a better pulp to work on?

From the results of this work, it is definite that the strength of neutral sulfite semichemical pulp can be improved by bleaching agents. We cannot say that we delignify the surfaces of the fibers (see first paragraph of this report), but we do apparently improve the nature of the bonded areas.

EM/jh

TABLE I

SURFACE BLEACHING OF SEMICHEMICAL PULPS
Preliminary Investigation
Commercial Aspen Neutral Sulfite

	Unbleached	Bleach 1	Bleach 2	Bleach 3	Bleach 4	Bleach 5	Bleach 6
Chemical	-	$Ca(ClO)_2$	$NaClO_2$	$KMnO_4$	Cl_2 and NaOH	Na_2O_2	ZnS_2O_4
Chemical applied on ovendry pulp, weight basis, %	-	4.0 as avail. chlorine	4.0 as avail. chlorine	3.16 as $KMnO_4$	1.7 as avail. chlorine, 1.7 as NaOH	1.0 as Na_2O_2	2.0 as ZnS_2O_4
Temperature, ° C.	-	35	37	35	27.0 27.0	43	32
Consistency, ovendry pulp basis, %	-	3.0	3.0	3.0	2.21 2.2	5.0	4.0
Residual chemical, %	-	0.0	96	0.0	0.0	47.4	-
Permanganate number, 60 cc. basis	49.6	42.0	48.2	43.9	44.8	47.7	48.0
Lignin, %	12.3	12.6	12.8	11.4	13.0	12.3	12.7
Yield, %	-	95.2	94.6	93.8	97.1	93.0	97.6
General Electric brightness, %	35.1	37.5	36.3	37.0	30.5	38.3	39.2
Freeness:							
Apparent density, 9.2	705	785	765	760	730	715	755
Apparent density, 10.2	285	445	330	320	375	445	420
Rating (9.2)	-	+1	+2	+3	+5	+6	+4
Rating (10.2)	-	+1	+5	+6	+4	+1	+3
Bursting strength, pt./100 lb.,							
Apparent density, 9.2	35	27	29	33	39	43	41
Apparent density, 10.2	61	59	64	63	64	62	67
Rating (9.2)	-	-3	-2	-1	+3	+1	+2
Rating (10.2)	-	-1	+2	+4	+2	+5	+1
Tear factor							
Apparent density 9.2	.66	.80	.77	0.75	0.77	0.77	0.84
Apparent density 10.2	.51	.58	.54	0.47	0.55	0.62	0.67
Rating (9.2)	-	+2	+3	+6	+3	+3	+1
Rating (10.2)	-	+3	+5	-1	+4	+2	+1
Tensile strength, lb./in./100 lb.							
Apparent density, 9.2	37.5	26.5	30.0	34.0	34.5	39.0	36.7
Apparent density, 10.2	55.0	48.5	55.5	54.0	49.0	51.0	50.5
Rating (9.2)	-	-5	-4	-3	-2	+1	-1
Rating (10.2)	-	-5	+1	-1	-4	-2	-3

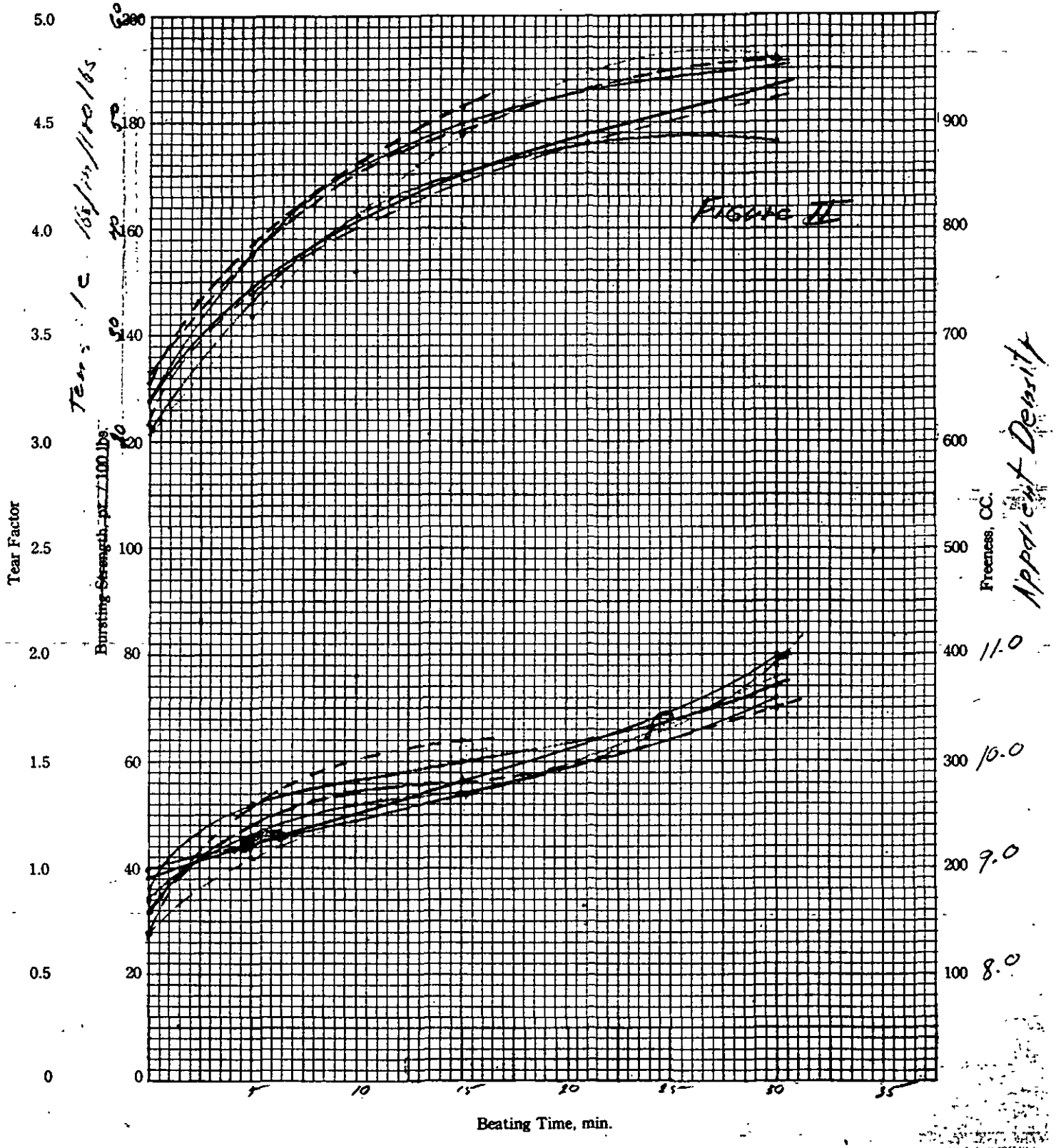
THE INSTITUTE OF PAPER CHEMISTRY

BEATING CURVES

Project _____ Date _____

File No. _____ Type of Pulp _____

Cook _____



Bleach 1 11 min
Unbleached — 48.6
1 ClO — 42.0
2 ClO2 — 43.2
3 NaOH — 43.9
4 Cl2 + NaOH — 44.8
5 NaClO2 — 47.7

