

#1915 THE INSTITUTE OF PAPER CHEMISTRY
(Thiosulfate In Neutral Sulfite
Semichemical Pulping) Reports (1) -

PROJECT REPORT FORM

cc: The Files
Dr. May
Dr. Whitney
Mr. Peckham
Dr. Stone
Mr. Voelker

✓ Project 1915
Co-operator Institute
Report No. 1
Date May 2, 1956
Notebook 1471
Page 7 to 49
Signed John R. Peckham
John R. Peckham

STUDY OF THE EFFECT OF THE PRESENCE OF SODIUM THIOSULFATE
IN NEUTRAL SODIUM SULFITE SEMICHEMICAL PULPING

OBJECTIVE

The project was initiated in an attempt to clarify the role, if any, played by sodium thiosulfate when it is present in varying amounts, in the cooking liquor used in neutral sodium sulfite semichemical pulping.

RAW MATERIALS

A supply of aspenwood obtained for use in Project 1849 was reserved for this investigation. The bolts were unpeeled and had been stored at the Institute in an outdoor, covered storage area for about 7 months. Chemicals used were reagent-grade sodium sulfite (Na_2SO_3), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$), and sodium bicarbonate (NaHCO_3).

METHOD OF ATTACK

It was proposed that several digester charges of aspenwood be pulped under conditions approximating those used in commercial practice, keeping all variables constant except the amounts of sodium thiosulfate dissolved in the cooking liquor. The resulting pulps were to be evaluated for yield, strength, and bleaching chemical requirement.

EXPERIMENTAL

The aspen bolts were peeled by hand, then passed through a 36" Carthage chipper set to deliver chips nominally 3/4" long. Large knots and slivers were removed manually and the remaining chips were screened on a 4-mesh screen, with the through fraction being discarded. The accepted chips were thoroughly mixed, then divided into digester charges of equal weight. Representative chip samples removed at this time were weighed, oven dried at $105 \pm 5^{\circ}\text{C}.$, and reweighed. The oven-dry content of the several digester charges was calculated from these data. The chips, stored in kraft-glassine multiwall bags, were kept in a room maintained at $5^{\circ}\text{C}.$ until used.

Pulping was carried out in a stainless steel digester of 44-liter capacity which is equipped for forced circulation and indirect heating. To facilitate the removal of the cooked chips from the digester, a removable liner which conforms closely to the interior contours of the vessel was used. The liner, containing the chips, was removed at the end of the cooking cycle and the hot chips were immediately processed in a 36" Bauer refiner fitted with B-957 plates maintained at a clearance of 0.005". Maximum feed rate was used, and consistency was estimated to be about 8% out of the refiner.

The defibered pulps were washed in a 60-gallon tank fitted with a perforated false bottom. Three changes of water were used, the pulp was stirred with a Patterson Uni-power stirrer for 10 minutes before the first drain, 5 minutes before the second, and allowed to stand overnight in the third dilution water. All effluent from the tank passed through a muslin-

covered wash box and fines recovered were returned to the pulp mass. After the last wash the pulp was thickened in a laundry centrifuge with the first effluent passed through the pulp cake a second time to retain fines. The dewatered pulp was broken into small crumbs, weighed, and the moisture content was determined. The yield of moisture-free pulp based on original moisture-free wood was calculated.

The pulps were screened on a small Valley flat screen fitted with 0.010" slotted plates. The rejects were oven dried, weighed, and discarded. The accepted portion was caught on a muslin-covered wash box where it was partially thickened before being transferred to the laundry centrifuge. The yield of screened pulp was calculated as described previously for the unscreened pulp.

The data obtained in pulping are shown in Table I. Cook 1 was made under conditions used previously in the pulping laboratory to produce a bleachable grade of neutral sulfite pulp from aspen. No $\text{Na}_2\text{S}_2\text{O}_3$ was included among the chemicals. The yield of pulp was 74.4%. In Cook 2, several conditions were changed to improve the pulp quality. The chemical charge was the same as in Cook 1, but the water ratio was increased from 3.96:1 to 4.95:1. Maximum temperature was raised to 176 instead of 165°C. and the time at temperature was increased to 180 min. The yield of pulp was 68.5%.

Cook 3 was made exactly like Cook 2 except that sodium thiosulfate, to the extent of 20% of the weight of the sodium sulfite, was added to the

TABLE I

PULPING CONDITIONS AND PRODUCT VARIABLES

	1	2	3	4	5
Cook					
Na ₂ S ₂ O ₃ content (basis Na ₂ SO ₃), %	0	0	28	40	60
Wood moisture (ovendry), %	29.2	29.0	29.1	29.1	29.0
Sodium sulfite (as Na ₂ SO ₃), %	17.83	17.83	17.83	17.83	17.83
Sodium thiosulfate (as Na ₂ S ₂ O ₃), %	0	0	3.57	7.13	10.7
Sodium bicarbonate (as NaHCO ₃), %	4.46	4.46	4.46	4.46	4.46
Water ratio (O.D. basis), cc./g.	3.96	4.95	4.95	4.95	4.95
Maximum temperature, °C.	165	176	176	176	176
Time to 125°C., min.	30	30	30	30	30
Time at 125°C., min.	60	60	60	60	60
Time, 125°C.-max. temp., min.	30	30	30	30	30
Time at max. temp., min.	150	180	180	180	180
Max. pressure, p.s.i.g.	136	117	117	117	117
Black liquor pH	—	7.5	7.65	7.9	7.95
Bauer conditions:					
Plates	B-957	B-957	B-957	B-957	B-957
Plate clearance, in.	0.005	0.005	0.005	0.005	0.005
Feed rate	7	7	7	7	7
Consistency (approx.)(ovendry), %	8	8	8	8	8
Load, amps	480	320	340	350	350
Yield (unscreened, ovendry basis), %	74.43	68.53	66.70	67.36	67.63
White liquor analysis:					
pH	—	8.60	8.35	8.4	8.4
Na ₂ SO ₃ , g./l.	—	38.4	38.0	37.90	37.80
Na ₂ S ₂ O ₃ , g./l.	—	—	7.75	15.63	23.07
NaHSO ₃ , g./l.	—	—	0.31	0.31	0.31
Na ₂ CO ₃ , g./l.	—	0.1	0.53	0.64	0.64
NaHCO ₃ , g./l.	—	8.3	9.32	9.23	8.64

cooking liquor. The yield of pulp was 66.7%.

Cooks 4 and 5 were made in the same manner as Cooks 2 and 3 except that the sodium thiosulfate content was increased to 40% of the sodium sulfite content in the case of Cook 4 and to 60% in Cook 5. The pulp yields were 67.4 and 67.6%, respectively.

The unbleached pulps of Cooks 2 through 5 were evaluated by forming and testing corrugating medium handsheets. The pulp was charged to a 1.5-lb. Valley beater and the clearance between roll and bedplate was reduced to zero by means of a fixed clearance device. When the freeness reached 450 cc. Canadian the pulp was made into handsheets on the 10 by 12-inch mold. Nominal sheet weight was 8.35 g. (ovendry basis). The sheets were pressed for 5 minutes at 50 p.s.i. and dried on a steam-heated dryer. The results of physical tests made on the handsheets are shown in Table II. Samples of the handsheets are included in the appendix of this report.

The unbleached pulps were also tested by making beater evaluations according to Institute Methods 403 and 411. The data concerning these tests are shown in Table III.

The pulps of Cooks 2 through 5 were bleached using a 3-stage process, as shown in Table IV. Bleaches 1 and 2 were carried out through the second stage and discarded when it became evident the pulps had been over-chlorinated. In Bleach 3, the pulp of Cook 2 was treated with 8% chlorine, extracted with 3% sodium hydroxide, and bleached to 80.1% G.E. brightness with sodium hypochlorite. Bleaches 4-6 were made in the same manner, the only deviation being

TABLE II
PHYSICAL PROPERTIES OF UNBLEACHED PULPS
CORRUGATING MEDIUM HANDSHEETS

Cook	2	3	4	5
Na ₂ S ₂ O ₃ content (basis Na ₂ S used), %	0	20	40	60
Basis weight, lb./1000 sq.ft.	25.7	26.5	26.2	27.7
Caliper, pt.	7.2	7.6	7.5	8.1
Apparent density	3.6	3.5	3.5	3.4
Single-flute flat-crush, lb./sq.in.	37.3	39.3	40.7	43.6
Single-flute flat-crush (basis 26-lb. sheet), lb./in.	37.7	38.6	40.4	41.0

TABLE III

STRENGTH PROPERTIES
Unbleached Poplar Neutral Sulfite Semichemical Pulp

Cook		2	3	4	5
		0	30	40	50
Na ₂ S ₂ O ₃ content, %	0 ¹	855	840	840	815
	5	820	810	820	785
Schopper-Riegler freeness, cc.	10	765	750	780	760
	20	595	580	680	680
	30	360	375	495	480
	40	170	195	250	295
Basis weight (25x40—500), lb.	0	46.8	44.9	46.4	46.2
	5	46.8	46.4	48.0	46.5
	10	50.6	46.2	47.0	46.4
	20	46.6	46.5	46.3	46.3
	30	46.9	46.0	47.8	46.2
	40	—	—	47.0	47.3
Apparent density	0	11.7	12.1	12.5	12.2
	5	12.6	13.3	13.0	12.9
	10	13.7	13.6	13.8	13.6
	20	15.0	15.5	14.5	14.5
	30	16.2	16.4	15.4	15.4
	40	—	—	16.2	16.9
Bursting strength, pt./100 lb.	0	49	56	56	61
	5	70	75	76	79
	10	83	84	85	94
	20	103	105	100	105
	30	113	110	106	110
	40	—	—	104	118
Tear factor	0	0.85	0.85	0.96	0.84
	5	0.83	0.84	0.85	0.84
	10	0.81	0.80	0.77	0.80
	20	0.69	0.67	0.73	0.71
	30	0.58	0.59	0.67	0.63
	40	—	—	0.55	0.53
Tensile strength, lb./in.	0	16.8	18.4	19.4	20.5
	5	22.8	24.8	24.8	25.3
	10	29.3	27.1	27.0	28.2
	20	30.2	32.3	31.4	32.7
	30	32.0	34.2	34.9	34.6
	40	—	—	34.8	37.3
¹ Beating time, min.					

(continued)

TABLE III CONTINUED

Cook		2	3	4	5
M.I.T. fold	0 ¹	13	28	29	29
	5	50	88	75	99
	10	196	217	112	155
	20	471	723	352	404
	30	1094	1350	982	470
	40	--	--	1230	833

¹ Beating time, min.

TABLE IV

BLEACHING CONDITIONS AND PRODUCT VARIABLES

Bleach	1	2	3	4	5	6
Cook	2	3	2	3	4	5
Sodium thiosulfate, %	0	20	0	20	40	60
<u>Chlorination Stage</u>						
Pulp charge (ovendry), g.	1000	1000	750	750	750	750
Consistency (ovendry), %	3.0	3.0	3.0	3.0	3.0	3.0
Temperature, °C.	20	20	20	20	20	20
Time, min.	45	50	30	40	45	45
Chlorine, %	10.0	10.0	8.0	8.0	8.0	8.0
Resid. chlorine (basis applied), %	--	--	--	--	--	--
<u>Caustic Extraction Stage</u>						
Pulp charge (ovendry)(assumed), g.	1000	1000	750	750	750	750
Consistency (ovendry), %	10.0	10.0	10.0	10.0	10.0	10.0
Temperature, °C.	50	50	50	50	50	50
Time, min.	60	60	60	60	60	60
NaOH, %	3.0	3.0	3.0	3.0	3.0	3.0
Yield, after chlorination and extraction, %	86.8	87.2	88.4	88.4	89.6	89.2
<u>Hypochlorite Stage</u>						
Pulp charge (ovendry), g.	--	--	576	580	588	580
Consistency (ovendry), %	--	--	10.0	10.0	10.0	10.0
Temperature, °C.	--	--	38	38	38	38
Time, min.	--	--	132	125	170	195
Chlorine, %	--	--	2.05	1.55	2.10	1.63
Residual Cl ₂ , %	--	--	--	--	--	--
Yield after chlorination, extraction, hypochlorite, %	--	--	86.7	87.2	87.8	86.3
Brightness, %	--	--	80.1	80.5	81.3	83.0
Total Cl ₂ used, %	--	--	10.05	9.55	10.10	9.63

in the amount of chlorine in the last stage.

The bleached pulps were beater evaluated following the procedures used for the unbleached pulps. The data are shown in Table V.

DISCUSSION OF RESULTS

The pulping data in Table I gave no indication of cooking differences induced by the inclusion of sodium thiosulfate in the chemical charge of the neutral sulfite digestions. Since the yields of pulp from Cooks 3-5 were less than that of Cook 2, it is indicated that the thiosulfate does not inhibit the action of the more active chemicals. The power requirements to defiber the four acceptable cooks were sufficiently similar to be within experimental error.

The unbleached pulp quality as indicated by the flat-crush tests on corrugated medium handsheets (Table II) was not adversely affected by the inclusion of thiosulfate. Indeed, in this case, a fairly uniform rate of increase in crush resistance was noted as the thiosulfate content was raised. Since there were variations in handsheet weight, the crush data was recalculated on the basis of a 26 lb./1000 sq.ft. sheet, as shown in the table. The differences in crush resistance were still evident. Inspection of the handsheets made from the unbleached pulps shows that those containing thiosulfate had a yellowish cast as compared to those made from pulp in which no thiosulfate was included. The sheets containing 60% of the chemical did not appear to differ materially from those containing 20%, however.

Strength properties of the unbleached pulps were obtained by beater evaluation as shown in Table III. The data were plotted against beating time in Figures 1-4 in the appendix. Pulp properties at two levels of freeness--700

TABLE V
STRENGTH PROPERTIES - BLEACHED POPLAR

Cook		2	3	4	5
Bleach		3	4	5	6
Na ₂ S ₂ O ₃ content, %		0	20	40	60
Schopper-Riegler freeness, cc.	0 ¹	840	810	820	830
	5	790	740	750	770
	10	685	670	660	700
	20	470	450	450	490
	30	265	250	245	300
	40	148	150	140	170
Apparent density	0	13.4	13.8	13.6	13.6
	5	14.2	14.2	14.9	14.6
	20	16.5	16.4	16.6	16.2
	30	16.1	16.3	17.2	16.9
Bursting strength, pt./100 lb.	0	70	80	82	77
	5	100	95	106	106
	10	109	113	125	119
	20	125	129	135	129
	30	126	121	138	136
Tear factor	0	0.98	0.96	0.93	0.95
	5	0.92	0.93	0.89	0.90
	10	0.86	0.84	0.82	0.82
	20	0.69	0.70	0.69	0.68
	30	0.60	0.59	0.58	0.61
Tensile strength, lb./in.	0	23.1	23.6	23.8	22.6
	5	30.0	29.8	30.3	29.8
	10	31.8	32.1	33.7	30.3
	20	37.0	35.0	33.7	34.7
	30	34.5	34.9	32.7	35.2
M.I.T. fold	0	68	75	83	48
	5	261	178	526	235
	10	553	628	924	472
	20	1531	1384	1579	827
	30	2547	2419	3271	1582

¹ Beating time in min.

and 400-cc. Schopper-Riegler were calculated from the graphs and appear in Table VI. There are some indications here that bursting strength at 700-cc. Schopper-Riegler freeness increased with increasing $\text{Na}_2\text{S}_2\text{O}_3$ content. This trend was not indicated at 400-cc. freeness. No distinct trends were noted in the other strength properties, although tensile strength was greater when the $\text{Na}_2\text{S}_2\text{O}_3$ was present than when it was absent. Folding strength at both freeness levels was highest at 20% $\text{Na}_2\text{S}_2\text{O}_3$ content and fell to a minimum at 60% content.

Bleaching data, shown in Table IV, gave no indication of a trend in ease of bleaching which could be correlated with sodium thiosulfate content. It was apparent, however, that there was no evidence of difficulty in bleaching the $\text{Na}_2\text{S}_2\text{O}_3$ containing pulps. The bleached pulp strengths, shown in Table V, were plotted against beating time in Figures 5-8 in the appendix. The strength data at 700- and 400-cc. freeness (Table VI) show no trends at all in strength properties at either freeness level. It is probably not surprising that small variables in bleaching should overshadow the minor differences that might be recognized in the unbleached pulp.

SUMMARY AND CONCLUSIONS

A study of pulping conditions and product variables in the preparation of aspen neutral sulfite pulp was made with sodium thiosulfate content of the liquor the only variable. There were no indications that the $\text{Na}_2\text{S}_2\text{O}_3$ had any effect upon ease of pulping or bleaching, although the unbleached pulp cooked without the thiosulfate was not as yellow in color as those cooked in its

TABLE VI
PHYSICAL PROPERTIES OF UNBLEACHED AND BLEACHED
ASPEN NEUTRAL SULFITE PULPS

Pulp	Cook 2 Bleached	Cook 2	Cook 3 Bleached	Cook 3	Cook 4 Bleached	Cook 4	Cook 5 Bleached
<u>Properties at 700-cc. Schopper-Riegler Freeness</u>							
Beating time, min.	14.5	10.5	13.5	7.5	19.0	8.0	10.0
Apparent density	14.2	15.2	14.7	15.0	14.4	15.1	15.3
Bursting strength, pt./100 lb.	93	113	95	106	99	119	119
Tear factor	0.76	0.83	0.76	0.88	0.72	0.85	0.82
Tensile strength, lb./in.	29.8	33.3	29.7	31.4	31.2	32.8	31.8
M.I.T. fold	280	570	360	400	310	650	470
<u>Properties at 400-cc. Schopper-Riegler Freeness</u>							
Beating time, min.	28.5	23.0	28.0	22.0	34.0	22.5	24.5
Apparent density	16.1	16.5	16.2	16.5	15.8	16.9	16.6
Bursting strength, pt./100 lb.	112	127	110	128	106	138	133
Tear factor	0.60	0.68	0.60	0.68	0.62	0.66	0.64
Tensile strength, lb./in.	31.9	36.8	33.8	35.0	35.3	33.8	34.7
M.I.T. fold	970	1770	1250	1600	960	2000	1220

presence. There was minor evidence to indicate that bursting and tearing strengths and flat-crush resistance of the unbleached pulps increased with the thiosulfate content, and that folding endurance suffered at the highest rate of addition. These trends were not in evidence in the bleached pulps. Bleaching of the pulps did not seem to be affected by changes in the $\text{Na}_2\text{S}_2\text{O}_3$ content of the pulping liquor.

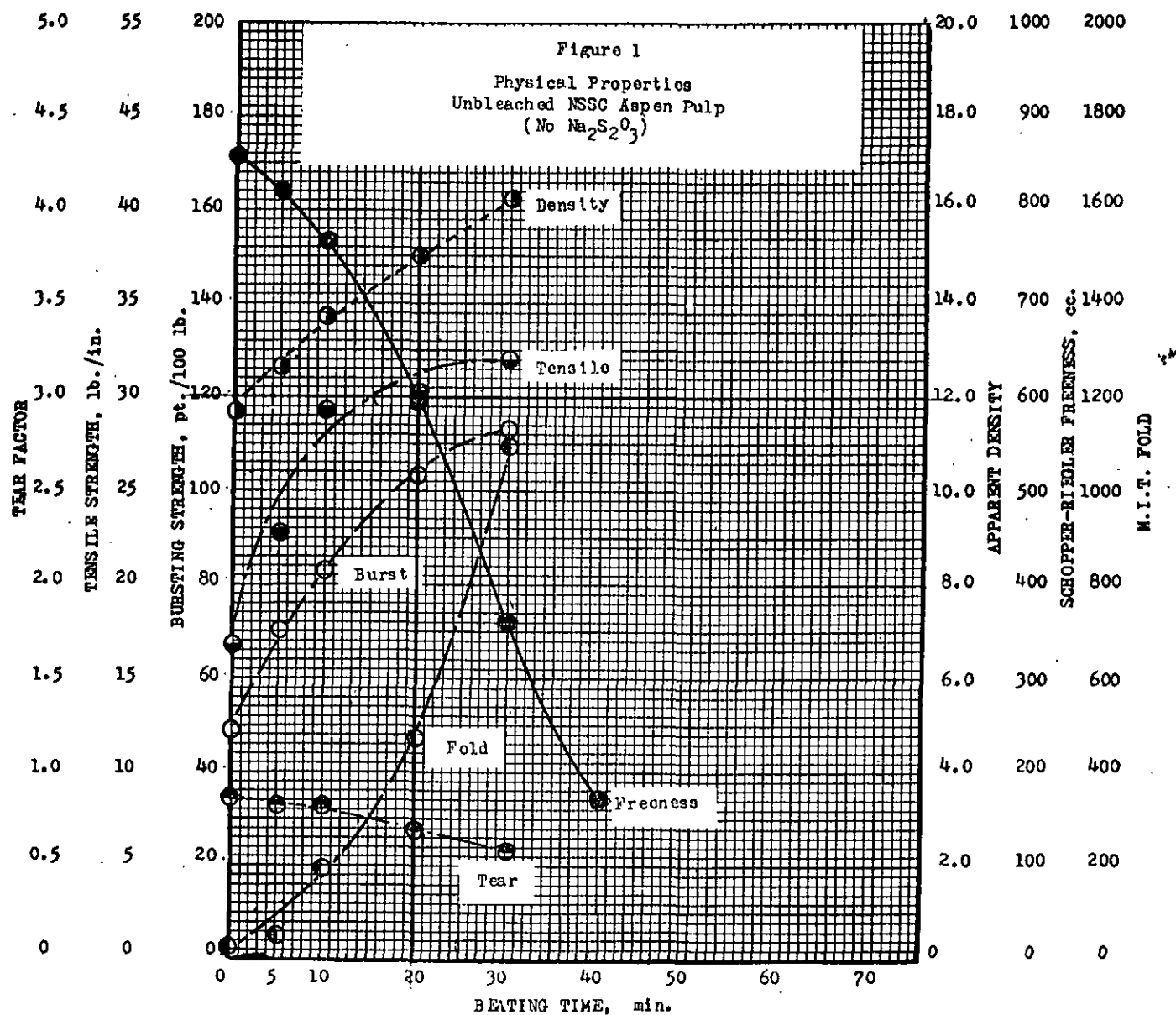
The white liquor analysis, included in Table I, is not commented on in this report.