THE INSTITUTE OF PAPER CHEMISTRY

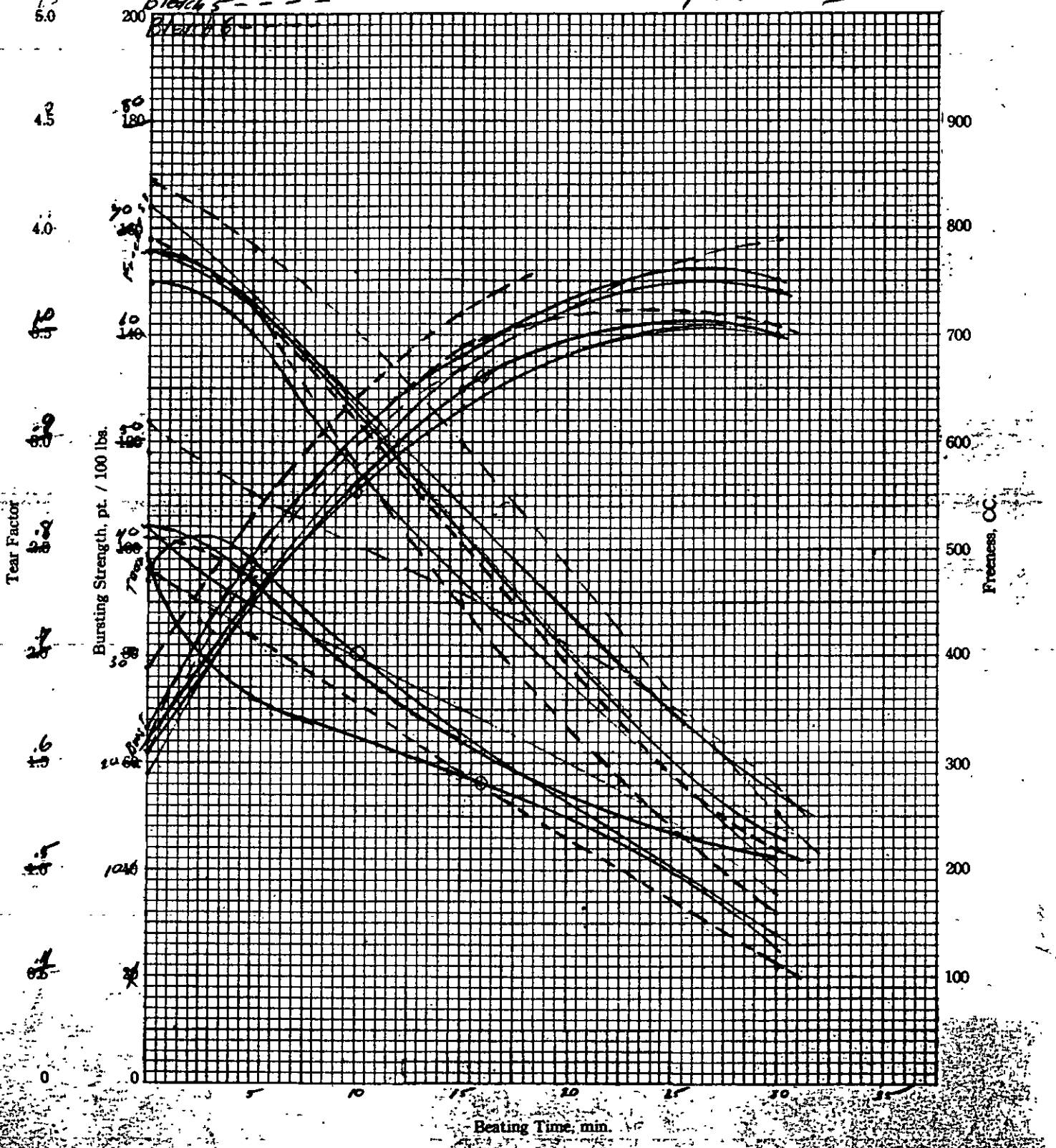
BEATING CURVES

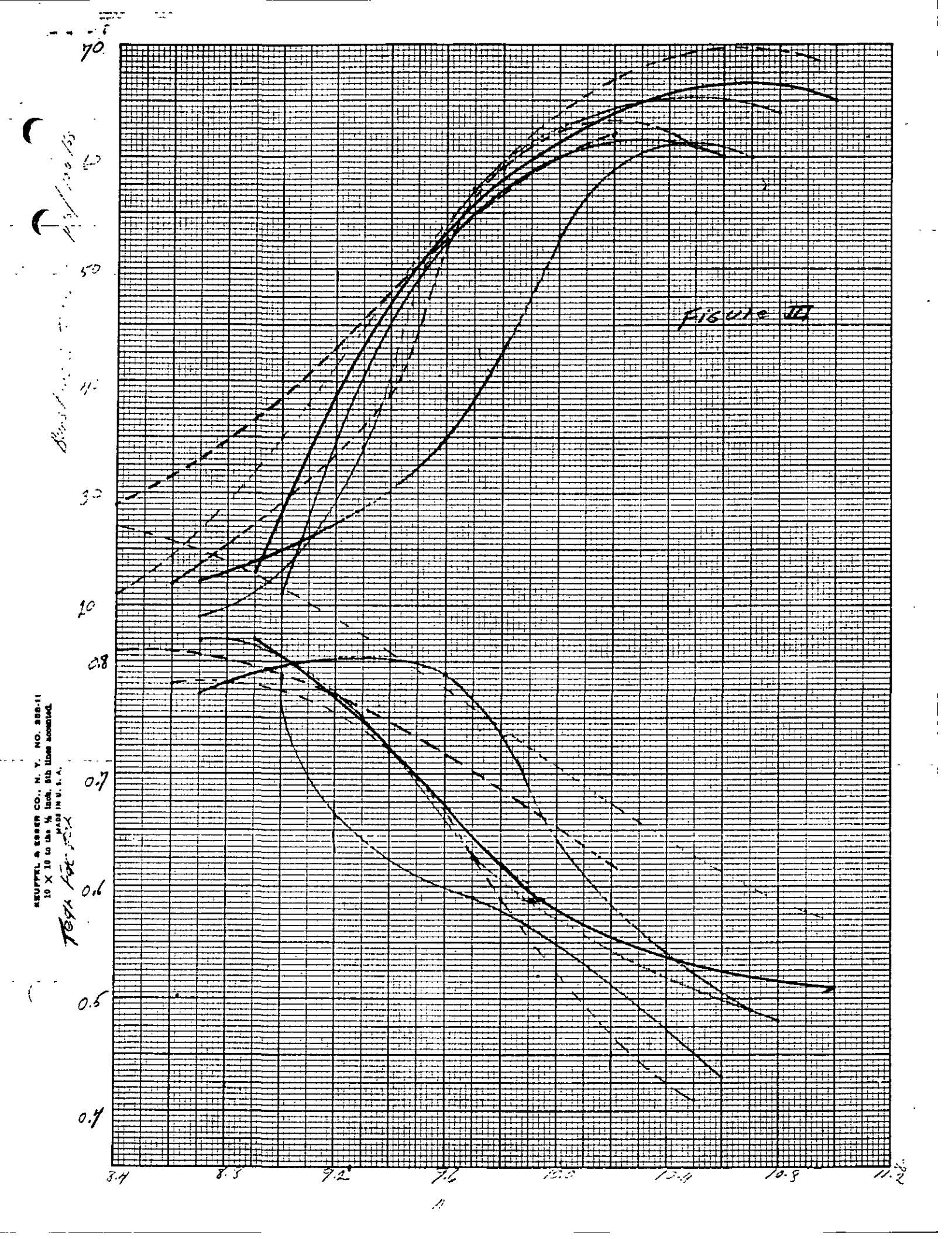
Project 1102-3 Date

File No. Unbleached Type of Pulp

Cook Bleach 1
Bleach 2
Bleach 3
Bleach 4
Bleach 5
Bleach 6

Figure I





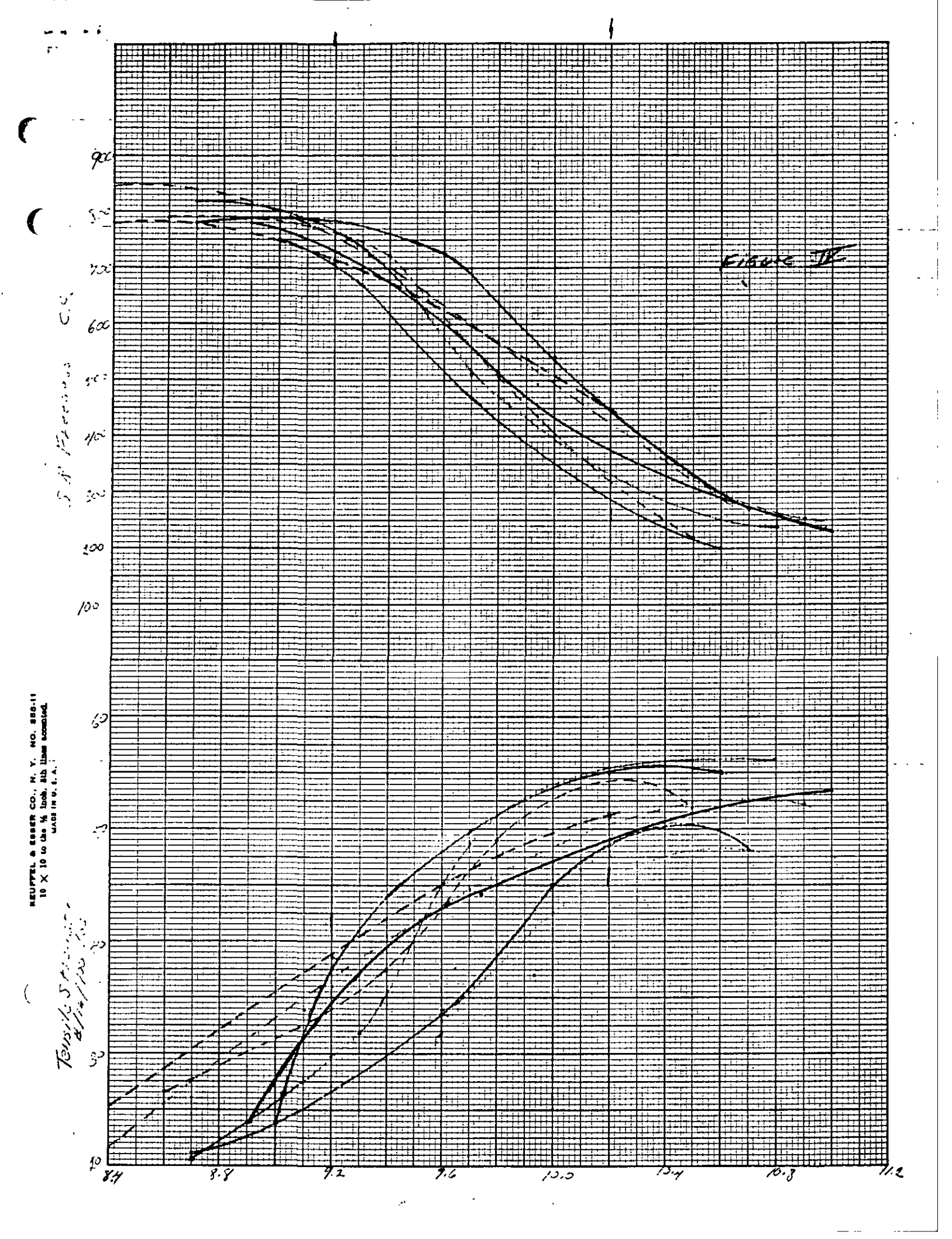


FIGURE III
900
800
700
600
500
400
300
200
100
50
40
30
20
10
8.4
8.8
9.2
9.6
10.0
10.4
10.8
11.2
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PROJECT NO. 1102-3
COOPERATOR Institute
REPORT NO. 8
DATE March 15, 1952
NOTE BOOK 898
PAGE 90-91, re 98-100
SIGNED R. S. Howard
Robert S. Howard

A BRIEF STUDY OF LIQUOR PH DURING NEUTRAL SULFITE PULPING

During the academic program in pulping, the pH of the cooking liquor of a neutral sulfite semichemical cook was measured periodically during the entire cook. The results showed a widely varying pH. As this varying pH could be one of the causes of equipment corrosion currently troubling the industry, two cooks were made in order to expand on the student work. The present report covers the conditions and results of these cooks.

RAW MATERIALS

Some seasoned, peeled poplar was chipped, screened, hand-sorted and bagged according to Pulping Group Procedure 40. At the time the digester charges were made, the moisture content of the wood was 21.0% and the digester charges weighed 4500 grams (airdry basis) or 3555 grams (ovendry basis).

C.p. chemicals were used in making the cooking liquor.

EXPERIMENTAL PROCEDURE AND RESULTS

Two cooks were made by the neutral sulfite semichemical process. Cooking conditions are shown in Table I and in Figures 1 and 2. The chips were charged to the digester in the stainless steel basket and at the end of the cook they were discarded.

TABLE I

PULPING CONDITIONS
NEUTRAL SULFITE SEMICHEMICAL PULPING OF POPLAR

Cook	1	2
Digester charge (airdry basis), g.	4500	4500
Digester charge (ovendry basis), g.	3555	3555
Water ratio (initial, O.D. basis), cc./g.	6.0	6.0
Sodium sulfite, %	18.0	18.0
Sodium carbonate, %	5.13	5.13
Cooking Schedule:		
Maximum temperature, °C.	170	*
Time to maximum, min.	120	
Time at maximum, min.	75	
Time of relief (to 0 p.s.i.), min.	15	
Total time (cover to blow), min.	210	

* No set schedule followed.

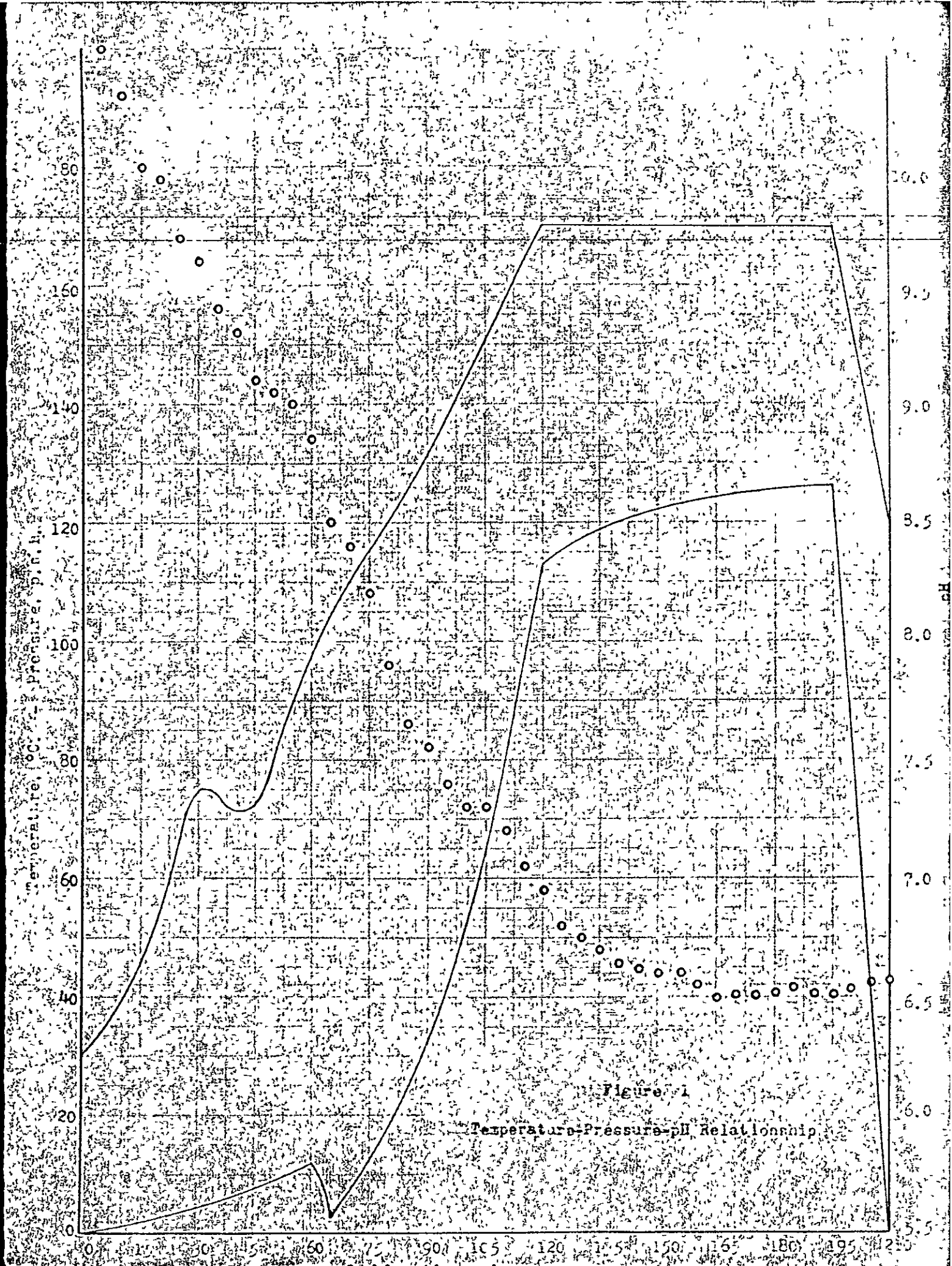
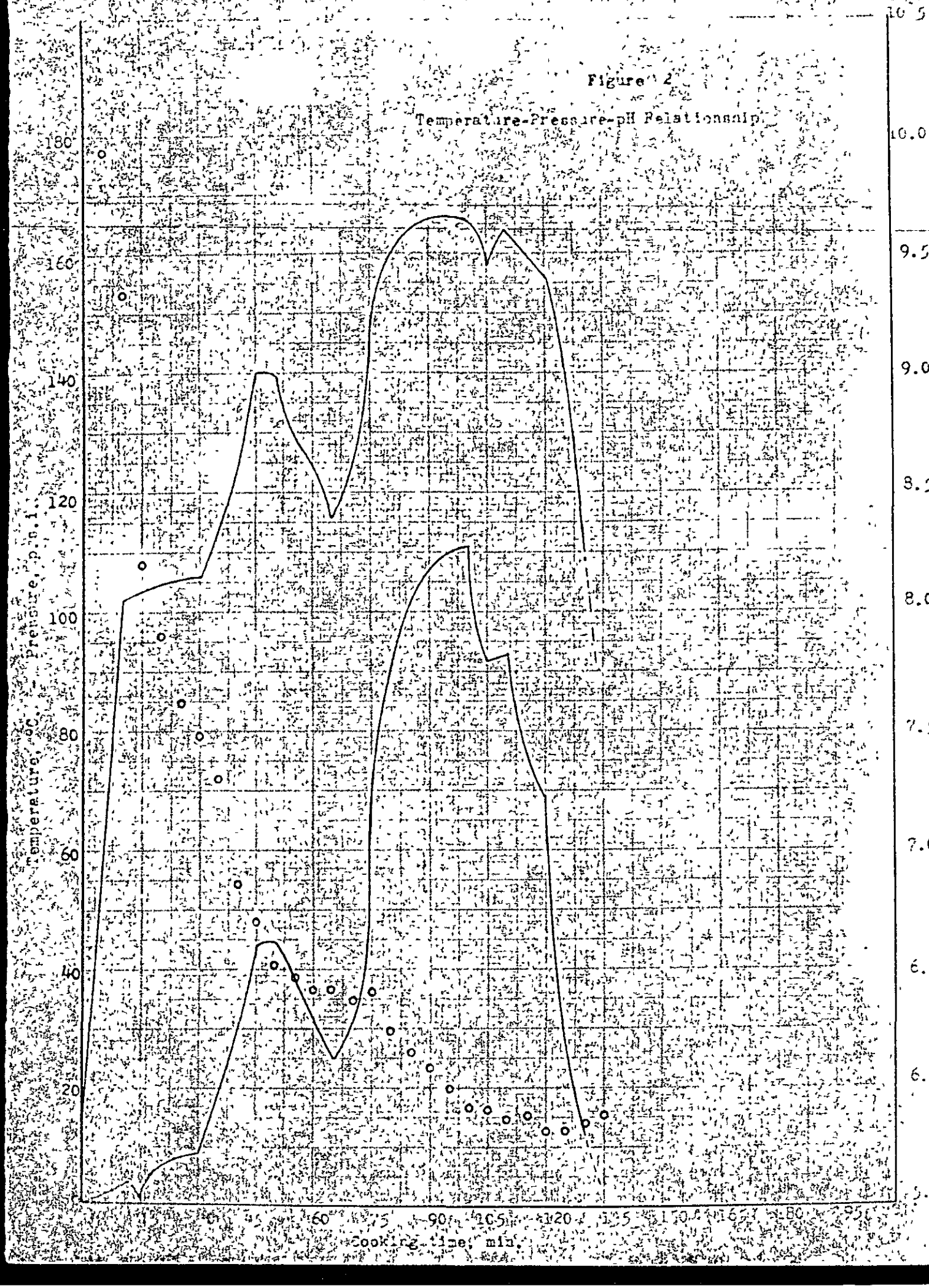


Figure 1

Temperature-Pressure-pH Relationship

Figure 2

Temperature-Pressure-pH Relationship



In Cook 1, a typical time-temperature schedule was followed, and liquor samples were withdrawn at five minute intervals throughout the cook. An initial high liquor ratio was used in order to furnish all the samples and still maintain sufficient liquor in the digester for satisfactory pulping.

Liquor samples (approximately 100 ml./sample) were withdrawn through a water-cooled condenser and then further cooled to 35-40°C. The pH of these samples was determined by using a Beckman-Glass Electrode-pH meter.

Cook 2 was a duplicate of Cook 1 in all except the time-temperature-pressure schedule. In this second cook, no definite schedule was followed; instead, large and rapid changes in temperature and pressure were effected in order to determine their effect on liquor pH. As in the previous cook, liquor samples were withdrawn, cooled, and the pH determined. The cooked chips were discarded on completion of the test. The results of pH determinations are listed in Table II and are related to temperature and pressure in Figures 1 and 2.

DISCUSSION

In following the liquor pH found in Cook 1, no great changes were found. There was a drop in pH as the temperature and pressure were increased. The changes in pH became increasingly smaller after maximum temperature was reached, finally maintaining a fairly constant value.

TABLE II

RESULTS OF PH DETERMINATIONS

COOK NO. 1

Sampling Time, min.	pH	Sampling Time, min.	pH	Sampling Time, min.	pH
5	10.50	75	8.20	145	6.62
10	10.30	80	7.90	150	6.60
15	10.00	85	7.65	155	6.60
20	9.95	90	7.55	160	6.55
25	9.70	95	7.40	165	6.49
30	9.60	100	7.30	170	6.51
35	9.40	105	7.30	175	6.51
40	9.30	110	7.20	180	6.52
45	9.10	115	7.05	185	6.54
50	9.05	120	6.95	190	6.51
55	9.00	125	6.80	195	6.51
60	8.85	130	6.75	200	6.53
65	8.50	135	6.70	205	6.56
70	8.40	140	6.64	210	6.57

TABLE II
(continued)

COOK NO. 2

Sampling Time, min.	pH	Sampling Time, min.	pH
5	9.93	75	6.40
10	9.33	80	6.24
15	8.20	85	6.15
20	7.90	90	6.08
25	7.62	95	6.00
30	7.48	100	5.92
35	7.30	105	5.91
40	6.86	110	5.87
45	6.70	115	5.88
50	6.52	120	5.82
55	6.47	125	5.82
60	6.42	130	5.85
65	6.42	135	5.88
70	6.37		

At the start of Cook 2, and in its early stages, large temperature increases in short periods of time brought the pH down fairly rapidly. The rate of pH drop seemed to level off somewhat when the temperature and pressure were held constant or decreased.

In comparing the results found in the two cooks it will be noted that the rapid rise in temperature early in Cook 2 lowered the average pH for the entire cook. There are indications that the temperature and pressure changes cause "breaks" in the pH curve in the later stages of the cook, but pH changes are small and not necessarily caused by variations in the cooking conditions. The "breaks" could possibly be error in pH measurement as the changes are beyond the accuracy of the pH meter.

The pH change found in the academic work was not verified by the cooks described in this report. The academic work was carried out in the rotary digesters where temperature control is very difficult, and this might account for the differences found. However, the temperature changes effected in Cook 2 did not cause the pH variation found in the student work.

It is unfortunate that pH determinations were necessarily made on cooled liquor samples. The pH conditions existing within the digester at relatively high temperatures and pressures are undoubtedly quite different than those found in the cooled liquor at atmospheric pressure. Continuous pH measurement utilizing electrodes enclosed in the liquor circulating system would be a superior method and the availability of this type of equipment should be investigated.

RSH/jh

PROJECT REPORT FORM

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COOPERATOR Institute
REPORT NO. 9
DATE June 24, 1955
NOTE BOOK 1109
PAGE 98 TO 106
SIGNED M. N. May
M. N. May

cc: The Files
May
Peckham

USE OF AMMONIA IN THE CHLORINATION STAGE OF BLEACHING

In U. S. Patent 2,478,379 issued to Alfred M. Dodson, assigned to the Hercules Powder Company, it is claimed that the addition of relatively small amounts of ammonia, ammonium salts, or amines to the chlorination stage of bleaching reduces degradation of the cellulose. It is said that a quantity of ammonia equal to about 6% or less of the amount of chlorine used in the chlorination stage is adequate. It is the purpose of this study to explore the effectiveness of this treatment.

PROCEDURE

A sample of unbleached kraft southern pine pulp was selected for this study. A three-stage chlorination-caustic extraction-hypochlorite sequence was used. Two identical bleaches were made, with the exception that ammonia was used in the second bleach in the amount of 6% of the chlorine applied in the chlorination stage. The conditions used in both bleaches are summarized in Table I. In the case where ammonia was added to the chlorination stage, this was added before the chlorine was applied. The pulp and the ammonia were mixed together for 10 minutes before starting the addition of chlorine. In both instances, the chlorine was added as chlorine gas. The cuprammonium viscosity of the

original unbleached pulp, the two chlorinated and washed pulps, and the two final bleached pulps, was determined using TAPPI Method T 206 m-44. Beater evaluations of the unbleached pulps and the two final bleached pulps were also made using Institute Method 403. Handsheets were prepared at each beating interval and were tested for basis weight, apparent density, burst, tear, and Schopper tensile.

The bleaching sequences used in this study were selected to give a final brightness of approximately 80% G.E. The brightness values actually obtained are included in Table I with the bleaching conditions.

DISCUSSION OF RESULTS

The bleaching sequence in which ammonia was used in the chlorination stage gave a pulp with a brightness about 4 points lower than in the case where ammonia was not used in the chlorination stage. The sequence in which ammonia was used gave a pulp with higher viscosity, both after chlorination and washing, also after the final hypochlorite treatment. It is quite possible, however, that the higher viscosity ties in with the somewhat lower brightness obtained when the ammonia was used in chlorination.

The physical properties of the two bleached pulps are compared at a common freeness level of 500-cc. Schopper-Riegler in Table III. Table III shows that the pulp which was chlorinated in the presence of ammonia had somewhat better burst, tear, and tensile properties than the pulp which was chlorinated without ammonia. However, this may be in

part due to the lower brightness in the pulp treated with ammonia.

CONCLUSIONS

These results indicate that the use of ammonia in the chlorination stage in the amount of 6% of the chlorine applied has the following effects in a 3-stage bleach of a kraft southern pine pulp when all other conditions are held constant:

(1) Reduces brightness

(2) Increases pulp viscosity

(3) Increases burst, tear, and tensile

mnm/jh

TABLE I

BLEACHING CONDITIONS

Bleach	Bl-1[1]	Bl-2[2]
CHLORINATION		
Charge (ovendry basis), g.	1000	1000
Temperature, °C.	20	20
Consistency, %	3.0	3.0
Chlorine, %	4.1	4.1
Ammonia, %	—	0.246
Retention time of chlorine, min.	60	60
Resid. chlorine (basis of applied), %	27.7	26.54
Yield after 1st stage, %	96.5	98.0
Cuprammonium viscosity, cp.	12.79	15.10
NaOH EXTRACTION		
Charge (ovendry basis), g.	950	965
Temperature, °C.	40	40
Consistency, %	10.0	10.0
NaOH, %	1.5	1.5
Time, min.	60	60
Yield after 2nd stage, %	100.0	98.24
HYPOCHLORITE		
Charge (ovendry basis), g.	930	927
Chlorine, %	2.0	2.0
Consistency, %	5.0	5.0
Temperature, °C.	40	40
Time, min.	240	240
Initial pH	9.2	9.0
Final pH	7.9	7.75
Resid. chlorine (basis of applied), %	18.76	12.05
G.E. brightness, %	79.7	76.1
Yield after hypochlorite, %	99.68	99.76
Cuprammonium viscosity, cp.	7.76	10.40
Cumulative yield, %	96.19	96.1
Brightness after Fade-Ometer exposure, %		
1/2 hr.	67.5	62.9
1 hr.	65.1	61.8
2 hr.	65.3	61.4

[1]Bl-1: Bleach without ammonia
[2]Bl-2: Bleach with ammonia

TABLE II

PHYSICAL PROPERTIES

Pulp		Unbl.	Bl-1	Bl-1X (Dup.)	Av. Bl-1	Bl-2	Bl-2X (Dup.)	Av. Bl-2
Schopper-Riegler freeness, cc.	0[1]	880	880	880	880	880	875	880
	5	875	870	870	870	870	870	870
	15	840	795	780	785	820	810	815
	30	670	395	370	380	520	500	510
	50	305	155	155	155	195	200	200
Basis weight (25x40--500), lb.	0	46.1	45.4	47.1	46.2	47.2	45.1	46.2
	5	45.3	45.2	45.4	45.3	47.9	44.7	46.3
	15	44.9	42.0	44.5	43.2	45.0	45.0	45.0
	30	45.0	44.3	44.8	44.6	45.0	44.9	45.0
	50	47.0	--	—	--	45.3	45.7	45.5
Apparent density	0	9.0	10.3	10.7	10.5	10.7	10.0	10.4
	5	11.0	11.6	12.3	12.0	12.0	11.8	11.9
	15	12.5	13.1	13.1	13.1	13.2	13.2	13.2
	30	14.1	14.8	14.9	14.8	14.5	14.0	14.2
	50	15.2	--	—	--	16.2	16.3	16.2
Bursting strength, pt./100 lb.	0	34	52	55	54	49	42	46
	5	71	79	82	80	81	76	78
	15	99	97	96	96	97	100	98
	30	110	108	107	108	113	110	112
	50	118	—	--	--	116	113	114
Tear factor	0	3.23	2.71	2.57	2.64	3.09	3.02	3.06
	5	2.58	1.77	1.67	1.72	1.96	2.06	2.01
	15	1.96	1.29	1.37	1.33	1.58	1.62	1.60
	30	1.64	1.17	1.12	1.14	1.31	1.27	1.29
	50	1.34	—	--	—	0.88	0.94	0.91
Schopper tensile, lb./in.	0	11.6	12.8	13.7	13.2	13.3	10.6	12.0
	5	19.7	18.9	19.2	19.0	19.6	18.5	19.0
	15	24.6	22.7	24.9	23.8	24.7	24.4	24.6
	30	26.9	25.9	27.6	26.8	28.4	28.8	28.6
	50	31.4	—	—	--	31.2	27.6	29.4

[1] Beating time, min.