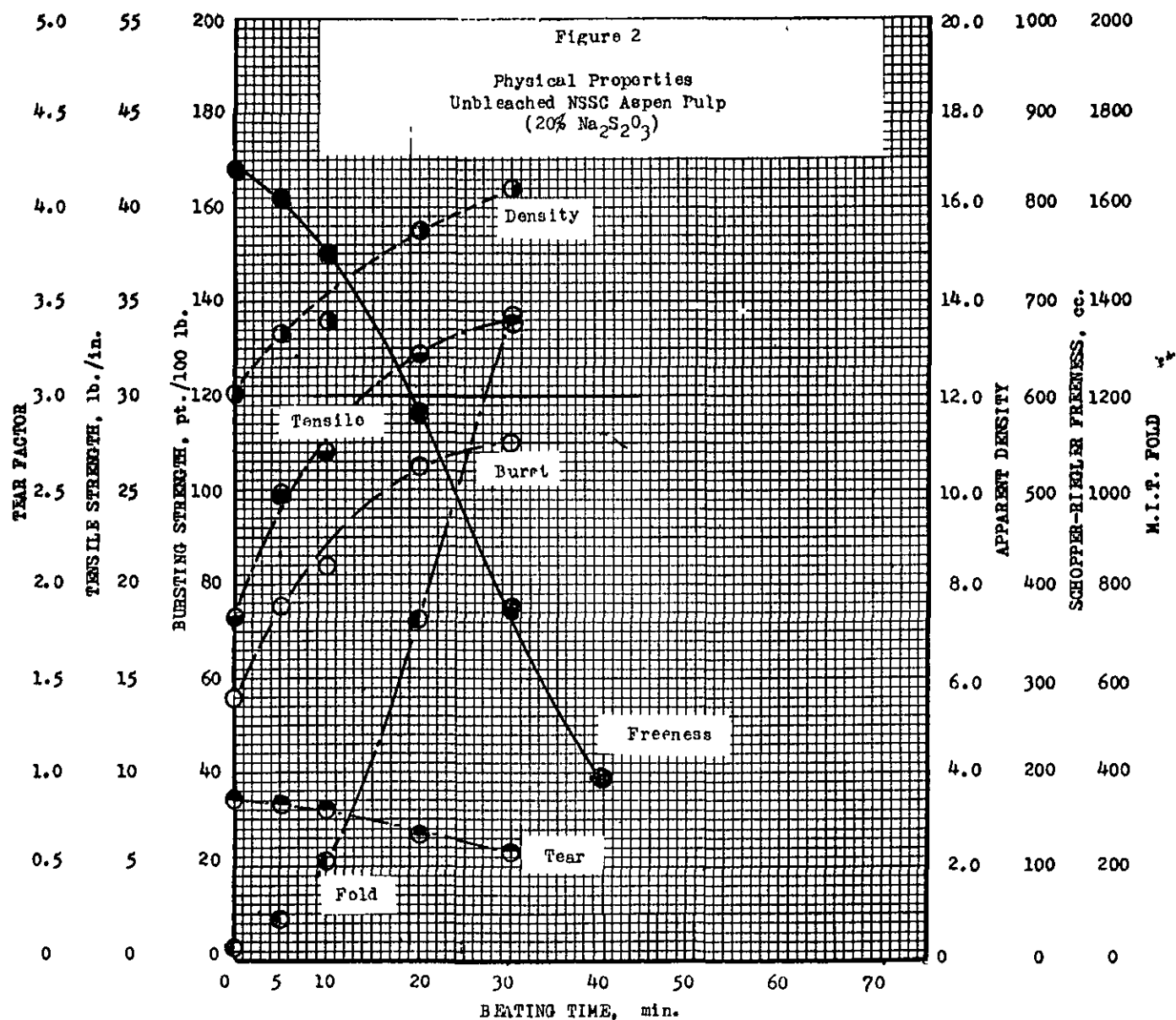
jrp/jh

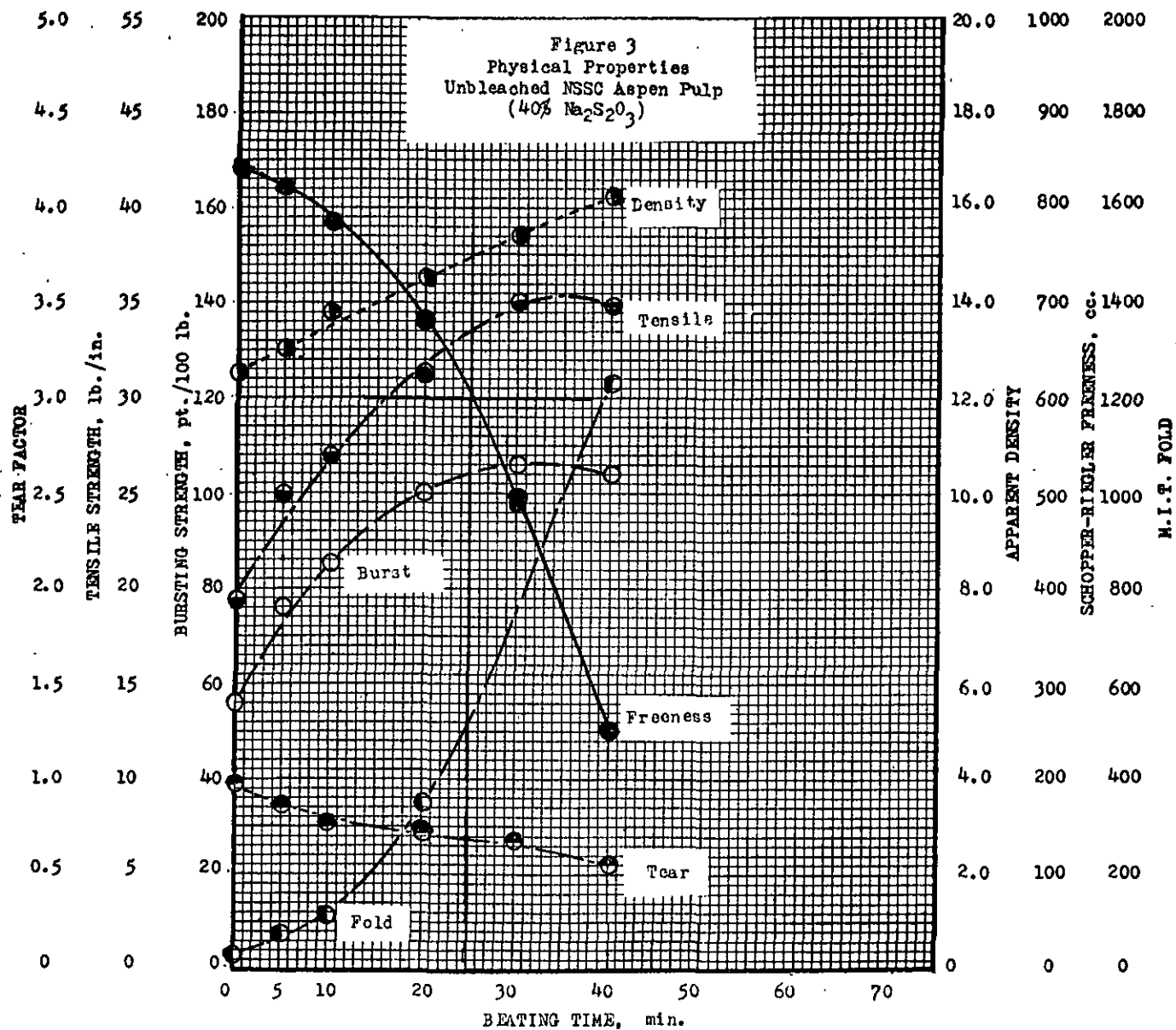
Project 1915
Report 1
May 2, 1956
Page 15