TABLE III

PHYSICAL PROPERTIES COMPARED AT A FREENESS OF 500-cc.
SCHOPPER-RIEGLER

Pulp	B1-1	B1-2
Bursting strength, pt./100 lb.	106	112
Tear factor	1.17	1.28
Schopper tensile, lb./in.	26.3	28.5

PROJECT REPORT FORM

PROJECT NO. 1102-3
COOPERATOR Institute
REPORT NO. Ten
DATE April 11, 1956
NOTE BOOK 1109
PAGE 119 TO 122
SIGNED John R. Peckham

cc: The Files
Dr. May
John Peckham

STUDY OF THE EFFECT OF THE PRESENCE OF FINES IN UNBEATEN AND BEATEN SULFITE PULP

The interest in this phenomenon was engendered by some tests undertaken in behalf of Charmin Tissue Mills under Project 1911. In this work we were presented with two pulps of different strength properties whose only notable physical difference as received was the greater amount of fines in the stronger pulp. However, when these two pulps were classified and recombined in fractions which agreed with those of the other pulp, an unexplained result occurred (see memo Project 1911 Peckham-Files March 14, 1956). The weaker pulp, when enriched with fines to the level found in the stronger pulp, increased in bursting and tensile strengths, although not to the level of the stronger pulp. The stronger pulp, when classified and recombined with a reduced quantity of fines to agree in composition with the weaker pulp, was a great deal stronger than it had been before the reduction of fines.

In this work, a sample of the weaker pulp (left over from Project 1911) was classified and each fraction was retained, including the "through 150-mesh" fraction. The classification results (a composite of 8 tests) agreed fairly well with previous tests (see Table I).

TABLE I
BAUER-McNETT CLASSIFICATION RESULTS

	Original Test	1102-3 test
On 14-mesh, %	38.7	30.9
Through 14, on 28-mesh, %	25.6	31.4
Through 28, on 48-mesh, %	9.1	9.9

	Original Test	1102-3 Test
Through 48, on 100-mesh, %	10.7	10.1
Through 100 mesh, %	15.9	17.7

The fractions of pulp retained on the various screens were recombined so that a pulp was on hand which was identical with the pulp "as received," except that the fines were not present. Handsheets were made from this pulp and tested in the usual manner. Strength properties of handsheets (120A in Table II) were similar to those found on handsheets made from the pulp with the fines present, with the exception of tear, which was higher.

A portion of pulp combined minus the fines fraction was beaten in the Jokro mill for 1 minute. Handsheets made from this pulp (120-B) showed sizeable increases in bursting and tensile strength. Some of the beaten pulp of 120-B was combined with the fines originally removed in a ratio of 85-15 and handsheets were formed (120-BX). At this level of refining there was a slight decrease in tearing strength when the fines were returned to the pulp, but bursting and tensile strengths were essentially unchanged.

Another aliquot of the fines-free pulp was beaten for 2.5 minutes in the Jokro mill and formed into handsheets without added fines (121-A) and with fines in 85-15 ratio (121-AX). The sheets of 121-A were high in bursting and tensile strength and low in tearing strength. The addition of fines in 121-AX reduced all physical properties with especial emphasis on bursting strength.

The same program was repeated with the fines-free pulp beaten for 5 minutes in the Jokro-mill (121-B) and with fines added to the beaten stock (122-A). The same adverse effect upon beaten pulp strength was evidenced with the addition of fines as had been previously experienced.

The results of these experiments supported the thesis (proposed in the previously cited memorandum) that presence of more fines in the stronger pulp was indicative of a refining action which had taken place but did not contribute to that strength. It is felt by the writer that this technique of refining and returning the fines to the beaten pulp is probably no more effective in increasing strength properties than would be beating the "as received" pulp to the same freeness level. It may be, however, that there would be more softness and water absorbency in paper made as described in these experiments.

jrp/jh

TABLE II

EFFECT OF THE PRESENCE OF FINES IN UNBEATEN AND BEATEN SULFITE PULP

Sample	As Rec'd.[1]	120-A	120-B	120-BX	121-A	121-AX	121-B	122-A
Canadian Standard freeness, cc.	710	725	725	685	690	640	635	570
Fines, %	15	None	None	15	None	15	None	15
Milling in Jokro mill, min.	None	None	1	1	2.5	2.5	5	5
Basis weight (25x40—500), lb.	45.2	45.1	45.8	44.7	45.3	45.4	45.2	45.8
Caliper, mils	3.7	3.7	3.5	3.4	3.3	3.3	3.1	3.3
Apparent density	12.2	12.2	13.1	13.1	13.7	13.8	14.6	13.9
Bursting strength, pt./100 lb.	43	45	55	54	71	63	85	76
Tear factor	1.11	1.29	1.16	1.05	0.99	0.90	0.91	0.79
Tensile strength, lb./in.	12.8	13.1	16.4	15.7	19.5	18.9	24.2	21.7

[1] Tested on 3/13/56

PROJECT REPORT FORM

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COOPERATOR I.P.C.
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SIGNED
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INFLUENCE OF AGING ON THE BLEACHING CHARACTERISTICS OF A CHLORINATED AND CAUSTIC EXTRACTED NORTHERN PINE KRAFT PULP

It has previously been found that storage or aging of certain chlorinated and caustic extracted pulps produced detrimental effects in subsequent hypochlorite bleaching treatments (Thesis work by Dr. Jappe). Specifically, these detrimental effects (excessive bleach demand, etc.) were noted with a semichemical pulp processing relatively high hemicellulose and lignin contents.

The present work was undertaken to determine if similar detrimental effects, due to aging, were generally noted with other types of pulp. In this work a northern pine kraft pulp was investigated and it was found that aging the chlorinated and caustic extracted pulp did not produce any detrimental bleaching effects in subsequent hypochlorite bleaching operations. Thus, detrimental bleaching effects are not necessarily incorporated when a caustic extracted pulp is allowed to age (in the dark at 40°F.) prior to hypochlorite bleaching treatment and the presence or absence of such effects is no doubt a function of the nature and type of pulp processed. In view of this situation, it was suggested that, when necessary, pulps required in project work be investigated to determine if an aging period would prove critical.

If aging proved critical, work schedules or control bleaches should be arranged and properly designed to compensate or eliminate these effects. Such approach to the problem would no doubt prove more beneficial and worth while than any further specific investigation concerning the effects of aging on randomly selected pulps.

RAW MATERIALS

The following raw materials were employed in the experimental bleaching study:

1. An unbleached northern pine kraft pulp obtained in wet bag form from the Thilmany mill. Permanganate number (25 ml. basis) = 17.8; pulp viscosity [Tappi Method T230 sm-50 (pipette)] = 24.7; G. E. brightness = 25.5 points.

2. Liquified chlorine gas (cylinder) for chlorination of the pulp.

3. A 50 g./l. solution of C.P. sodium hydroxide for caustic extraction of the chlorinated pulp and for pH control during the calcium hypochlorite bleaching processes.

4. A calcium hypochlorite bleach liquor prepared from high test hypochlorite. Approximate available chlorine concentration = 33 g./l.

EXPERIMENTAL

Method of Attack

A 1000 gram sample (ovendry basis) of unbleached northern pine kraft pulp was chlorinated and caustic extracted (see Tables I and II). The resulting caustic extracted pulp was then aged (in the dark at 40°F.) for various periods--0, 2, 4 and 10 days--and the effects of aging were determined by investigating the permanganate number, viscosity, and G. E. brightness properties of the pulp (see Table III). In addition, a series of calcium hypochlorite bleaches were performed at each aging period to determine the effects of aging on the hypochlorite bleaching characteristics of the pulp (see Table IV).

Calcium Hypochlorite Bleaching

At each aging period, the caustic extracted pulp was subjected to the following series of small scale calcium hypochlorite bleaches:

Bleach	Available Chlorine Applied With Hypochlorite Black Liquor, %	pH Control Point	Temperature, °C.	Pulp Consistency (Ovendry basis), %	Retention Time
A	1.8	8.5	35	12	1 hour
B	1.8	8.5	35	12	To exhaustion
C	1.4	8.5	35	12	1 hour
D	1.4	8.5	35	12	To exhaustion
E	1.0	8.5	35	12	1 hour
F	1.0	8.5	35	12	To exhaustion

In all of these bleaches, the following constant conditions were adhered to:

1. Pulp charge (ovendry basis) = 25 g.
2. Pulp consistency (ovendry pulp basis) = 12%.
3. Temperature = 35°C.
4. pH control point = 8.5 (the pH of the bleach was controlled by adding 0.2 ml. of a 50 g./l. sodium hydroxide solution whenever the pH dropped to 8.5).
5. Washing and sampling procedure for bleached pulp.
   a. At the end of the required retention period, the bleach was diluted to 4 liters with filtered tap water, stirred with a small Lightnin' mixer, and dewatered on a Büchner funnel.
   b. (a) above was repeated.
   c. (a) above was repeated.
   d. After the third dewatering step, 1/2 of the pad was removed and allowed to air dry for a pulp viscosity determination. The remainder of the pad was split into 2 portions and a G. E. brightness sheet was formed from each portion. (G. E. brightness sheets were formed by diluting the pulp with about 500 ml. of distilled water, stirring with a malted milk mixer, and forming on a Büchner funnel.)
   e. The G. E. brightness sheets were conditioned overnight at 50% R.H. and 73°F. before brightness readings were obtained.
   f. After the initial brightness of the sheets had been determined, the fading characteristics of the pulp were investigated by fading the sheets for one hour in an air circulating oven maintained at 105°C.

TABLE I

CHLORINATION OF NORTHERN PINE KRAFT PULPS

Date chlorination was performed	5-21-56
Pulp charge (ovendry basis), g.	1000
Pulp consistency (ovendry pulp basis), %	3.0
Temperature, °C.	19-21
pH of pulp slurry before addition of chlorine	8.4
Chlorine applied (based on weight of ovendry pulp charge), %	7.0
Time required for the addition of chlorine gas, min.	16
pH of pulp slurry after addition of chlorine	1.75
Retention time after addition of chlorine, min.	60
pH of pulp slurry after retention period	1.7
Chlorine consumed during retention period (based on weight of ovendry pulp), %	5.74

Following the retention period, the stock was dumped on a muslin-covered wash box, thoroughly washed with filtered tap water, and dewatered to a consistency of about 20%.

TABLE II

CAUSTIC EXTRACTION OF CHLORINATED NORTHERN PINE KRAFT PULP

Date caustic extraction was performed	5-21-56
Pulp charge (ovendry pulp basis), g.	1000 (assumed)
Pulp consistency (ovendry pulp basis), %	12
Sodium hydroxide[1] (based on weight of ovendry pulp), %	2
Temperature, °C.	40
Retention time, min.	60
Pulp yield after chlorination and caustic extraction treatments, %	94.4
Pulp viscosity[2] after the caustic extraction treatment, cp.	16.6
G. E. brightness of the pulp after the caustic extraction treatment, pt.	32.5

[1]The sodium hydroxide was applied as a 50 g./l. solution.
[2]TAPPI Method T230 sm - 50 (pipette).

Following the retention period, the stock was dumped on a muslin-covered wash box, thoroughly washed with filtered tap water, dewatered to a consistency of about 25%, placed in a pliofilm bag, and stored in the dark at 40°F. until required for subsequent hypochlorite bleaching experiments.