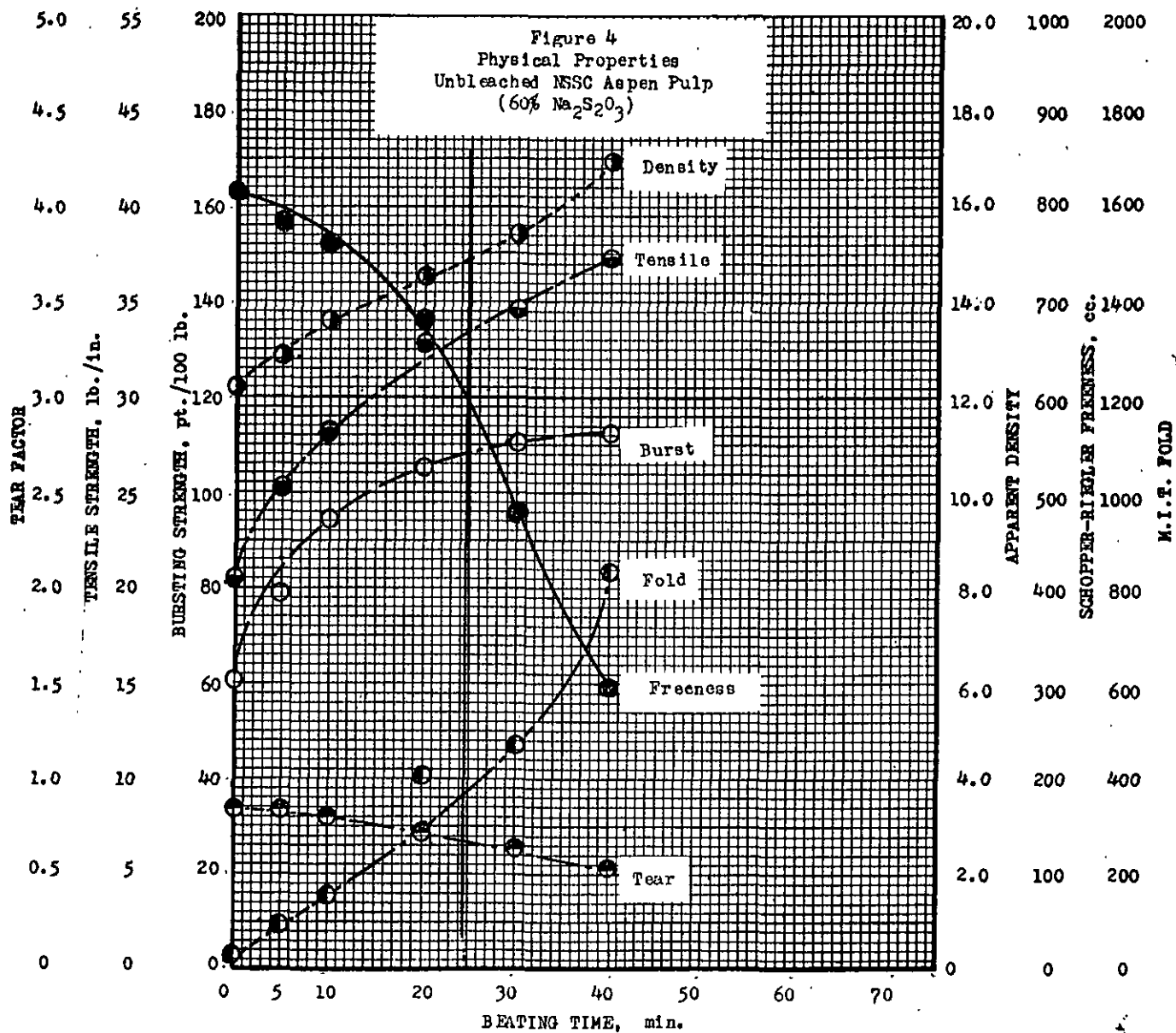
APPENDIX

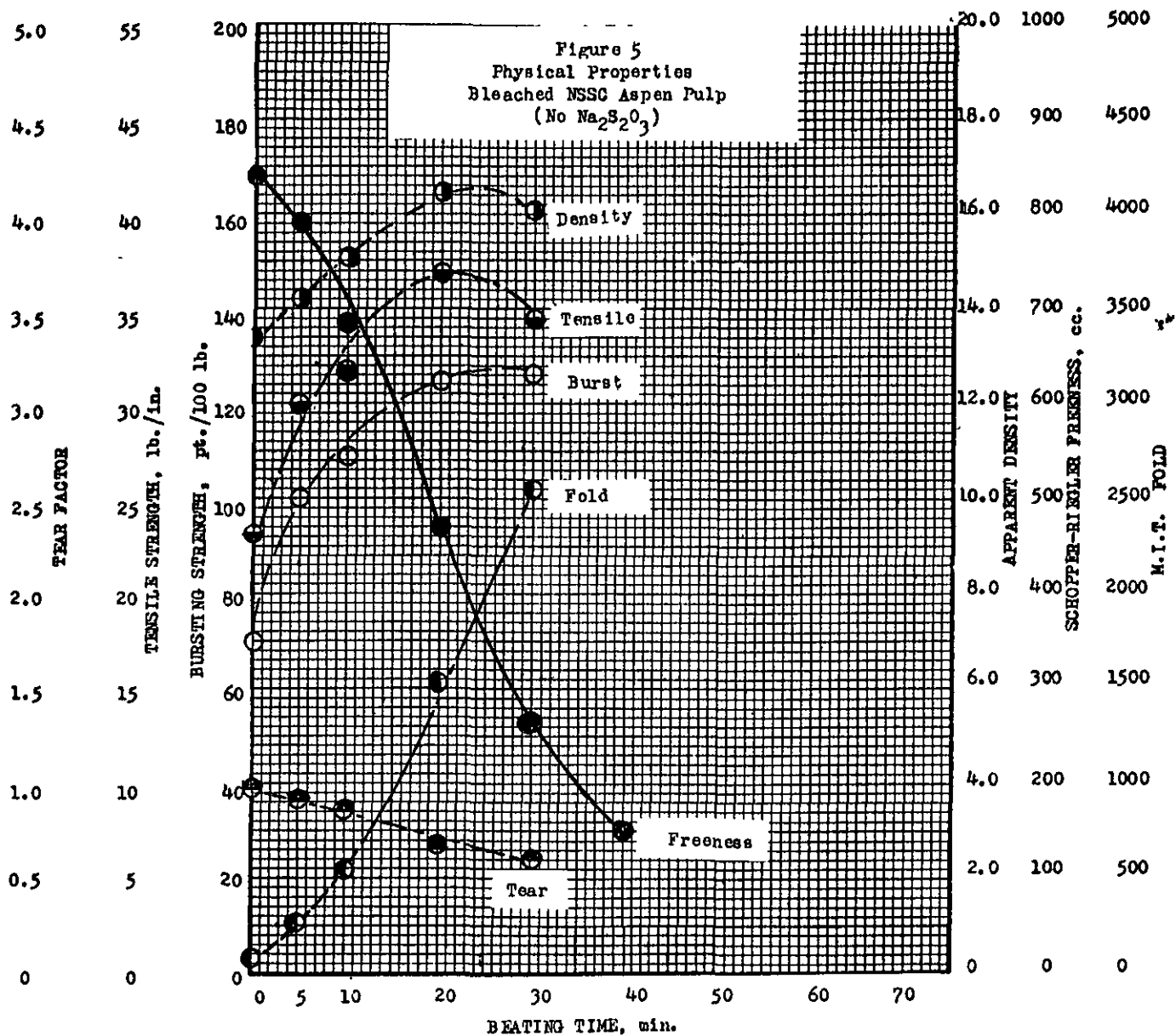
Figures 1 - 8

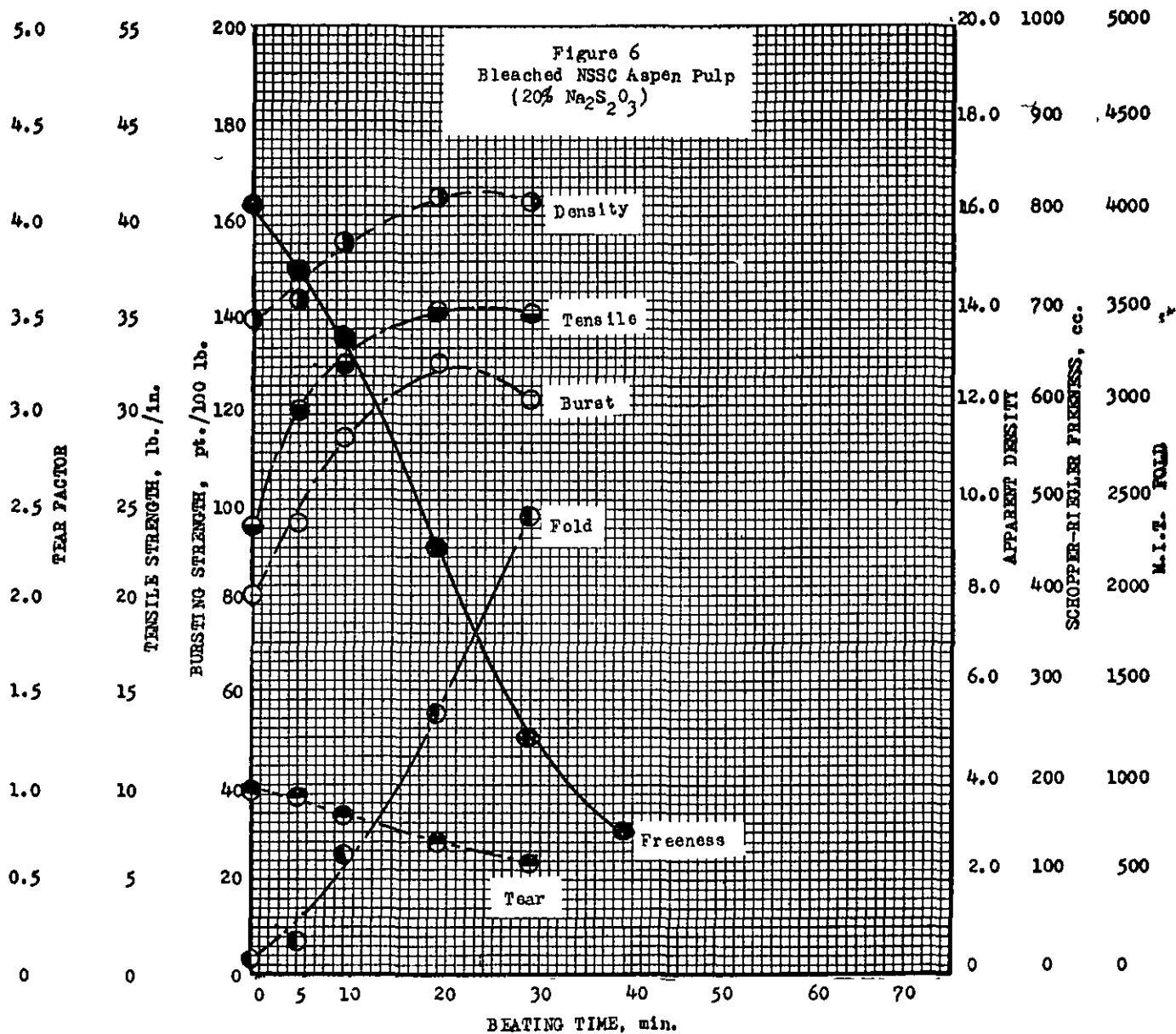


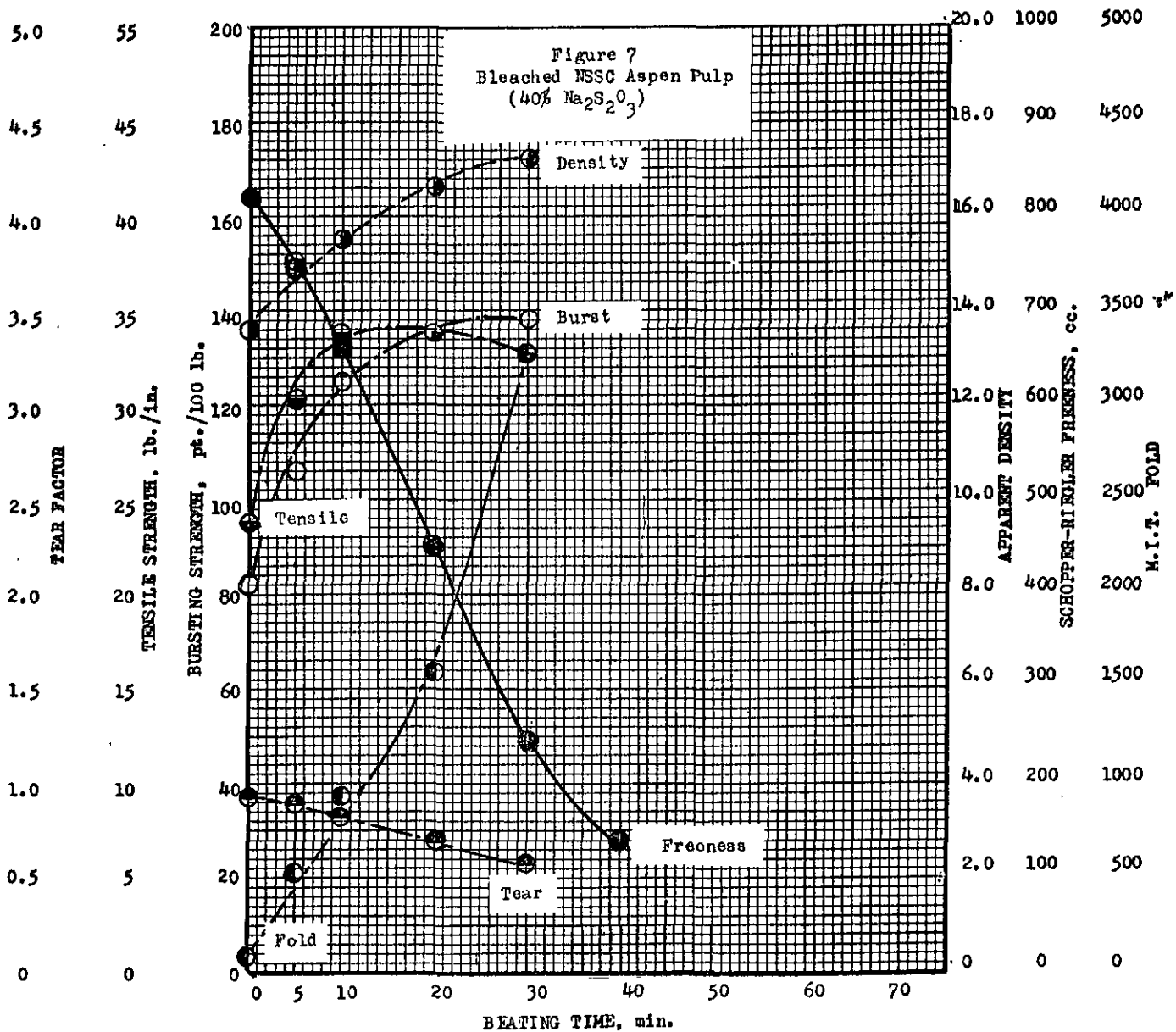


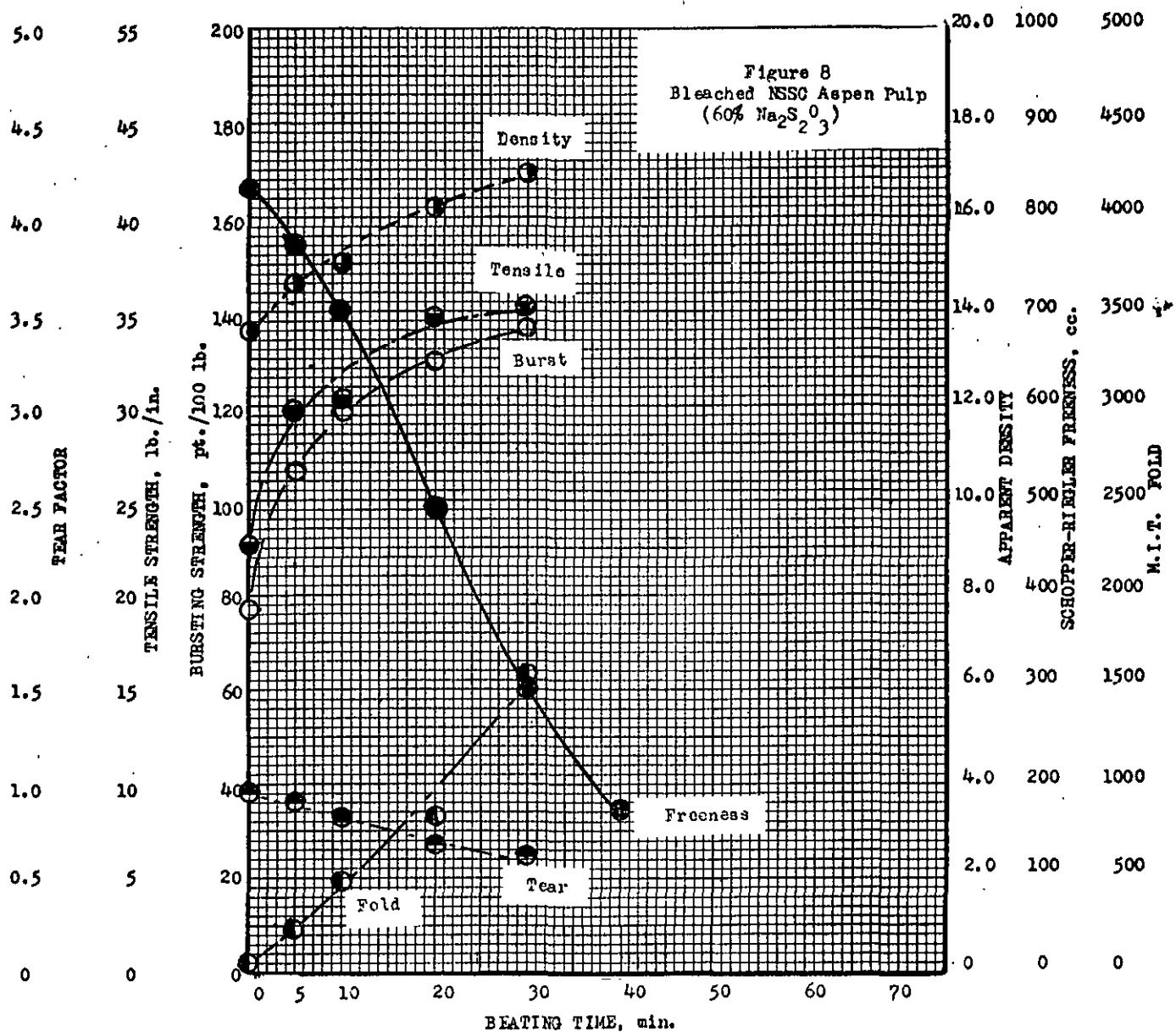












Cook 2

Cook 3



Cook 4



Cook 5

PROJECT REPORT FORM

cc. The Files
May
Peckham
Voelker
Jappe
Whitney
Ingmanson

✓ Project 1915
Co-operator Institute
Report No. 2
Date May 27, 1957
Notebook 1471
Page 51 to 156
Signed: J. R. Peckham
J. R. Peckham

STUDY OF THE EFFECT OF THE PRESENCE OF SODIUM THIOSULFATE
IN NEUTRAL SODIUM SULFITE SEMICHEMICAL PULPING

INTRODUCTION

Project Report One dealt with experiments wherein aspen chips were subjected to a series of neutral sodium sulfite digestions with all variables held constant except the sodium thiosulfate content. The results of these tests indicated that, under the conditions chosen, the presence of sodium thiosulfate in amounts up to 60% of the sodium sulfite used, had no deleterious effect upon the resultant pulp.

This report is concerned with a second phase of the study, and the results caused by the presence of sodium sulfide in the cooking chemical are investigated.

SUMMARY

A continuation of a study of the effect of the presence of sodium thiosulfate in neutral sodium sulfite cooking liquor was undertaken. A description of three phases of the investigation and the results obtained follow.

(1) With aspenwood as the raw material, a standard set of cooking conditions was maintained which featured a high level both of sodium sulfite and thiosulfate. To this liquor was added varying amounts of sodium sulfide.

Increases in the level of addition of this substance did not affect pulp yield, but it lowered pulp brightness with a consequent increase in bleach demand. It could not be demonstrated that the unbleached pulp strength suffered from the addition of the sulfide, but increases in strength were certainly not indicated. Any variations in pulp strength that were noted were apparently leveled out by the bleaching process.

(2) With the same supply of aspenwood, and the same high level of sodium sulfite in the cooking liquor, the sodium sulfide content of the liquor was held constant at 1.67% and sodium thiosulfate was varied. This had no appreciable effect upon either yield or pulp brightness, but decreasing the thiosulfate content increased the bleach demand of the pulp significantly. It was of especial interest that complete removal of thiosulfate from the liquor did not continue the trend toward harder bleaching, but seemed to reverse it back to a point held by a moderate dosage of thiosulfate. No differences in strength properties of the pulps, unbleached or bleached, were noted.