TABLE III

EFFECT OF AGING ON THE PROPERTIES OF A CHLORINATED AND CAUSTIC EXTRACTED NORTHERN PINE KRAFT PULP

Aging Period, days	Permanganate Number of Aged Pulp (25-ml. basis)	G. E. Brightness of Aged Pulp, pt.	Viscosity[1] of Aged Pulp, cp.
0	4.6	32.5	16.56
2	4.35	34.3	--
4	4.5	33.2	--
10	4.15	34.5	16.25
32	4.6	--	--
35	4.9	34.0	--

[1] TAPPI Method T230 sm 50 (pipette).

Note: The pulp was aged in the dark at 40°F. (pulp consistency = 26.5%).

TABLE IV

EFFECT OF AGING ON THE CALCIUM HYPOCHLORITE BLEACHING CHARACTERISTICS OF A CHLORINATED AND CAUSTIC EXTRACTED NORTHERN PINE KRAFT PULP

Bleach	Date Bleach Was Performed	Bleaching Conditions: Aging Period For Caustic Extracted Pulp[1] Days	Available Chlorine Applied (Based on Ovendry Pulp Charge), %	Available Chlorine Consumed (Based on Ovendry Pulp Charge), %	Sodium Hydroxide Required (Based For pH Control on Ovendry Pulp Charge), %	Retention Time, min.	Bleached Pulp Properties: G. E. Brightness of Bleached Pulp, %	G. E. Brightness of Bleached Pulp After One Hour Oven Fading, pt.	Viscosity[2] of Bleached Pulp, cp.
A	5-21-56	0	1.80	1.29	0.12	60	73.9	64.3	11.51
B	5-21-56	0	1.80	1.80	0.56	296	79.9	70.3	9.54
C	5-21-56	0	1.40	1.22	0.12	60	74.4	64.4	12.00
D	5-21-56	0	1.40	1.40	0.28	190	75.0	65.8	11.54
E	5-21-56	0	1.00	—	0.08	60	68.6	60.2	13.52
F	5-21-56	0	1.00	1.00	0.16	67	68.3	60.1	13.72
A	5-23-56	2	1.80	1.30	0.12	60	74.3	64.5	12.23
B	5-23-56	2	1.80	1.80	0.56	337	81.1	69.8	10.32
C	5-23-56	2	1.40	1.15	0.16	60	72.1	62.8	14.36
D	5-23-56	2	1.40	1.40	0.32	221	75.8	66.8	12.97
E	5-23-56	2	1.00	0.96	0.12	60	69.2	60.2	15.74
F	5-23-56	2	1.00	1.00	0.12	89	68.4	59.8	15.52
A	5-25-56	4	1.80	1.28	0.16	60	75.0	65.2	11.68
B	5-25-56	4	1.80	1.80	0.56	330	80.1	70.5	9.80
C	5-25-56	4	1.40	1.16	0.16	60	72.9	64.1	12.70
D	5-25-56	4	1.40	1.40	0.36	216	76.1	66.9	11.96
E	5-25-56	4	1.00	0.97	0.16	60	68.4	60.3	14.44
F	5-25-56	4	1.00	1.00	0.12	74	68.8	60.3	14.59
A	5-31-56	10	1.80	1.36	0.20	60	74.8	66.0	11.15
B	5-31-56	10	1.80	1.80	0.60	328	81.2	70.9	9.62
C	5-31-56	10	1.40	1.18	0.12	60	73.2	63.8	12.09
D	5-31-56	10	1.40	1.40	0.32	195	76.7	67.3	11.68
E	5-31-56	10	1.00	0.99	0.12	60	67.4	59.2	14.38
F	5-31-56	10	1.00	1.00	0.12	78	70.3	61.6	14.08

[1] The pulp was aged in the dark at 40°F. (pulp consistency = 26.5%).
[2] TAPPI Method T230 sm 50 (pipette).

Constant Bleaching Conditions:

Pulp charge (ovendry pulp basis), g. = 25
Pulp consistency (ovendry pulp basis), % = 12
Temperature, °C. = 35
pH control point = 8.5

RESULTS

The results of the experimental work have been summarized in Tables I through IV (see preceding section of report) and in Figures 1 through 5. A study of these results indicated the following:

1. Aging the chlorinated- and caustic-extracted pulp produced no consistent or marked effect on the permanganate number, G. E. brightness, or cupriethylenediamine viscosity properties of the pulp.

2. Aging the chlorinated- and caustic-extracted pulp apparently had little, if any, effect on the G. E. brightness characteristics of the pulp after hypochlorite bleaching treatment--i.e., aging produced no consistent or marked effect on the pulp brightnesses obtained after hypochlorite bleaching (Figure 1).

3. Aging the chlorinated and extracted pulps apparently had little, if any, effect on the oven fading characteristics of the pulp after hypochlorite bleaching treatments--i.e., aging produced no consistent or marked effect on the oven faded brightnesses obtained after hypochlorite bleaching (Figure 2).

4. Aging the chlorinated- and caustic-extracted pulp produced no consistent effect on the viscosity characteristics of the pulp after hypochlorite bleaching treatments. Actually, hypochlorite bleached pulps

prepared from chlorinated- and caustic-extracted pulps aged 0, 4 or 10 days exhibited essentially similar pulp viscosity properties. However, hypochlorite-bleached pulps prepared from chlorinated- and caustic-extracted pulp aged for 2 days apparently produced slightly higher pulp viscosity properties. Further work should perhaps be done to determine if this apparent increase in pulp viscosity was actually a real effect or if it was merely due to some unrealized experimental variable. The fact that the effect is not consistent with aging (i.e., the hypochlorite bleached pulp properties did not consistently increase or decrease as the aging period for the caustic-extracted pulp was increased) would strongly indicate that some unrealized experimental variable might be involved (Figure 3).

5. Aging the chlorinated- and caustic-extracted pulp produced no consistent or marked effect on the rate of available chlorine consumption during subsequent hypochlorite bleaching treatments (Figure 4).

6. Aging the chlorinated- and caustic-extracted pulp produced no consistent or marked effect on the quantity of sodium hydroxide required for pH control during subsequent hypochlorite bleaching treatments (Figure 5).

CONCLUSIONS AND DISCUSSION

Actually the preceding work was much too limited to allow a summation of any general or inclusive conclusions. It does appear, however, that detrimental bleaching effects are not necessarily incorporated when a caustic-extracted pulp is allowed to age (in the dark and at 40°F.) prior to hypochlorite bleaching treatments.

Thus, in certain bleaching work undertaken at the Institute, a work schedule involving brief periods of storage or aging for caustic-extracted pulps would be satisfactory. A prime consideration, however, would be the nature and type of pulp under investigation. It has been indicated, for example, (thesis work by Dr. Jappe) that the aging of caustic-extracted pulp having high hemicellulose and lignin contents produced marked effects on subsequent hypochlorite bleaching treatments. In view of these facts and the variety of pulps generally bleached at the Institute, it would be most difficult to assign a general guide which would indicate when an aging period for a caustic-extracted pulp would be critical. Additional work, similar to this study, could be undertaken with a large variety of pulps to attempt to formulate such guide; however, the work would necessarily be relatively extensive and perhaps quite involved. As an alternate to such attack, the following general considerations could perhaps be incorporated into all bleaching studies undertaken at the Institute.

1. There is a possibility that storage of caustic-extracted pulps would influence the results obtained in subsequent hypochlorite bleaching treatments. Also, the influence of the aging period would perhaps be more marked for pulps having high hemicellulose and lignin contents--i.e., semichemical pulps.

2. Whenever feasible, hypochlorite bleaching treatments should be conducted immediately after the caustic extraction stage.

3. If the design of bleaching experiments necessitates the storage of caustic-extracted pulp prior to hypochlorite treatments, a brief investigation could be conducted to determine the effects of this aging period on resulting hypochlorite bleaching characteristics. (This should be done especially if the pulp has a relatively high hemicellulose and lignin content.) Perhaps the fastest and simplest procedure for conducting such investigation would be essentially as follows:

a. Perform 2 small-scale (25-g. each) hypochlorite bleaches on the pulp immediately after the caustic extraction stage.

b. Use a different level of available chlorine application for each of the 2 bleaches and employ a retention time of one hour. Otherwise follow the bleaching, washing, sampling, and testing techniques described in the experimental section of this report (see constant conditions, page 3).

c. Repeat (a) and (b) above after the caustic-extracted pulp has been stored and aged.

d. If storage of the caustic extracted pulp proved critical, a different work schedule should be arranged or the bleaching program should be designed to compensate the effects of aging--i.e., a number of control bleaches might be conducted throughout the work for comparison purposes.

Actually the above experimental design could be fairly flexible, depending upon the nature of the particular bleaching project and the information desired.

It would appear that investigations based on the above considerations and conducted on pulps actually used in project work would prove more beneficial and worth while than a further specific investigation of the effects of aging on randomly selected pulps.

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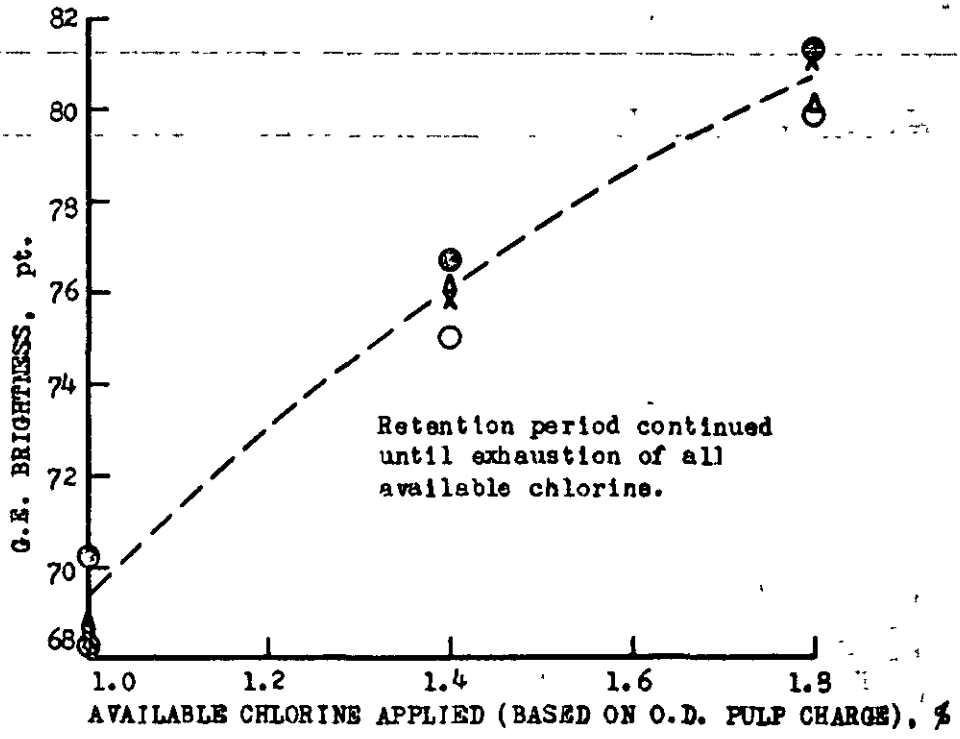
Figure 1

EFFECT OF AGING ON THE HYPOCHLORITE BLEACHING CHARACTERISTICS OF A CHLORINATED- AND CAUSTIC-EXTRACTED NORTHERN PINE KRAFT PULP