(3) The effect of thiosulfate presence in a cooking liquor containing a low level of sodium sulfite was investigated. The yield from the aspen chips was somewhat higher than when more sulfite was used and the pulps were darker and harder to bleach. The pulp containing thiosulfate had a brownish color as compared to a red color for the pulp made without thiosulfate. This brown color was deepened when the buffer proved to be inadequate to maintain an alkaline pH throughout the cook. The strength properties of the unbleached and bleached pulps showed no trends which could be attributed to the presence or absence of thiosulfate except that the pulp made without thiosulfate had a low flat-crush resistance when made into corrugating medium handsheets. The

general level of strength properties of the pulps made with the minimum amount of sodium sulfite was lower than when an excess of cooking chemical was used. This could be attributed to the slightly higher yield of pulp.

Duplicate cooks were made in all cases, but few tests were completed to characterize the success of the replication. On the basis of pulp yield, it is indicated that the techniques involved are probably reproducible.

EXPERIMENTAL

PULPING

The aspenwood used in this portion of the work came from a Populus tremuloides sample which remained from another study (Project 1800). The chips contained about 40% moisture (airdry chip basis). The preparation of wood, cooking procedures, and yielding and evaluation techniques were those described in Project Report One.

Cook 6 (Table I) was a baseline effort and the results were compared with those of Cook 2, Project Report One. The yield of pulp was very similar in both cooks. In Cooks 7 through 9 the conditions used in Cook 6 were duplicated with the exception that three increasing levels of sodium sulfide were included with the cooking chemicals. Cook 10 was made to duplicate Cook 8 in order to obtain sufficient pulp for bleaching experiments. Cooks 11 through 13 were made like Cook 9 with the exception that the thiosulfate level was reduced in successive cooks until none at all was present in Cook 13. Cook 14 was a duplicate of Cook 11 in all respects, again necessary in order to supply enough pulp for bleaching experiments.

TABLE I

PULPING CONDITIONS AND PRODUCT VARIABLES

Cook	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Wood moisture, %	39.1	39.3	37.8	39.3	39.2	39.3	39.2	39.2	39.4	39.1	44.0	44.1	44.1	44.0	44.0	44.0	43.8	43.9	44.0
Sod. sulfite (as Na_2SO_3), %	17.83	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	8.0	8.0	8.0	18.0	18.0	18.0	18.0	18.0	8.0	8.0
Sod. bicarbonate (as NaHCO_3), %	4.46	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	6.0	7.5	7.5	4.5	4.5	4.5	4.5	4.5	7.5	7.5
Sod. sulfide (as Na_2S), %	--	0.6	1.12	1.67	1.12	1.67	1.67	1.67	1.67	--	--	--	0.56	1.12	1.67	1.67	1.67	--	--
Sod. thiosulfate (as $\text{Na}_2\text{S}_2\text{O}_3$), %	--	7.21	7.21	7.21	7.21	5.0	1.0	--	5.0	7.21	7.21	--	7.21	7.21	7.21	1.0	--	7.21	--
Water ratio (ovendry chip basis), cc./g.	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Max. pressure, p.s.i.	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117
Bauer load, amps	220	220	250	250	260	250	280	300	260	250	300	300	--*	--**	340	340	350	--**	360
Yield (unscreened), %	67.2	67.9	67.7	66.9	68.3	68.4	68.2	68.1	68.5	69.6	71.5	72.8	69.1	70.1	68.4	69.5	69.1	70.8	72.2
G.E. brightness, %	42.8	38.6	26.5	20.9	26.0	21.7	23.7	23.9	21.6	16.4	16.3	18.6	37.6	29.4	22.7	25.1	24.9	15.8	18.0
<u>White Liquor Analysis</u>																			
pH	8.3	9.1	9.3	9.4	--	9.4	9.5	9.5	--	8.1	8.1	8.2	9.0	--	9.6	9.4	9.4	8.2	8.2
Na_2SO_3 , g./l.	37.4	34.3	32.7	38.6	--	36.2	35.7	35.7	--	14.8	12.9	11.9	32.5	--	39.1	37.7	37.8	10.1	16.6
$\text{Na}_2\text{S}_2\text{O}_3$, g./l.	16.4	19.3	18.7	18.5	--	12.8	3.48	0.95	--	16.3	16.9	--	18.8	--	18.5	3.79	--	16.8	--
NaHSO_3 , g./l.	2.71	--	--	--	--	--	--	--	--	1.46	1.35	1.42	--	--	--	--	--	0.83	1.56
Na_2CO_3 , g./l.	0.53	2.54	4.24	3.50	--	5.51	5.62	5.62	--	0.42	0.64	0.53	2.54	--	6.04	6.47	6.80	0.53	0.53
NaHCO_3 , g./l.	11.5	5.21	7.56	9.83	--	6.89	5.76	5.96	--	13.5	17.6	17.1	9.33	--	5.80	5.19	5.51	18.2	17.1
NaHS , g./l.	--	3.14	3.48	2.19	--	3.14	3.76	3.92	--	--	--	--	3.70	--	3.20	4.04	3.70	--	--

Constant conditions:

#4 Stationary digester
 Bauer plates: B-957
 Plate clearance, in. 0.005
 Bauer feed rate: 7
 Bauer cons. (est.), % 8

Max. temp., °C. 176
 Time to 125°C., min. 30
 Time at 125°C., min. 60
 Time, 125°C. to max., min. 30
 Time at max. temp., min. 180

*Defibered in Sprout-Waldron
 **Data not obtained.

In an effort to verify claims (1) that under certain conditions the presence of thiosulfate may be deleterious, Cooks 14 through 16 were made to investigate the effect of its presence in the cooking liquor when the active chemical level is low. In Cook 14 the buffer content was insufficient to maintain an alkaline pH, so Cook 15 was made with an increase in sodium bicarbonate content. Cook 17 was made without either sulfide or thiosulfate.

It should be noted that Cook 15 exhausted the supply of aspen chips prepared for this investigation and that all of the cooks from 16 through 24 were made using a fresh batch prepared in the usual manner. The wood bolts were taken from the same lot of Populus tremuloides that was used for Cooks 6 through 15.

Cooks 18 through 24 were made to provide duplicate data for that already compiled.

BLEACHING

Bleaching experiments were based on a three-stage sequence in which sufficient chlorine was added in the first stage to allow the achievement of approximately 80% G.E. brightness with the use of 3% or less of chlorine in the hypochlorite stage. The conditions used and the results obtained are shown in Table II.

Bleach 7 was made using the pulp of baseline Cook 6, and the conditions used were the same as those used in Bleach 3, Cook 2, with the exception that 2.6% chlorine was used in the third stage instead of 2.05%. The brightness achieved was 79.6 as compared to 80.1% in Bleach 3. Bleach 8, using the pulp of Cook 7 (7.21% $\text{Na}_2\text{S}_2\text{O}_3$ and 0.56% Na_2S) was bleached in the same manner as

TABLE II

BLEACHING CONDITIONS AND PRODUCT VARIABLES

Bleach	7	8	9	9X	10	11	11A	11B	12	13	15	16	17	18 (10A)
Cook	6	7	8	10	9	11	11	14	12	13	15	16	17	20
Na ₂ S ₂ O ₃ , %	--	7.21	7.21	7.21	7.21	5.0	5.0	5.0	1.0	--	7.21	7.21	--	7.21
Na ₂ S, %	--	0.56	1.12	1.12	1.67	1.67	1.67	1.67	1.67	1.67	--	--	--	1.67
<u>CHLORINATION STAGE</u>														
Pulp charge (moisturefree), g.	750	750	750	750	750	750	750	750	750	750	750	750	750	750
Time, min.	35	34	26	20	20	20	45	60	60	60	60	50	15	35
Chlorine, %	8.0	8.0	8.0	12.0	12.0	12.0	15.0	19.0	25.0	24.0	23.0	20.0	18.0	15.0
Resid. chlorine (basis Cl ₂ applied), %	--	--	--	--	--	--	--	Trace	9.45	17.05	3.04	--	--	--
<u>CAUSTIC-EXTRACTION STAGE</u>														
Pulp charge (moisturefree--assumed), g.	750	750	750	750	750	750	750	750	750	750	750	750	750	750
<u>HYPOCHLORITE STAGE</u>														
Pulp charge (moisturefree), g.	580	610	--*	522	512	--*	--*	540	517	550	526	512	512	565
Time, hr.	3.5	4.0	--	4.0	4.0	--	--	4.0	1.42	4.0	4.0	4.0	4.0	4.0
Chlorine, %	2.6	2.25	--	2.0	4.5	--	--	0.5	0.3	0.4	0.68	0.66	1.0	0.9
Residual chlorine, %	--	2.4	--	11.3	2.0	--	--	10.6	--	Trace	11.3	10.8	10.7	9.36
Brightness, %	79.6	79.5	--	80.0	77.1	--	--	80.5	79.9	80.9	81.5	78.8	79.0	80.5
Chlorine used (total), %	10.6	10.3	--	14.0	15.9	--	--	19.5	22.9	20.3	22.9	20.6	18.9	15.7
Yield, %	83.1	87.9	--	81.7	82.0	--	--	83.6	78.1	82.3	78.5	81.2	79.3	84.9

Constant conditions:

	<u>Chlorination</u>	<u>Caustic-Extraction</u>	<u>Hypochlorite</u>
Consistency (moisturefree), %	3.0	10.0	10.0
Temperature, °C.	20	50	38
Time, min.	--	60	--
NaOH, %	--	3.0	--

*Bleach was abandoned when bleach demand tests indicated insufficient chlorination.

Bleach 7, with quite similar results in terms of bleach consumption and brightness level attained. Bleach 9 (Cook 8) was chlorinated with 8% Cl_2 , duplicating the level applied in Bleaches 7 and 8. Chlorine demand tests indicated that this pulp, cooked with 7.21% $\text{Na}_2\text{S}_2\text{O}_3$ and 1.12% Na_2S , would probably take a high level of hypochlorite addition to reach 80 brightness, so the experiment was abandoned.

Bleach 9X, using pulp from Cook 10 (a duplicate of Cook 8) was chlorinated with 12% Cl_2 . This pulp, after caustic extraction, was bleached with 2% chlorine in the hypochlorite stage and 80.0% brightness was achieved.

The pulp used in Bleach 10 had been made with a liquor containing 1.67% Na_2S , but since it did not appear badly discolored, it also was chlorinated with 12% Cl_2 . The addition of 2% Cl_2 in the hypochlorite stage resulted in a pulp of 77.1% G.E. brightness, indicating a greater chlorine demand for this pulp than for that of Cook 9.

The pulp of Cook 11, made with 1.67% Na_2S and 5% $\text{Na}_2\text{S}_2\text{O}_3$, was different from the pulps of Cooks 8 and 10 only in the lower level of $\text{Na}_2\text{S}_2\text{O}_3$ applied. Chlorination in the case of Bleach 11 was carried out with 12% applied and in this case tests indicated that too little Cl_2 had been used. Bleach 11A was made with 15% Cl_2 in the first stage. Again, bleach demand tests were indicative of the necessity for drastic applications of hypochlorite to attain 80 brightness. Bleach 11B utilized the pulp of Cook 14 which duplicated Cook 11 in all respects. In this experiment, 19% Cl_2 was applied in the first stage, 0.5% in the third stage, and the bleached pulp measured 80.5% G.E. brightness.

The pulp of Cook 12 had been made with only 1% $\text{Na}_2\text{S}_2\text{O}_3$ accompanying the 1.67% Na_2S . In Bleach 12 this stock was treated with 25% Cl_2 in the first stage and 0.3% in the third stage to a brightness of 79.9%.

Cook 13, made without $\text{Na}_2\text{S}_2\text{O}_3$ and with 1.67% of Na_2S , provided the raw material for Bleach 13. Chlorine applied in the first stage was 24% and 0.4% as hypochlorite was effective in producing bleached pulp of 80.9 brightness.

Cook 15 was made with a low level of sodium sulfite as compared to the cooks made previously and 7.21% of $\text{Na}_2\text{S}_2\text{O}_3$ was also included. This pulp, when bleached (Bleach 15) needed 23% Cl_2 in the first stage and 0.68% in the hypochlorite stage to attain 81.5% brightness.

Cook 16 was made similarly to Cook 15 but with two changes. First, a new batch of wood from the same original lot was used, and secondly, a higher NaHCO_3 content was maintained. This pulp, though having a somewhat higher yield than that from Cook 15, was bleached with 20% Cl_2 in the first stage instead of 23% and 81.2% brightness was developed with the use of 0.66% Cl_2 as hypochlorite. Cook 17, made without $\text{Na}_2\text{S}_2\text{O}_3$ and at the low Na_2SO_3 level, was only slightly easier to bleach than Cook 16 (refer to Bleach 17).

Bleach 18 was a repeat of Bleach 10, made on the pulp of Cook 20, which was the duplicate of Cook 9, but with more chlorine in the first stage. Brightness of 80.5% was achieved.

TESTING

The unbleached pulps which were of interest were formed into handsheets on a 10 by 12-inch mold after beating to 450-cc. Canadian Standard freeness. These sheets were tested for basis weight, caliper, and flat-crush resistance. The

results of the tests are shown in Table III. Beater evaluations (Institute Methods 403 and 411) were made on unbleached and bleached pulps. The data for the unbleached fiber are included in Table IV, those for bleached pulps in Table V.

DISCUSSION OF RESULTS

The discussion of results can logically be divided into several segments. First to be considered is the effect of the addition of sodium sulfide to neutral sulfite liquors containing 7.21% $\text{Na}_2\text{S}_2\text{O}_3$ and a high level of sodium sulfite. In this series of digestions, Cook 6 was a baseline effort to tie the new wood supply to the one used in Cooks 1-5 earlier in this project. Neither cook contained sodium sulfide or sodium thiosulfate. The yields were found to be very similar (68.5 and 67.2%). Strength properties of the two pulps were similar except that that of Cook 6 had a higher bursting strength than the pulp of Cook 2, and an appreciably higher flat-crush resistance in the corrugating medium handsheets. Cooks 7, 8, and 9--containing increasingly large amounts of sodium sulfide, with $\text{Na}_2\text{S}_2\text{O}_3$ constant at 7.21%, showed little recognizable trend in yield. Strength properties of the pulps, shown in Table V, vary in what might be recognized as a trend only in bursting strength. A quite definite fall-off in that property occurred at the 1.12% Na_2S level but did not become worse at 1.67% Na_2S . Tensile strength showed this relationship with Na_2S addition only when the pulps were compared at 700-cc. freeness. At 400-cc. freeness and at 15.5 apparent density, the tensile strengths agreed well within the limits of experimental error. Folding strength declined with the first two additions of sulfide but made an apparent recovery at the 1.67% level of addition.

TABLE III
TEST RESULTS ON CORRUGATING MEDIUM HANDSHEETS

Cook	6	7	8	9	11	12	13	16	17
Na ₂ SO ₃ , %	17.8	18.0	18.0	18.0	18.0	18.0	18.0	8.0	8.0
Na ₂ S ₂ O ₃ , %	--	7.21	7.21	7.21	5.0	1.0	--	7.21	--
Na ₂ S, %	--	0.56	1.12	1.67	1.67	1.67	1.67	--	--
Yield, %	67.2	67.9	67.7	66.9	68.4	68.2	68.1	71.5	72.8
Basis weight, lb./1000 sq. ft.	26.4	26.8	26.9	26.5	27.0	26.3	26.4	27.1	26.7
Caliper, mils	7.2	6.7	7.4	7.1	8.1	8.2	7.9	8.7	8.8
Apparent density	3.7	4.0	3.6	3.7	3.3	3.2	3.3	3.1	3.0
Single-flute flat-crush, p.s.i.	45.4	48.4	43.3	41.1	39.2	37.7	40.8	39.1	33.3

TABLE IV

PHYSICAL PROPERTIES OF UNBLEACHED PULPS

	6	7	9	10	12	13	14	15	16	17	20
Riegler freeness, cc.	865	860	855	855	805	845	835	830	820	850	805
	850	835	835	825	--	--	--	850	790	820	790
	840	835	800	800	750	780	790	805	680	790	705
	785	795	755	765	720	745	725	760	570	690	635
	715	720	695	675	675	730	710	700	360	560	510
	620	635	675	580	605	650	600	600	250	440	395
	515	505	540	530	525	570	525	545	--	275	245
	360	415	460	435	470	510	465	455	--	--	--
	--	--	370	--	380	390	390	--	--	--	--
ght (25 x 40--	46.6	45.9	46.0	45.7	46.5	45.7	46.4	46.5	46.1	46.3	46.0
	46.0	46.4	46.9	46.8	--	--	--	45.7	46.1	46.1	45.8
	46.7	46.8	45.4	46.2	46.6	46.3	46.0	46.5	46.3	46.3	46.3
	46.8	46.1	46.0	46.2	46.0	46.6	47.1	46.8	46.7	46.0	46.9
	46.6	46.6	46.3	46.3	46.2	46.5	46.3	46.8	46.9	46.3	46.5
	46.7	46.4	46.4	46.1	46.1	46.6	46.4	47.0	--	46.3	46.5
	46.4	46.5	47.8	47.1	46.9	46.9	47.3	47.0	--	--	--
	45.8	46.5	46.6	46.8	46.9	46.8	46.5	46.9	--	--	--
	--	--	46.6	--	47.2	46.9	46.4	--	--	--	--
density	10.6	10.7	10.7	11.1	11.3	11.1	11.3	10.8	11.5	11.0	12.1
	11.8	11.9	11.4	12.0	--	--	--	11.4	12.5	11.5	12.7
	12.6	12.6	11.9	12.5	12.6	12.5	12.8	12.6	14.0	12.9	14.0
	13.8	13.6	12.8	13.6	13.5	13.3	13.5	13.4	15.6	13.9	15.1
	14.6	14.6	13.6	14.5	14.0	13.7	14.5	14.6	16.8	14.9	15.5
	15.1	15.5	14.5	14.9	14.4	14.6	15.0	14.7	--	16.0	16.6
	15.5	16.0	15.4	15.7	15.6	15.1	15.8	15.7	--	--	--
	16.4	16.6	16.1	16.1	15.6	15.6	16.0	16.2	--	--	--
	--	--	16.1	--	16.3	15.6	16.6	--	--	--	--
strength, pt./100 lb.	33	28	26	29	37	34	35	27	40	28	50
	51	52	38	48	--	--	--	32	50	35	62
	71	69	47	61	59	57	55	51	80	57	86
	92	93	64	82	79	71	75	65	99	74	110
	112	111	81	94	89	86	86	83	101	95	115
	127	120	96	110	101	104	104	91	--	106	123
	139	134	111	118	108	112	114	103	--	--	--
	134	132	118	121	121	119	120	114	--	--	--
	--	--	118	--	117	124	116	--	--	--	--
time, min.											

(cont'd)

Seating time, min.

TABLE V

PHYSICAL PROPERTIES OF BLEACHED PULPS

bleach book	7 6	8 7	9X 10	10A 20	11B 14	12A 12	13 13	15 15	16 16	17 17
chopper-Riegler freeness, cc.	0 ¹ 830 5 800 10 785 20 720 30 640 40 570 50 440 60 370 70 --	840 -- 780 710 660 570 495 400 295	815 780 700 595 440 310 200 -- --	790 740 605 490 350 -- -- -- --	800 730 630 520 350 280 -- -- --	760 710 600 460 305 230 -- -- --	0 ¹ 765 5 735 20 545 35 355 50 255 -- -- -- --	800 750 665 540 380 260 -- -- --	830 720 610 455 350 260 -- -- --	790 750 670 515 370 260 -- -- --
apparent density	0 12.9 5 13.6 10 14.0 20 14.8 30 -- 40 -- 50 16.6 60 17.3 70 --	12.6 -- 14.4 15.4 16.2 16.5 16.7 17.0 17.8	13.8 14.5 15.5 16.5 17.5 -- -- -- --	14.6 15.4 16.5 17.3 18.0 -- -- -- --	15.0 15.4 16.2 17.1 17.4 -- -- -- --	15.1 15.4 16.8 17.8 18.0 -- -- -- --	0 15.5 5 15.4 20 16.6 35 18.0 50 17.5 -- -- -- --	14.6 15.5 16.6 17.6 17.3 -- -- -- --	14.3 15.5 16.3 17.1 17.3 -- -- -- --	14.4 14.9 16.0 16.7 17.8 -- -- -- --
tensile strength, pt./100 lb.	0 57 5 83 10 99 20 117 30 148 40 147 50 157 60 156 70 --	58 -- 111 136 149 157 162 153 155	72 102 140 157 166 -- -- -- --	92 116 144 156 153 -- -- -- --	107 116 153 155 153 -- -- -- --	108 125 157 162 159 -- -- -- --	0 107 5 124 20 149 35 152 50 145 -- -- -- --	97 114 142 150 150 -- -- -- --	96 114 135 147 139 -- -- -- --	82 100 131 142 134 -- -- -- --
tear factor	0 1.01 5 0.99 10 0.97 20 0.89 30 -- 40 -- 50 0.75 60 0.66 70 --	1.01 -- 0.93 0.91 0.88 0.78 0.75 0.72 0.65	1.04 1.04 0.91 0.84 0.72 -- -- -- --	1.15 1.10 0.95 0.81 0.75 -- -- -- --	1.14 1.06 0.95 0.87 0.79 -- -- -- --	1.11 1.10 0.90 0.76 0.73 -- -- -- --	0 1.16 5 1.10 20 0.90 35 0.77 50 0.70 -- -- -- --	1.11 1.05 0.95 0.79 0.73 -- -- -- --	1.11 1.10 0.90 0.78 0.71 -- -- -- --	1.11 1.04 0.91 0.77 0.69 -- -- -- --
beating time, min.										

TABLE V CONCLUDED

Bleach Cook	7	8	9X	10A	11B	12A	13	15	16	17
	6	7	10	20	14	12	13	15	16	17
Tensile strength, lb./in. (corrected to basis weight of 45 lb.)	0 ¹ 5 10 20 30 40 50 60 70	18.2 24.5 27.7 32.3 -- -- 39.5 38.8 --	21.7 27.4 34.8 34.8 35.2 -- -- -- --	25.3 30.9 36.3 39.0 39.2 -- -- -- --	28.0 32.1 37.1 36.6 38.4 -- -- -- --	26.3 30.8 38.3 36.0 33.4 -- -- -- --	28.1 32.4 39.9 40.5 37.1 -- -- -- --	27.3 29.9 36.0 36.1 35.7 -- -- -- --	25.8 30.6 36.6 37.9 37.9 -- -- -- --	22.6 25.9 33.6 35.4 33.4 -- -- -- --
M.I.T. fold	0 5 10 20 30 40 50 60 70	29 82 167 410 -- -- 1635 1659 --	104 306 1352 2103 3193 -- -- -- --	91 172 1395 1346 2821 -- -- -- --	181 427 1280 2319 1834 -- -- -- --	258 633 1756 2096 3191 -- -- -- --	235 471 2095 3274 3921 -- -- -- --	120 270 1657 2380 2423 -- -- -- --	157 437 1715 2496 2724 -- -- -- --	54 181 935 1798 2042 -- -- -- --

¹Beating time, min.

When the unbleached pulps were compared on the basis of their utility as corrugating medium, it was found (see Table III) that flat-crush resistance appeared to decrease when the 1.12% level of sulfide addition was reached.

The most notable difference which appeared in the pulps used to investigate the effect of the addition of sodium sulfide was in their color and their reaction to the bleaching sequence used. The brightness of the unbleached pulps declined as sodium sulfide was increased in the cooking liquor, and--as might then be expected--they became more difficult to bleach. This phenomenon had been mentioned in the work of Keller and McGovern (2), so was not unexpected. Figure 1 shows the relationship of unbleached pulp brightness to chlorine consumption. In the case of Bleach 7, Cook 6, the chlorination stage utilized 8% Cl_2 which exhausted in 35 minutes. After caustic extraction, the pulp bleached to 79.6% brightness with the addition of 2.6% chlorine as hypochlorite. The pulp of Cook 7 was equally easy to bleach. When the pulp of Cook 8 was chlorinated with 8% Cl_2 , the chlorine exhausted in 26 minutes and, after extraction, this pulp demonstrated in chlorine demand tests that unrealistic amounts of hypochlorite would be needed to bring the brightness to the desired level. In order to pursue this experiment a new supply of unbleached pulp was obtained by making Cook 10. This pulp was treated with 12% Cl_2 in the first stage, which took 20 minutes to exhaust. After caustic extraction, 2.0% chlorine in the hypochlorite stage raised the brightness to 80.0 (Bleach 9X).

The pulp cooked with 1.67% Na_2S (Cook 9) was bleached with the same amount of chlorine used in the first stage of Bleach 9X. The chlorinated pulp, after extraction, reached only 77.1% brightness after the addition of 4.5% Cl_2 in the hypochlorite stage. The bleach was repeated as Bleach 10A, using the

pulp of Cook 18, and the chlorine in the first stage was increased to 15%. With this change, the pulp reached a brightness of 80.5 with the addition of 0.9% Cl_2 in the last stage. Figure 2 shows the relationship between sodium sulfide content of the cooking liquor and chlorine demand of the resultant pulp when the sodium thiosulfate content of the cooking liquor was held at 7.21%.