○ 0 days aging
× 2 days aging
△ 4 days aging
⊗ 10 days aging

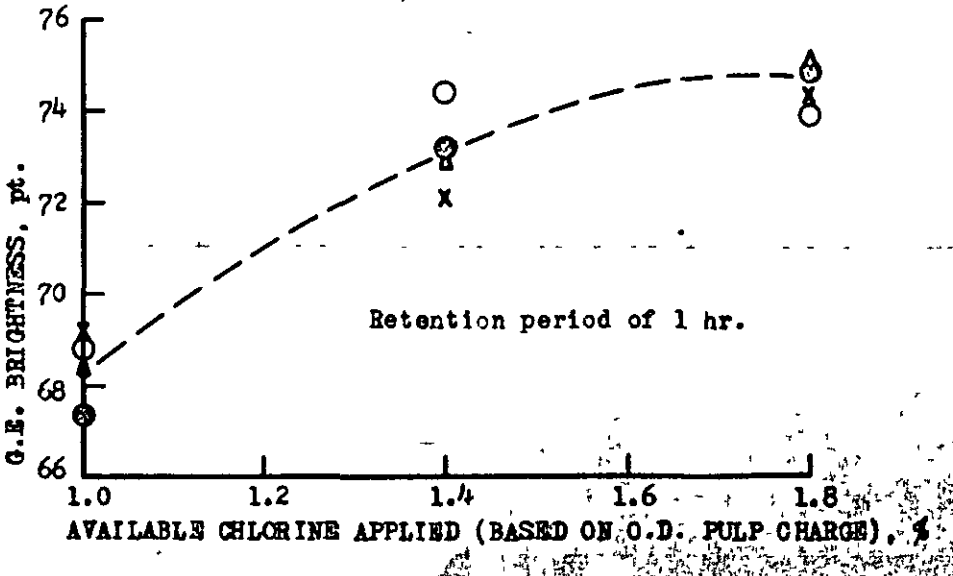
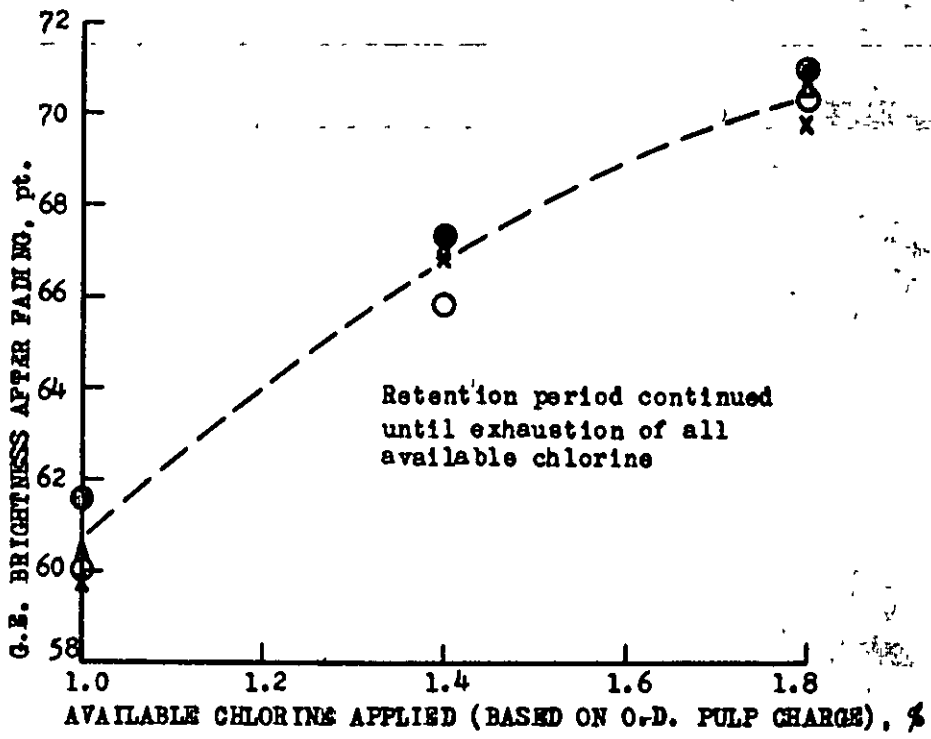


Figure 2

EFFECT OF AGING ON THE HYPOCHLORITE BLEACHING CHARACTERISTICS OF A CHLORINATED- AND CAUSTIC-EXTRACTED NORTHERN PINE KRAFT PULP



○ 0 days aging
x 2 days aging
Δ 4 days aging
● 10 days aging

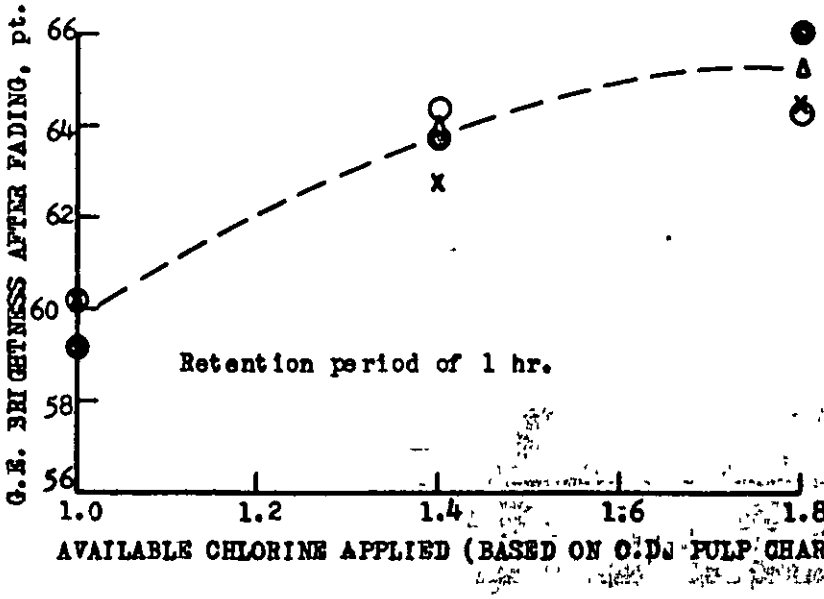
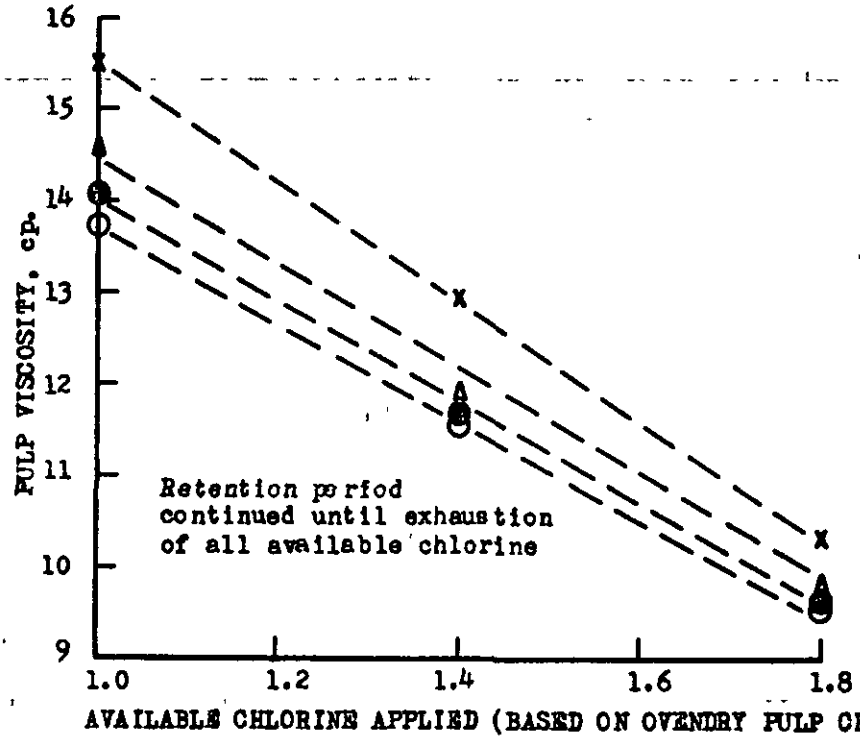


Figure 3

EFFECT OF AGING ON THE HYPOCHLORITE BLEACHING CHARACTERISTICS OF A CHLORINATED- AND CAUSTIC-EXTRACTED NORTHERN PINE KRAFT PULP



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X 2 days aging
Δ 4 days aging
● 10 days aging

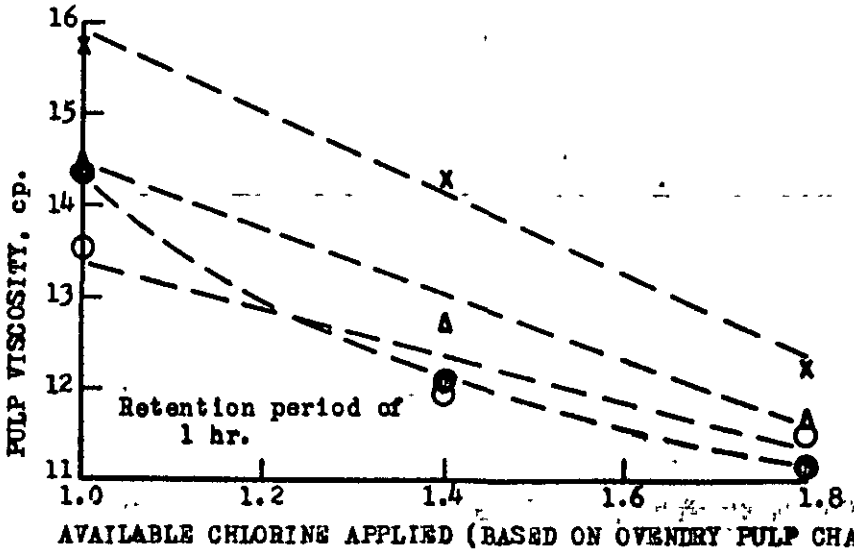
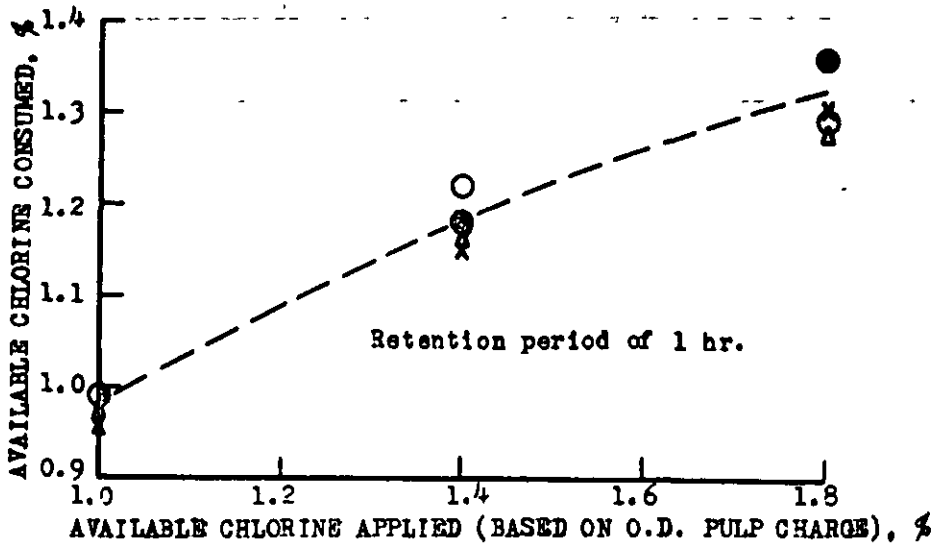


Figure 4

EFFECT OF AGING ON THE HYPOCHLORITE BLEACHING CHARACTERISTICS OF A CHLORINATED AND CAUSTIC-EXTRACTED NORTHERN PINE KRAFT PULP



○ 0 days aging
× 2 days aging
△ 4 days aging
● 10 days aging

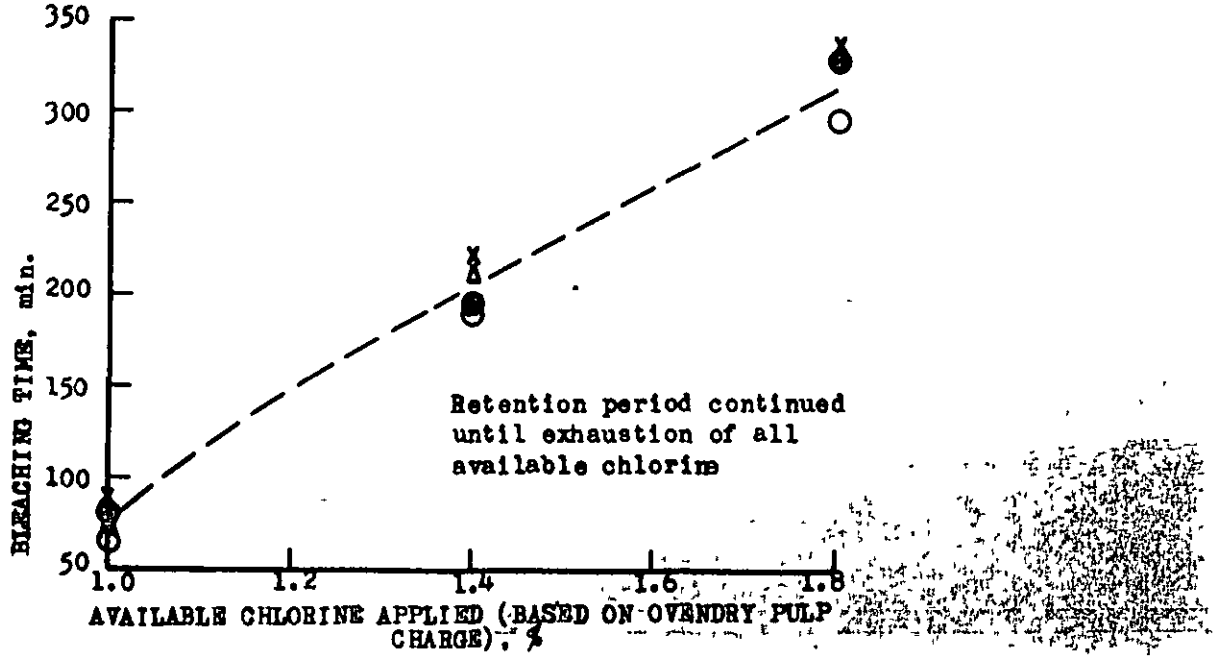
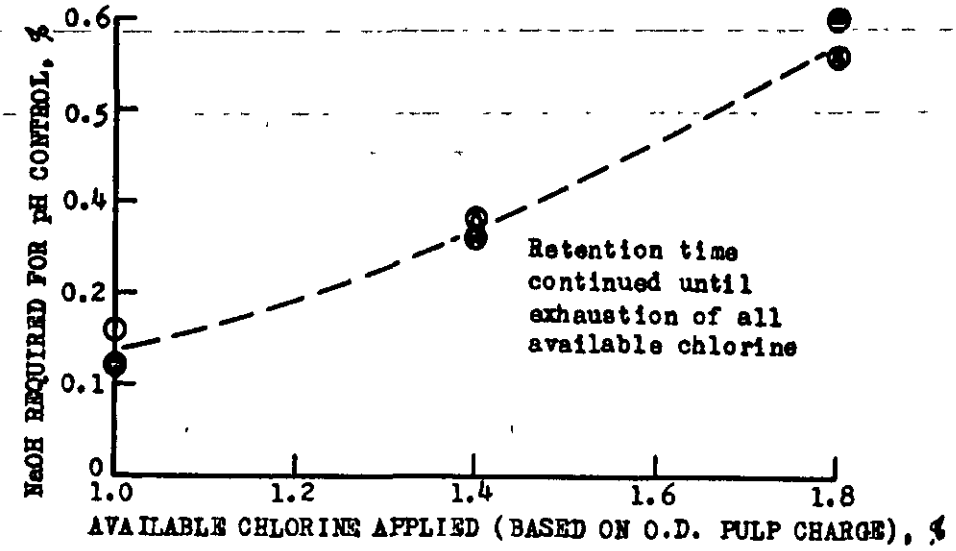
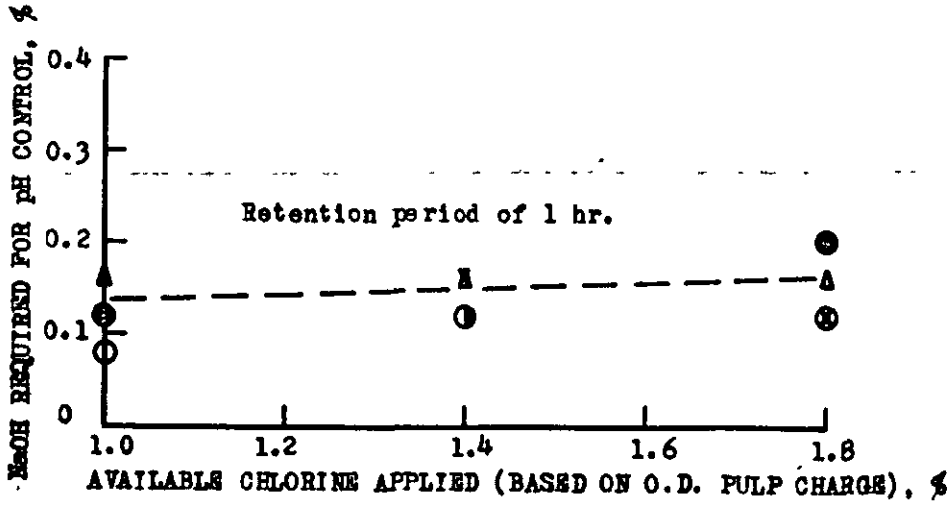


Figure 5

EFFECT OF AGING ON THE HYPOCHLORITE BLEACHING CHARACTERISTICS OF A CHLORINATED- AND CAUSTIC-EXTRACTED NORTHERN PINE KRAFT PULP



○ 0 days aging
X 2 days aging
Δ 4 days aging
● 10 days aging



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EFFECT OF TEMPERATURE ON SCHOPPER-RIEGLER FREENESS

INTRODUCTION

The freeness test is quite insensitive to changes in fiber character in the early stages of beating. For example, bursting and tensile strengths may easily triple or quadruple in value during the first ten minutes of beating, while the freeness shows as little as 10 or 15 cc. difference between the two samples. On the other hand, when beating has progressed to the intermediate stage, several hundred cc. change in freeness value may correspond to only a few points difference in sheet properties. Since it is known that reduction of temperature depresses the fluidity of a pulp-water suspension, it was thought that perhaps small changes in drainage characteristics could be detected at low water temperature which would not be recognizable at the usual level of 20°C. While investigating this point, handsheets were made at the various beating intervals so that some correlation between freeness and pulp properties could be made.

EXPERIMENTAL

The No. 3 one and one-half pound valley beater was used in this work. The design of the experiment was to accumulate sufficient pulp for the tests by the expedient of making two consecutive beater runs on bleached Weyerhaeuser sulfite pulp and combine the appropriate interval samples. From each composite sample sufficient pulp was removed to make duplicate freeness tests at three levels of water temperature. The remainder

of the pulp was used for handsheet preparation. The Schopper-Riegler 2-gram freeness test was used and handsheets were made and tested according to Institute methods 403 and 411. The data involved are shown in Table I.

DISCUSSION OF RESULTS

Measurement of freeness at temperature levels in the range of 6°C. did increase the latitude of freeness measured in the first 20 minutes of beating by 75%, but the majority of the variation was found in the last 10 minutes of that time. Measurements at higher temperature levels were, as expected, nearer the readings taken at 20°C.

While the basis for undertaking this work was the theory that freeness readings taken at very low temperatures might show greater variation than would be predicted by application of the temperature correction chart, this did not prove to be the case. Table II shows that corrections made in the usual manner would have brought the measurements made at low temperatures into good agreement with the values obtained at 20°C.

CONCLUSIONS

Measuring Schopper-Riegler freeness at temperatures as low as 6°C. did not make the test sufficiently more sensitive in the high freeness range to justify the use of this device.

jrp/ms

TABLE I

PHYSICAL PROPERTIES OF WEYERHAEUSER BLEACHED SULPHITE

		Temperature, °C. 6 - 9	13 - 14	17 - 18	19 - 20
Schopper-Riegler freeness, cc.	0[1]	870-880	875-875	880-880	880-880
	5	870-870	865-875	875-870	870-880
	10	855-855	865-865	860-870	860-870
	20	815-810	825-830	835-840	840-840
	35	690-690	715-710	720-730	715-730
	50	480-460	510-495	510-520	540-550
	65	285-285	315-330	340-350	360-360
Basis weight, (25 x 40/500), lb.	0	51.8			
	5	49.0			
	10	50.9			
	20	48.1			
	35	44.7			
	50	47.5			
	65	46.7			
Caliper, mils	0	5.2			
	5	4.5			
	10	4.3			
	20	3.8			
	35	3.2			
	50	3.2			
	65	3.0			
Apparent density	0	10.0			
	5	10.9			
	10	11.8			
	20	12.7			
	35	14.0			
	50	14.8			
	65	15.6			
Bursting strength, pt./100 lb.	0	9			
	5	20			
	10	34			
	20	61			
	35	87			
	50	101			
	65	101			
Tear factor	0	1.25			
	5	2.02			
	10	2.20			
	20	1.35			
	35	1.01			
	50	0.86			
	65	0.79			
Tensile strength, lb./in.	0	4.1			
	5	8.0			
	10	11.7			
	20	17.2			
	35	22.8			
	50	27.0			
	65	28.4			

[1] Beating time min.

TABLE II

SCHOPPER-RIEGLER FREENESSES

Interval, Min.	Reading at 20°C.	Reading at 6°C.	Corrected Reading at 6°C.	Reading at 13°C.	Corrected Reading at 13°C.
0	880	375	890	875	880
5	875	870	885	870	880
10	865	855	870	865	875
20	840	810	830	825	835
35	720	690	720	710	725
50	545	470	530	500	530
65	360	285	335	320	350

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STUDY OF THE EFFECTS PRODUCED BY DRYING AN UNBLEACHED KRAFT PULP PRIOR TO A SINGLE-STAGE HYPOCHLORITE BLEACHING TREATMENT

A brief series of experimental investigations were conducted to determine the effects of air drying and oven drying on the bleaching characteristics of a kraft pulp. On the basis of this relatively limited exploratory work, it would appear that drying the kraft pulp prior to bleaching produced no adverse effects on the bleaching characteristics of the stock--i.e., the G.E. brightness, oven fade stability, bleaching time, and chemical demand characteristics actually tended to show improvement. Drying, however, adversely affected the bursting and tensile strength properties of the pulp both before and after bleaching.

RAW MATERIALS

The materials employed in this exploratory study consisted of:

(1) A Canadian Jackpine kraft pulp (Thilmany). Ovendry content = 41%; permanganate number (25-ml. basis) = 14.8; G.E. brightness = 26.7%.

(2) Calcium hypochlorite bleach liquor prepared from granular high-test hypochlorite (approximate available chlorine content = 35 g./l.).

(3) Solution of C.P. sodium hydroxide for pH control (concentration = 50 g./l.).

The pulp, obtained in a wet lap form, was fluffed in the laboratory pulp breaker, placed in pliofilm bags, and stored in the dark at 40°F. until it was required for the bleaching studies. Subsequent evaluation of this stock in the 1.5-lb. Valley beater indicated the strength characteristics presented in Table I.

EXPERIMENTAL ATTACK
(See Appendix for Detailed Experimental Procedures)

A series of five small-scale calcium hypochlorite bleaches, employing 0, 3, 5, 7, and 9% available chlorine, were conducted on a sample of the undried (59% moisture) Thilmany kraft pulp, a sample of air dried (6% moisture) Thilmany kraft pulp, and a sample of oven-dried (10 hr. at 105°C., 2% moisture) Thilmany kraft pulp.

The bleaching characteristics of the various unbleached pulps were subsequently evaluated by determining the G.E. brightness levels attained at various available chlorine consumptions, the quantity of sodium hydroxide required for pH control during the bleaching treatments, the time required for the bleaching treatments, and the yield and oven fade characteristics of the bleached pulps. In addition, the strength characteristics of the various bleached and unbleached stocks were evaluated by determining the Schopper-Riegler freeness and handsheet shrinkage properties of the pulps and the basis weight, caliper, apparent density, bursting strength, tearing strength, tensile strength, and zero-span tensile strength properties of handsheets prepared from the pulps.

RESULTS

The results of the investigations concerning the drying of a kraft pulp prior to a hypochlorite bleaching treatment have been summarized in Table II and Figures 1 and 2. A study of these results indicates that:

(1) Drying, particularly oven drying, increased the G.E. brightness of the unbleached pulp. It should be noted, however, that the pulp was dried in crumb form and thus, the observed increase in brightness may have been a combined effect of drying and subsequent washing during the formation of brightness sheets.

(2) Drying the pulp did not adversely affect the G.E. brightness levels attainable with a given consumption of available chlorine and the dried pulps actually appeared to respond slightly better to hypochlorite bleaching than the undried pulp (see Figure 1).

(3) Air drying the unbleached pulp prior to bleaching produced essentially no effect on the oven fading characteristics of the bleached pulps. Oven drying the pulp prior to bleaching, however, produced bleached pulps which had improved stability to oven fading (see Figure 2).

(4) Drying--particularly oven drying--decreased the bleaching time required to bleach the pulp to a given brightness level. Also, the predrying operations tended to slightly reduce the quantity of caustic required during the bleaching treatment.

TABLE I

BEATER EVALUATION OF THE KRAFT PULP EMPLOYED IN THE BLEACHING STUDIES
(Evaluation performed with the student beater)

ating ime, in.	Schopper-Riegler Freeness, ml.	Handsheet Shrinkage, %[2]	Basis Weight (25x40--500), lb.	Caliper, mils	Apparent Density	Bursting Strength, pt./100 lb.	Tear Factor	Tensile Strength, lb./in./100 lb.	Zero-Span Tensile Strength, lb./in./100 lb.
0[1]	870	2.58	47.8	4.3	11.1	66.5	2.18	42.2	113
5	865	2.81	47.2	3.9	12.1	96.6	1.46	60.2	116
15	840	3.37	47.2	3.5	13.5	134	1.21	70.4	124
30	750	4.82	46.7	3.2	14.6	152	0.99	82.4	133
50	490	6.20	47.0	3.1	15.2	159	0.94	85.3	127
70	255	8.89	47.4	2.9	16.3	144	0.91	87.3	130

[1] A 360-g. (ovendry basis) charge of pulp was beaten at a consistency of 1.57% with a 6.5 kg. bedplate loading and 900 ml. slurry samples were removed at each beating interval.