The strength properties of the bleached pulps are shown in Tables V and VI. The indications seem to be that the bleaching process tended to level out any differences which might have existed in the unbleached pulps. However, in the unbleached pulps the sulfide containing pulps had a lower handsheet density at a given freeness than the sulfide-free pulp and in the bleached product the situation was reversed.

The Effect of the Thiosulfate Level Upon the Action of Sodium Sulfide in the Cooking Liquor

When it became apparent that the pulps made with increasing quantities of Na_2S present in the cooking liquor were progressively harder to bleach, the influence of the level of $\text{Na}_2\text{S}_2\text{O}_3$ upon this phenomenon was investigated. Starting with Cook 9, which contained 1.67% Na_2S and 7.21% Na_2SO_3 , the latter chemical was successively reduced to 5.0% in Cook 11, 1.0 in Cook 12, and zero in Cook 13. The yields were very similar, which fortifies the conclusion generally held that $\text{Na}_2\text{S}_2\text{O}_3$ is not an active pulping ingredient.

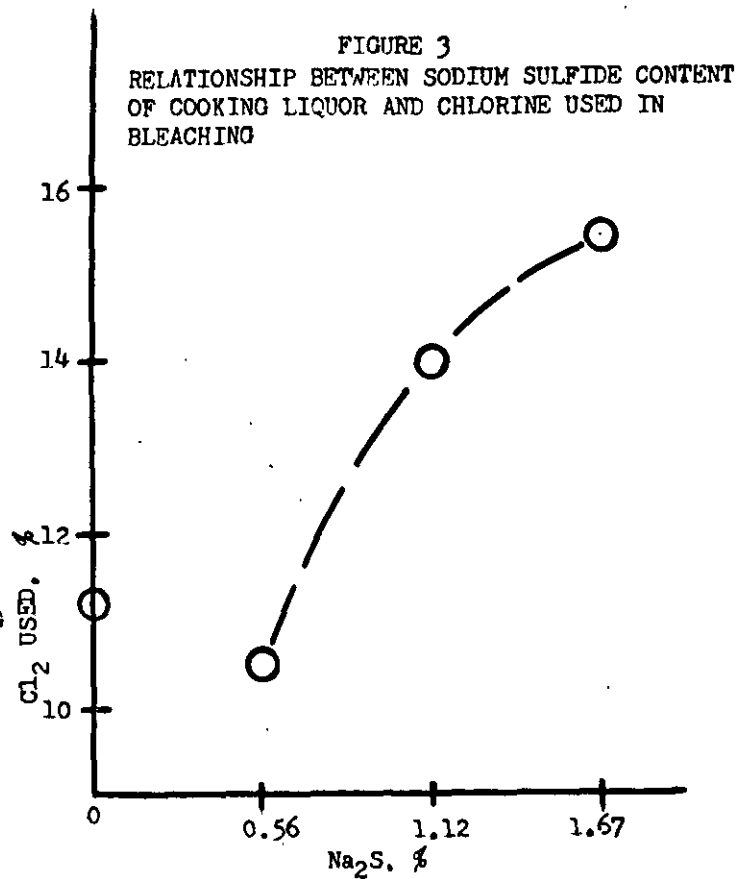
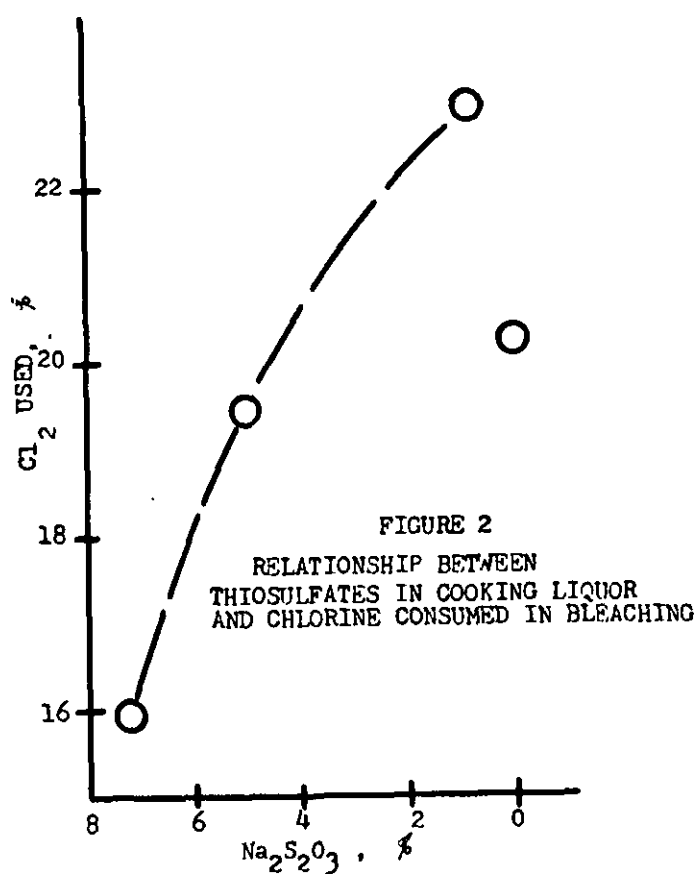
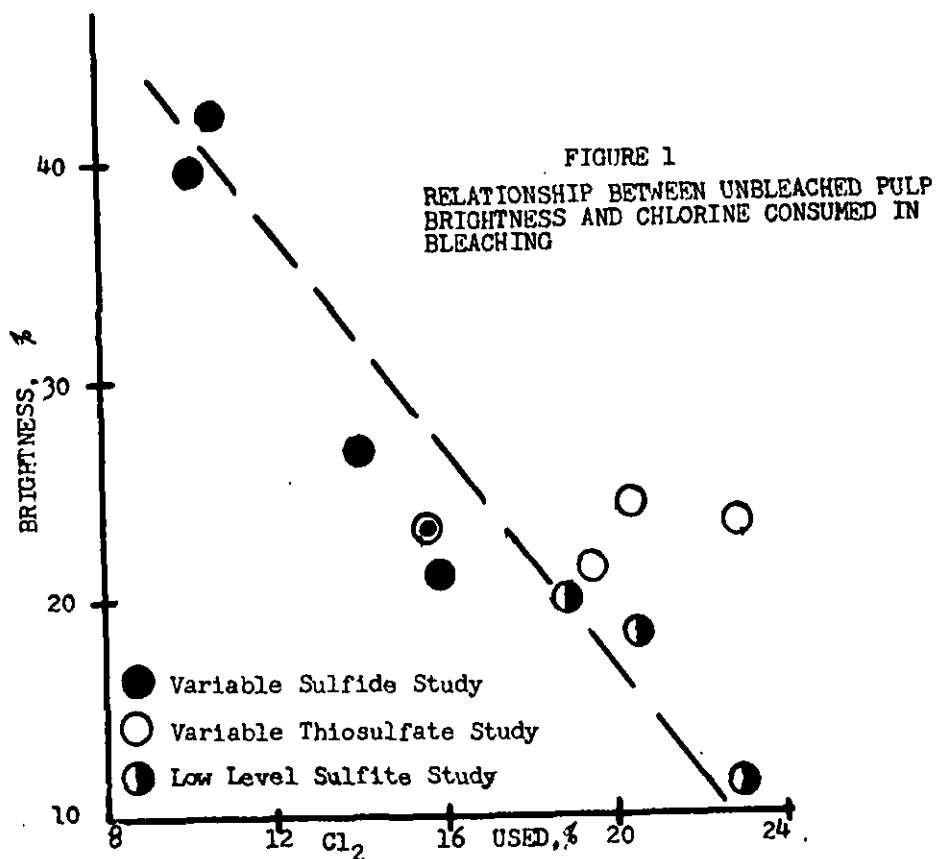
When the physical characteristics of the pulps of this group are analyzed, we see that flat-crush resistance decreased as the thiosulfate is removed, but that there is a regain in the pulp which was cooked without thiosulfate (Table III).

TABLE VI

COMPARISON OF PHYSICAL PROPERTIES OF PULPS MADE WITH VARIATIONS IN SODIUM SULFITE CONTENT OF COOKING LIQUOR

Pulp	Cook 6		Cook 7		Cook 10		Cook 20	
	Unbleached	Bleach 7	Unbleached	Bleach 8	Unbleached	Bleach 9X	Unbleached	Bleach 10A
$\text{Na}_2\text{S}_2\text{O}_3$, % Na_2S , % Pulp yield (basis oven-dry wood), %	--	--	7.21	7.21	7.21	7.21	7.21	7.21
	--	--	0.56	0.56	1.12	1.12	1.67	1.67
	67.2	55.8	67.9	59.6	68.3	56.0	68.4	58.0
<u>Properties at 700-cc. Schopper-Riegler</u>								
Beating time, min.	32.0	22.5	32.5	21.5	25.5	15.0	23.0	8.0
Apparent density	14.6	14.9	14.7	15.5	14.1	15.5	14.1	15.8
Bursting strength, pt./100 lb.	117	129	116	136	92	139	95	129
Tear factor	0.80	0.91	0.78	0.89	0.91	0.94	0.92	1.03
Tensile strength, lb./in.	31.7	33.2	32.1	35.8	28.3	35.5	26.7	33.8
M.I.T. fold	450	480	420	610	130	1220	200	310
<u>Properties at 400-cc. Schopper-Riegler</u>								
Beating time, min.	58.5	55.5	61.0	60.0	63.0	38.0	64.0	31.0
Apparent density	16.2	17.0	16.7	17.0	16.1	17.7*	16.3	17.7
Burst, pt./100 lb.	136	157	132	160	122	167*	122	155
Tear factor	0.62	0.68	0.60	0.68	0.61	0.67*	0.66	0.77
Tensile, lb./in.	33.7	39.5	34.5	39.7	33.7	34.2*	33.6	39.3
M.I.T. fold	1110	1675	985	2300	780	3400*	1350	2600
<u>Properties at 15.5 Apparent Density</u>								
Beating time, min.	49.0	31.5	43.0	21.5	45.0	15.0	46.5	6.0
Schopper-Riegler, cc.	525	630	590	700	570	700	535	730
Burst, pt./100 lb.	138	143	128	136	114	140	117	121
Tear factor	0.66	0.85	0.72	0.89	0.75	0.89	0.81	1.06
Tensile, lb./in.	33.5	36.1	33.6	35.8	33.4	34.9	33.0	32.5
M.I.T. fold	1055	800	650	610	395	1220	640	220

*These data extrapolated from Figure H.



The beater evaluation data on the unbleached pulps of this series (Tables IV and VII) do not seem to indicate any trends in pulp strength attributable to the variation of thiosulfate in the cooking liquor, with sodium sulfide content held constant.

When the pulps were bleached the chlorine used to obtain 80% brightness increased as the thiosulfate content decreased. However, when the thiosulfate was dispensed with entirely (Cook 13, Bleach 13), the demand did not increase over that noted in the case of Cook 12, Bleach 12 (1% thiosulfate) but rather decreased to agree fairly well with the chlorine demand of Cook 14, Bleach 11B (5% thiosulfate). In this case the brightness of the unbleached pulps apparently had no direct bearing upon the bleach demand. Figure 1 compares this relationship with that found in other cooks made in this investigation. The relationship between thiosulfate content and bleach demand is illustrated in Figure 3. As in the case of the unbleached pulps, the bleached pulps had no consistent physical properties variations (see Table VII) which could be attributed to the variation in thiosulfate present in the cooking liquors.

A Study of the Effect of Thiosulfate Content in Cooks Containing Minimum Amounts of Sodium Sulfite

Because it has been said that the thiosulfate content of neutral sulfite cooking liquors is more critical when the sodium sulfite content is low, Cooks 15-17 were made with only 8% sodium sulfite instead of 18%. In Cook 15, the amount of buffer was insufficient to keep the liquor on the alkaline side, so Cook 16 was made with a greater amount of NaHCO_3 present. Also, this and subsequent cooks were made with a fresh batch of

TABLE VII

COMPARISON OF THE PHYSICAL PROPERTIES OF PULPS
MADE WITH VARIATIONS IN SODIUM THIOSULFATE CONTENT OF COOKING LIQUOR

Pulp	Cook 20	Cook 14	Cook 12	Cook 13	Cook 20 Bl. 10A	Cook 14 Bl. 11B	Cook 12 Bl. 12	Cook 13 Bl. 13
Na ₂ S ₂ O ₃ , %	7.21	5.00	1.00	--	7.21	5.00	1.00	--
Yield, % (basis oven-dry wood)	68.4	68.5	68.2	68.1	58.0	57.3	53.2	56.0
Cl ₂ used, %	--	--	--	--	15.7	19.45	22.9	20.3
<u>Properties at 700-cc. Schopper-Riegler Freeness</u>								
Beating time, min.	23.0	26.0	24.5	28.5	8.0	8.5	6.0	8.5
Apparent density	14.1	14.2	13.7	13.9	15.8	15.7	15.8	16.1
Burst, pt./100 lb.	95	86	84	86	129	143	137	131
Tear factor	0.92	0.91	0.88	0.92	1.03	1.02	1.05	1.04
Tensile, lb./in.	26.7	27.0	26.7	26.2	33.8	34.0	31.2	35.2
M.I.T. fold	200	175	160	175	310	580	760	700
<u>Properties at 400-cc. Schopper-Riegler Freeness</u>								
Beating time, min.	64.0	69.0	67.5	70.0	31.0	32.5	27.5	30.5
Apparent density	16.3	16.5	15.9	15.6	17.7	17.3	17.9	17.7
Burst, pt./100 lb.	122	117	119	124	155	153	162	154
Tear factor	0.66	0.68	0.72	0.70	0.77	0.80	0.75	0.80
Tensile, lb./in.	33.6	33.0	33.5	34.5	39.3	37.7	35.2	40.7
M.I.T. fold	1350	630	940	940	2600	2000	2520	2880
<u>Properties at 15.5 Apparent Density</u>								
Beating time, min.	46.5	49.0	57.5	58.0	6.0	6.0	4.0	2.5
Schopper-Riegler Freeness, cc.	535	530	475	515	730	730	720	750
Burst, pt./100 lb.	117	113	118	119	121	136	128	115
Tear factor	0.81	0.77	0.75	0.76	1.06	1.04	1.08	1.12
Tensile, lb./in.	33.0	32.7	34.0	33.3	32.5	33.0	29.8	31.2
M.I.T. fold	640	585	690	450	220	420	540	340

chips, which were however obtained from the same lot of aspen bolts. A comparison between Cooks 16 and 17 indicates the differences attributable to thiosulfate content only, Cook 16 containing 7.21% $\text{Na}_2\text{S}_2\text{O}_3$, Cook 17 containing none. Cook 15 was also investigated in hopes of obtaining data indicative of the effect of the depressed pH of the spent cooking liquor.

The crush resistance of the pulp of Cook 17, containing no thiosulfate, was quite low. The same property of the low sulfite cook containing thiosulfate was comparable to all except the best pulps investigated. More regarding this relationship should probably be learned.

The physical properties of the unbleached pulps of Cooks 15, 16, and 17 are shown in Table IV and compared in Table VIII. The data would indicate that little difference in pulp quality could be attributed to either the change in chip supply or the acidity of the spent liquor of Cook 15. The properties of the pulps of Cooks 16 and 17 should indicate the effect of the presence of thiosulfate in the low chemical cooks. Again it is demonstrated that the effects, if any, are minimal.

The bleachabilities of the three pulps are really not directly comparable, since each was chlorinated with a different amount of chlorine. However, the pulp of Cook 15, which was made with too little buffer, was the lowest brightness pulp obtained and was apparently considerably more difficult to bleach than Cook 16. Cook 17, made without thiosulfate, was brighter and apparently bleached more easily than Cook 16. In pulp strength, the bleached pulp of Cook 15 was at least as good as that from the other two cooks. In the early stages of beating it seemed even to be better than the other low chemical pulps. Eliminating thiosulfate from the cooking liquor

TABLE VIII
COMPARISON OF PHYSICAL PROPERTIES OF PULPS
MADE WITH LOW SODIUM SULFITE LEVEL IN THE COOKING LIQUOR

Pulp	Cook 15	Cook 16	Cook 17	Cook 15 Bl. 15	Cook 16 Bl. 16	Cook 17 Bl. 17
Na ₂ S ₂ O ₃ , %	7.21	7.21	--	7.21	7.21	--
Black liquor pH	5.8	6.8	5.6	--	--	--
Chlorine, %	--	--	--	22.9	20.6	18.9
Yield, % (basis oven-dry wood)	69.6	71.5	72.8	54.6	58.0	57.7
<u>Properties at 700-cc. Schopper-Riegler</u>						
Beating time, min.	48.0	20.0	31.5	11.0	8.0	11.0
Apparent density	14.2	14.0	13.7	16.2	15.6	15.6
Burst, pt./100 lb.	79	80	71	133	122	117
Tear factor	0.89	0.90	0.88	0.96	1.00	0.96
Tensile, lb./in.	26.3	24.5	25.2	34.0	32.7	31.7
M.I.T. fold	90	130	85	1000	640	520
<u>Properties at 400-cc. Schopper-Riegler</u>						
Beating time, min.	102.0*	47.0	66.0**	33.0	30.0	32.0
Apparent density	16.4	16.6	16.1	17.4	17.3	17.4
Burst, pt./100 lb.	118	102	107	151	147	141
Tear factor	0.67	0.66	0.67	0.72	0.73	0.73
Tensile, lb./in.	33.7	29.2	31.5	35.8	38.3	34.6
M.I.T. fold	980	450	670	2500	2600	1990
<u>Properties at 15.5 Apparent Density</u>						
Beating time, min.	76.5	34.0	58.0	5.0	7.5	10.0
Schopper-R. freeness, cc.	570	545	475	760	705	705
Burst, pt./100 lb.	101	99	101	117	120	114
Tear factor	0.77	0.77	0.74	1.04	1.00	0.97
Tensile, lb./in.	31.2	27.6	31.6	31.2	32.5	31.2
M.I.T. fold	350	280	470	260	600	460

*Data extrapolated from Figure T.

**Data extrapolated from Figure V.

raised brightness and lowered bleach demand, but no advantages in physical properties were discernable. The relationship between unbleached pulp brightness and bleach demand is shown in Figure 1.

Duplicate Pulping to Ascertain Reproducibility of Procedures

Cooks 18 through 24 were made to determine the degree of confidence which could be accorded our results on individual experiments. Excepting for the pulp of Cook 20, which was bleached, the only comparison made in the duplicate pulps was in yield level. The pairs of cooks were: 7 and 18; 8 (also 10) and 19; 9 and 20; 12 and 21; 13 and 22; 16 and 23; 17 and 24. Cook 11 was not duplicated in this series because Cook 14 constituted a second experiment under the same conditions.

Referring to Table IX, it will be seen that the wood of the second lot of chips gave a consistently higher yield of pulp at any set of conditions than was obtained from the first lot of chips. This brings up the question of whether there really was a significant difference in wood from the same batch or if a small error had been made in weight or moisture content of one or the other of the lot of chips. The latter would seem to be the most reasonable conjecture. Pulps made from the same lot of chips were very similar in yield. In the only case in which unbleached pulp strengths, brightnesses, etc., were recorded (Cooks 9 and 20, see Table X), the pulp of Cook 20 would appear to be somewhat superior to that of Cook 9 in physical characteristics, although not outstandingly so. The pulps from the duplicate cooks are available for further testing if deemed necessary.

TABLE IX
RESULT OF REPLICATE PULPING TESTS

Cook	7	18	8	10	19	9	20	11	14
Lot of chips	1	2	1	1	2	1	2	1	1
Na ₂ SO ₃ , %	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
NaHCO ₃ , %	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Na ₂ S ₂ O ₃ , %	7.21	7.21	7.21	7.21	7.21	7.21	7.21	5.0	5.0
Na ₂ S, %	0.56	0.56	1.12	1.12	1.12	1.67	1.67	1.67	1.67
Pulp brightness, %	38.6	37.6	26.5	26.0	29.4	20.9	22.7	21.7	21.6
Pulp yield, %	67.9	69.1	67.7	68.3	70.1	66.9	68.4	68.4	68.5

Cook	12	21	13	22	16	23	17	24
Lot of chips	1	2	1	2	2	2	2	2
Na ₂ SO ₃ , %	18.0	18.0	18.0	18.0	8.0	8.0	8.0	8.0
NaHCO ₃ , %	4.5	4.5	4.5	4.5	7.5	7.5	7.5	7.5
Na ₂ S ₂ O ₃ , %	1.0	1.0	--	--	7.21	7.21	--	--
Na ₂ S, %	1.67	1.67	1.67	1.67	--	--	--	--
Pulp brightness, %	23.7	25.1	23.9	24.9	16.3	15.8	18.6	18.0
Pulp yield, %	68.2	69.5	68.1	69.1	71.5	70.8	72.8	72.2

TABLE X

COMPARISON OF PHYSICAL PROPERTIES OF UNBLEACHED PULPS FROM DUPLICATE COOKS

Pulp	9	20
Lot of chips	1	2
Na ₂ SO ₃ , %	18.0	18.0
Na ₂ S ₂ O ₃ , %	7.21	7.21
Na ₂ S, %	1.67	1.67
Chlorine used to bleach, %	15.9	15.7
Yield, %	66.9	68.4

Properties at 700-cc. Schopper-Riegler

Beating time, min.	29	23
Apparent density	13.6	14.1
Bursting strength, pt./100 lb.	80	95
Tear factor	0.88	0.92
Tensile strength, lb./in.	24.0	26.7
M.I.T. fold	160	200

Properties at 400-cc. Schopper-Riegler

Beating time, min.	66.5	64.0
Apparent density	16.4	16.3
Bursting strength, pt./100 lb.	118	122
Tear factor	0.69	0.66
Tensile strength, lb./in.	32.5	33.6
M.I.T. fold	1130	1350

Properties at 15.5 Apparent Density

Beating time, min.	51.5	46.5
Schopper-Riegler freeness, cc.	530	535
Bursting strength, pt./100 lb.	112	117
Tear factor	0.76	0.81
Tensile strength, lb./in.	29.5	33.0
M.I.T. fold	565	640

CONCLUSIONS

Sufficient tests have been made to warrant the following conclusions:

When sodium sulfite is maintained at a high initial level (in this case 18% Na_2SO_3 based on wood):

- (1) The addition of thiosulfate up to 7.21% (based on wood) has no demonstrable effect on yield, color, bleachability or strength of the resultant pulp.
- (2) In the presence of thiosulfate at the 7.21% level, increasing dosages of sodium sulfide in the cooking liquor tend to make the pulp darker and more difficult to bleach. Brightness of the unbleached pulp seems to have a linear relationship with chlorine demand.
- (3) The addition of the sulfides at this thiosulfate level may cause a decrease in flat-crush resistance of corrugating medium made from the pulp.
- (4) Physical properties of the unbleached and bleached pulps display no trends which could be attributed to the sodium sulfide level in the cooking liquor.
- (5) When sodium sulfide content of the cooking liquor was held constant, decreasing the thiosulfate present had the effect of increasing the chlorine demand of the pulp without appreciably changing the unbleached brightness.
- (6) A liquor containing no thiosulfate gave a pulp which was harder to bleach than one made with a liquor containing 7.21% thiosulfate, but it was brighter and easier to bleach than one containing 1% thiosulfate.
- (7) Lowering the thiosulfate level in a cooking liquor containing 1.67% sodium sulfide had no appreciable effect upon flat-crush resistance of corrugating

medium handsheets nor upon other physical properties of the unbleached pulp.

(8) Although the chlorine demand increased as thiosulfate content decreased with a constant sulfide content, the bleached pulps were decidedly similar in physical characteristics.

(9) When the sodium sulfite content of the cooking liquor was kept at a minimum level, the presence of thiosulfate in the liquor had the effect of darkening the pulp.

(10) If the cooking liquor did not stay alkaline, the darkening of the pulp became more pronounced.

(11) The presence of thiosulfate in the cooking liquor apparently did not affect pulp strength in either the bleached or the unbleached pulp, but there is some indication that it was deleterious to the flat-crush resistance of corrugating medium handsheets.

(12) Strength properties of the pulps made at low sodium sulfite content were only moderately lower than those made with an excess of sodium sulfite. This was true for both the unbleached and the bleached pulps.

(13) Replicate cooks on the same batch of wood chips agreed well as to yield.

(14) Strength properties of replicate cooks showed what appeared to be significant differences at relatively high freeness values, but the differences were minimized when the comparison was made later in the beating cycle.

(15) More conclusions might be reached with greater confidence if some method of comparison of strength data could be devised which gives the proper weight to the important physical properties. At the moment, for example, the analyst is faced with the dilemma of deciding whether a pulp displaying high

burst and moderate tear is better than one having moderate bursting strength and low tear, and whether this actually indicates strength differences, when--as often happens--the pulps have identical tensile strengths. And to add to the confusion, apparent differences in strength properties at one freeness or apparent density level are many times minimized or reversed at a different comparison level.

FUTURE WORK

Sufficient material is available to investigate some of the chemical properties of the pulps. Primarily, permanganate number or chlorine number, lignin, pentosan and cellulose content would be valuable data. The nature of the coloring material in the pulps and isolation of the chlorine consuming constituents in the difficultly bleached pulps should provide information of extreme value.

LITERATURE CITED

- (1) Textor, Clinton K. U.S. Patent 2,022,073.
- (2) Keller, E. L., and McGovern, J. N. Neutral sulfite semichemical pulping of aspen. Tappi 32:400-405(September, 1949).

APPENDIX

Figures A through U