[2] Handsheet shrinkage determinations were made according to Institute Method 406. In the present work, however, the handsheets were pressed for 5 minutes at 50 p.s.i. before the oven-dried shrinkage perimeter was measured.

TABLE II

RESULTS OBTAINED BY DRYING A KRAFT PULP PRIOR TO A HYPOCHLORITE BLEACHING TREATMENT

Condition of Unbleached Pulp Prior to Bleaching Treatment	Hypo. Bleach Liq. Avail. Chlorine (Based on OD Pulp Charge), % Applied	Consumed	G.E. Brightness, %	G.E. Brightness After Oven Fading,[1] %	Sodium Hydrox. Req'd. for pH Control, %[2]	Bleach. Time, min.	Bleached Pulp Yield, %	Schopper-Riegler Freeness, ml.	Handsheet Shrinkage, %	Basis Wt. (25x40-500), lb.	Caliper, mils	Appar. Dens.	Burst. Strength, pt./100 lb.	Tear Fact.	Tensile Strength, lb./in./100 lb.	Zero-Zpan Tensile Strength, lb./in./100 lb.
Undried (59% moisture content)	0	0	26.7	--	--	--	--	870	2.91	45.5	4.0	11.4	65.5	2.11	40.4	88.8
	3	3	36.4	34.5	0.2	42	97	870	3.09	46.9	4.1	11.4	71.4	1.94	40.2	87.6
	5	5	51.0	46.9	0.8	58	101	860	3.23	47.3	4.1	11.5	72.1	1.90	42.7	83.1
	7	7	65.8	58.4	1.6	133	98	860	3.49	46.0	3.9	11.8	65.2	1.57	41.8	77.4
	9	9	74.4	66.6	2.3	240	98	870	3.81	45.4	3.9	11.6	62.1	1.17	40.9	64.5
Air dried (6% moisture content)	0	0	27.3	27.6	--	--	--	870	2.65	46.2	5.0	9.2	31.2	2.71	23.1	83.5
	3	3	37.6	35.8	0.1	20	97	875	2.83	45.8	4.5	10.2	43.9	2.88	28.7	83.8
	5	5	53.5	48.4	0.7	41	102	875	3.00	46.1	4.3	10.7	48.8	2.45	30.0	81.6
	7	7	66.1	59.8	1.3	132	97	865	3.09	46.0	4.4	10.5	42.2	2.13	29.8	64.8
	9	9	75.3	67.1	2.0	201	100	870	3.32	46.2	4.3	10.7	47.2	1.47	30.0	61.7
Ovendried 10 hr. at 105°C. (2% moisture content)	0	0	28.2	28.3	--	--	--	880	2.30	47.0	5.2	9.0	19.6	2.17	16.2	99.4
	3	3	38.1	36.8	0.3	20	98	875	2.41	47.3	5.0	9.5	26.2	2.60	20.0	107.0
	5	5	52.5	49.0	0.3	35	98	865	2.37	44.4	4.5	9.9	30.2	2.73	22.9	99.5
	7	7	67.1	61.8	1.4	86	96	870	2.76	44.9	4.5	10.0	34.3	2.49	24.4	90.9
	9	9	74.6	68.4	2.1	177	97	875	3.02	45.1	4.2	10.7	35.5	1.75	26.7	83.4

[1]The G.E. brightness sheets were faded for 1 hour in an air-circulating oven maintained at 105°C.

[2]ovendry pulp basis

Figure 1

Effect of Drying on the Bleaching Properties of the Pulp

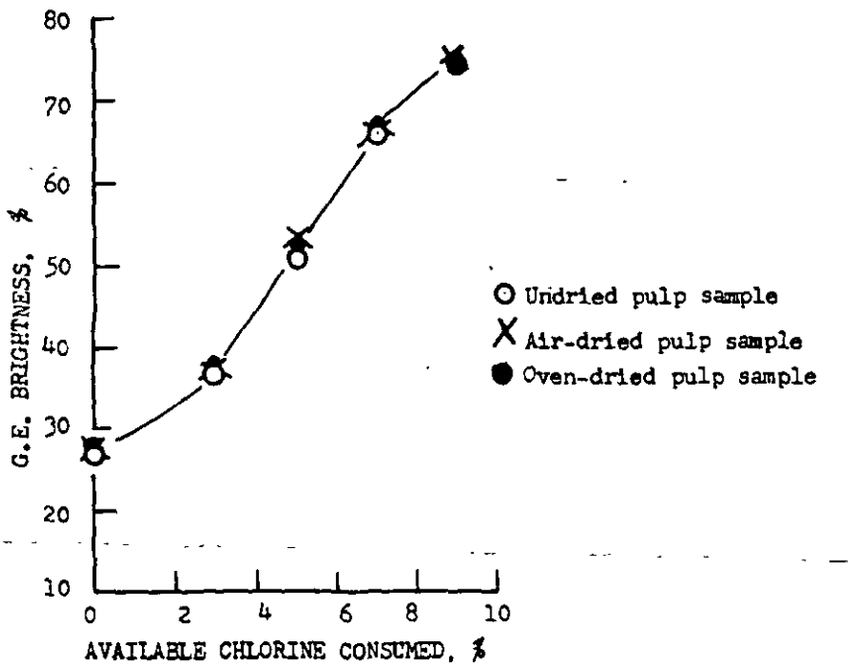
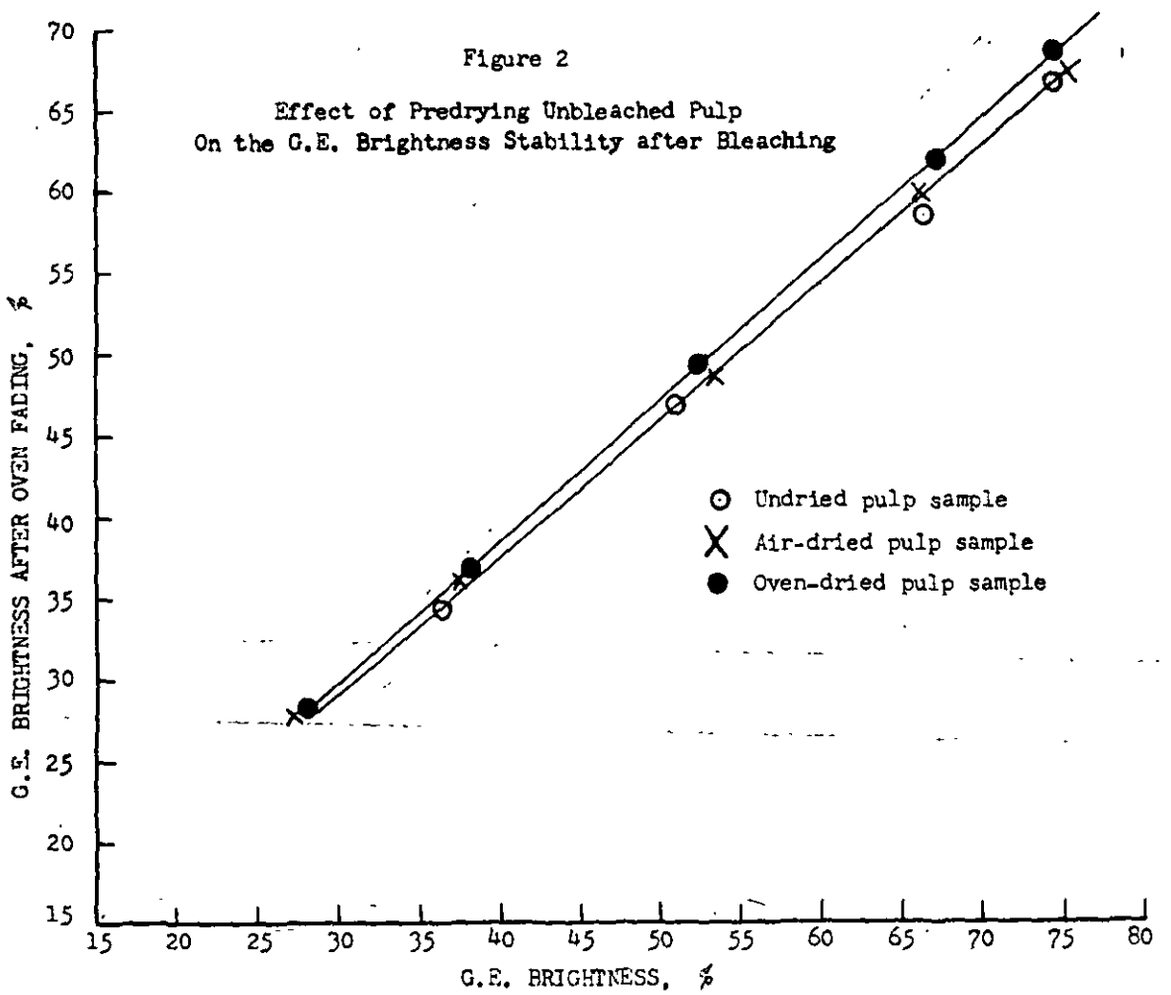


Figure 2

Effect of Predrying Unbleached Pulp
On the G.E. Brightness Stability after Bleaching



(5) The drying operations did not greatly affect the freeness properties of the unbleached and bleached pulps. The air-drying pretreatment, however, tended to slightly reduce the zero-span tensile strength of the pulps and the oven drying pretreatment apparently improved the zero-span tensile strength properties of the pulps.

(6) In general, the drying operations produced unbleached and bleached pulps possessing higher tearing strength characteristics and lower handsheet shrinkage, apparent density, tensile strength, and bursting strength properties.

CONCLUSIONS AND DISCUSSION

The over-all effect of drying a pulp prior to bleaching was detrimental because it lowered the tensile and bursting strength of both the unbleached and the bleached pulps. Apparently, however, the drying operations produced no adverse effects on the bleaching characteristics of the stock--i.e., the G.E. brightness, oven fade stability, bleaching time, and chemical demand characteristics actually tended to show improvement as a result of drying.

In view of this situation, an investigation of the causes for the improved bleaching characteristics of an oven-dried pulp might prove profitable. Conceivably these improved characteristics (higher G.E. brightness, better oven fade stability, and shorter bleaching periods) may be the result of the surface migration of certain pulp constituents during the drying operation. If this in fact were the case, it may be possible to produce the same effect by means other than drying, and thus

simultaneously improve the bleaching characteristics and preserve the strength properties of the stock.

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APPENDIX
DETAILED EXPERIMENTAL PROCEDURES

I. EXPERIMENTAL PROCEDURE FOR CONDUCTING SMALL-SCALE BLEACHES

(1) Constant conditions:

(a) Pulp charge (ovendry basis) = 45 g.

(b) Pulp consistency (ovendry pulp basis) = 12%

(c) Temperature = 35°C.

(d) pH control point = 8.5

(e) NaOH addition (50 g./l.) prior to start of bleach = 1.0 ml.

(2) Bleaching procedure (use double plastic bags for pulp containers)

(a) During the course of the bleach, allow the pH to drop to 8.5 and then add 1.0 ml. of 50 g./l. NaOH. Repeat as necessary.

(b) Allow bleach to proceed to exhaustion or a maximum of 4 hr.

(c) Record bleaching time, NaOH addition required, and residual available chlorine.

(3) Washing and sampling procedure at end of bleach.

(a) At the end of the bleaching treatment, dilute the charge to about 14.5 liters with filtered tap water.

(b) Determine the weight of the slurry, the consistency of the slurry, and calculate the yield of the bleached pulp.

(c) Dewater the slurry on a filter paper, dilute the dewatered pulp to about 14 liters with filtered tap water, and determine consistency of the stock.

(d) Remove two 2-gram (ovendry basis) samples and perform duplicate Schopper-Riegler freeness determinations.

(e) Remove a 5-gram (ovendry basis) sample and dewater on a filter paper. Split the dewatered stock into two equal portions, dilute each to about 500-ml. with distilled water and from 2 G.E. brightness sheets.

(f) Remove a 15-gram (ovendry basis) sample, dilute to about 10 liters and form 5 TAPPI standard handsheets for strength testing and 3 handsheets for handsheet shrinkage measurements.

(g) Perform the shrinkage tests according to Institute Method 406, but press the sheets between blotters for 5 minutes at 50 p.s.i. before measuring the oven-dried shrinkage perimeter.

(h) Test the 5 standard TAPPI handsheets for basis weight (25x40--500), caliper, apparent density, bursting strength, tearing strength, tensile strength, and zero-span tensile strength.

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