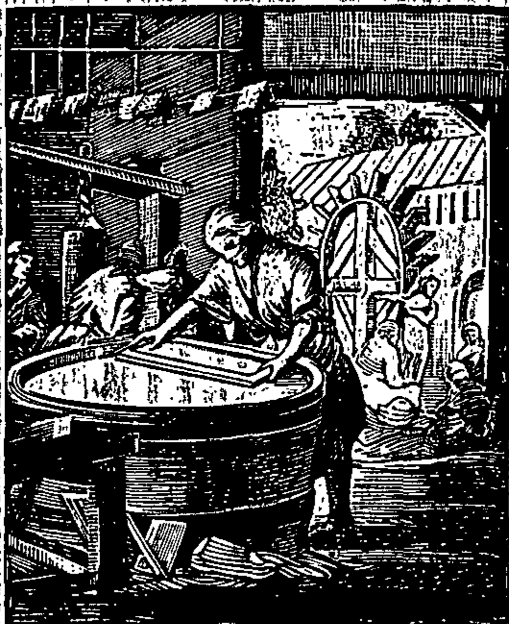

INSTITUTE OF PAPER CHEMISTRY
Appleton · Wisconsin

CONFIDENTIAL

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER MATERIALS:

A FINAL REPORT ON PROCESS STUDIES AND PAPERMAKING CHARACTERISTICS

Project 2500

Report Nineteen
A Progress Report
to
THE GRANTORS

July 5, 1973

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SELECTIVE DELIGNIFICATION OF WOOD AND OTHER MATERIALS:

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SUMMARY

As the last part of a plan to investigate the chlorine dioxide-alkali semichemical pulping of softwoods using chip impregnation with alkali before fiberization, a series of loblolly pine pulps with about 70-85% yield has been made using process conditions which are fully described. The amount of chlorine dioxide used is 4.5-7.5% and it is demonstrated that this oxidant can be substituted on a chemical equivalent basis by chlorine dioxide and chlorine with up to at least 45% chlorine. This means it would be unnecessary to remove chlorine from the gas stream of a chlorine dioxide generator. About one-fourth as much power is required for primary refining compared with when using kraft cooked chips.

The papermaking properties of the about 70-85% yield loblolly pine pulps, which are relatively shive-free and similar in color to high-yield kraft pulp, have been investigated by handsheet evaluation and determination of hydrodynamic properties. There is a clear trend to higher burst, breaking length, stretch, tensile stiffness, ring crush and degrees-to-crack as yield decreases. At 70% yield these strength properties are shown to be near comparable, at sheet densities of about 0.44-0.54 g./cc., to those of a 56% yield kraft pulp (from the same lot of chips) for which sheet densities were 0.53-0.63 g./cc.

For comparable amounts of beating, the filtration resistances of these chlorine dioxide-alkali pulps are shown to be no higher than for a 56% yield kraft pulp when chips were impregnated with alkali before fiberization.

Without alkali impregnation, filtration resistance is relatively higher than for the kraft pulp.

For comparable strength levels, the about 70% yield pulp has a somewhat higher filtration resistance than the kraft pulp. The advantage of increasing the yield of chlorine dioxide-alkali pulps above about 70% is accompanied by the disadvantage of increased filtration resistance for the same strength development.

An intermediate level of burst factor is reached by 70-80% yield pulps. Previous indications on cost suggest that this yield range and the amounts of chemicals used in the related process conditions bracket an attractive pulp cost situation.

As the last part of a plan covering the investigation of hardwood holopulps the results of a web former run using furnishes that include a clay filler are formally reported. Generally, similar sheet properties are obtained when the 70% of the furnish that is bleached red maple kraft pulp is substituted by a bleached red maple holopulp. Both furnishes have similar filtration resistance. Sheets made from the furnish with holopulp have 14% filler compared with 8% for the kraft pulp.

Preparation and testing of red maple holopulps made using chlorine dioxide and chlorine with w/w ratios of 85:15 to 15:85 is described. The results show that for the same process conditions up to 45 w/w % chlorine can be included on a chemical equivalent basis without disadvantage. This reduces the amount of chlorine dioxide needed to about 6% during lignin modification for a high brightness pulp and means the gas stream of a chlorine dioxide generator could be used without the need to remove any chlorine.

INTRODUCTION

The main objectives in this part of the project are to define whether an acceptable unbleached softwood semichemical chlorine dioxide-alkali pulp particularly for linerboard might be made at favorable cost, and to achieve a lower bleached hardwood cost basis through lower chemical cost. Pursuit of these objectives follows earlier activity in this area which was covered in Progress Report Sixteen.

SOFTWOODS — LOBLOLLY PINE

BACKGROUND

From earlier work on softwoods, particularly as described in Progress Reports Thirteen and Sixteen, the position was reached where the essential steps under consideration for producing a high-yield unbleached chlorine dioxide-alkali pulp were:

impregnation/fiberization,
lignin modification,
alkali extraction, and
primary refining.

It was demonstrated that fiberization at a temperature corresponding to steam pressures above atmospheric resulted in less fiber damage and that treatment with alkali before lignin modification resulted in greater lignin removal for the addition of a certain amount of oxidant. For the treatment with alkali before lignin modification, the alternative of chip impregnation with alkali before fiberization has become the focus of most attention.

The primary refining step is included because the yield under consideration is up to at least 80%, which is above the fiber liberation point. Preliminary test work to provide a basis for selecting process conditions for the production of enough pulp to obtain information on papermaking characteristics, was described in Progress Report Sixteen. Some of those results, which are particularly relevant to the selection of process conditions used when making pulps described in this report, are included in Appendix I.

The process conditions in Appendix I that are associated with the use of alkali in chip impregnation and extraction after lignin modification, can be simplified and expressed solely in terms of the amount of alkali, as in Table I. This shows the four combinations of alkali in the set of conditions used, which required the addition of 8 to 15% sodium hydroxide. Other process conditions like temperature, time, and consistency applicable to the impregnation and extraction steps were held constant so that the significant differences in these two steps are shown in Table I.

TABLE I

AMOUNTS OF ALKALI IN IMPREGNATION AND EXTRACTION

Sodium Hydroxide, %	
Impregnation	Extraction
4.0	4.0
4.0	8.0
7.0	4.0
7.0	8.0

The important aspects of pulp yield, lignin content, and oxidant addition from Appendix I may be summarized as shown in Fig. 1. When the amount of oxidant used in lignin modification is 4.5, 6.0, or 7.5% for the set of conditions represented in Table I, each set of results is represented in Fig. 1 by a quadrilateral. Since the set of conditions associated with the use of alkali in the impregnation and extraction steps was a constant factor, the difference in the positions of the quadrilaterals in Fig. 1 must be primarily related to the amount of oxidant used. Furthermore, the relative positions of the quadrilaterals make it apparent that increasing the usage of oxidant not only results in the alkali removing more lignin [(A-B) and (A-C)], but also results in the alkali removing an amount of carbohydrate [(D-E) and (D-F)].

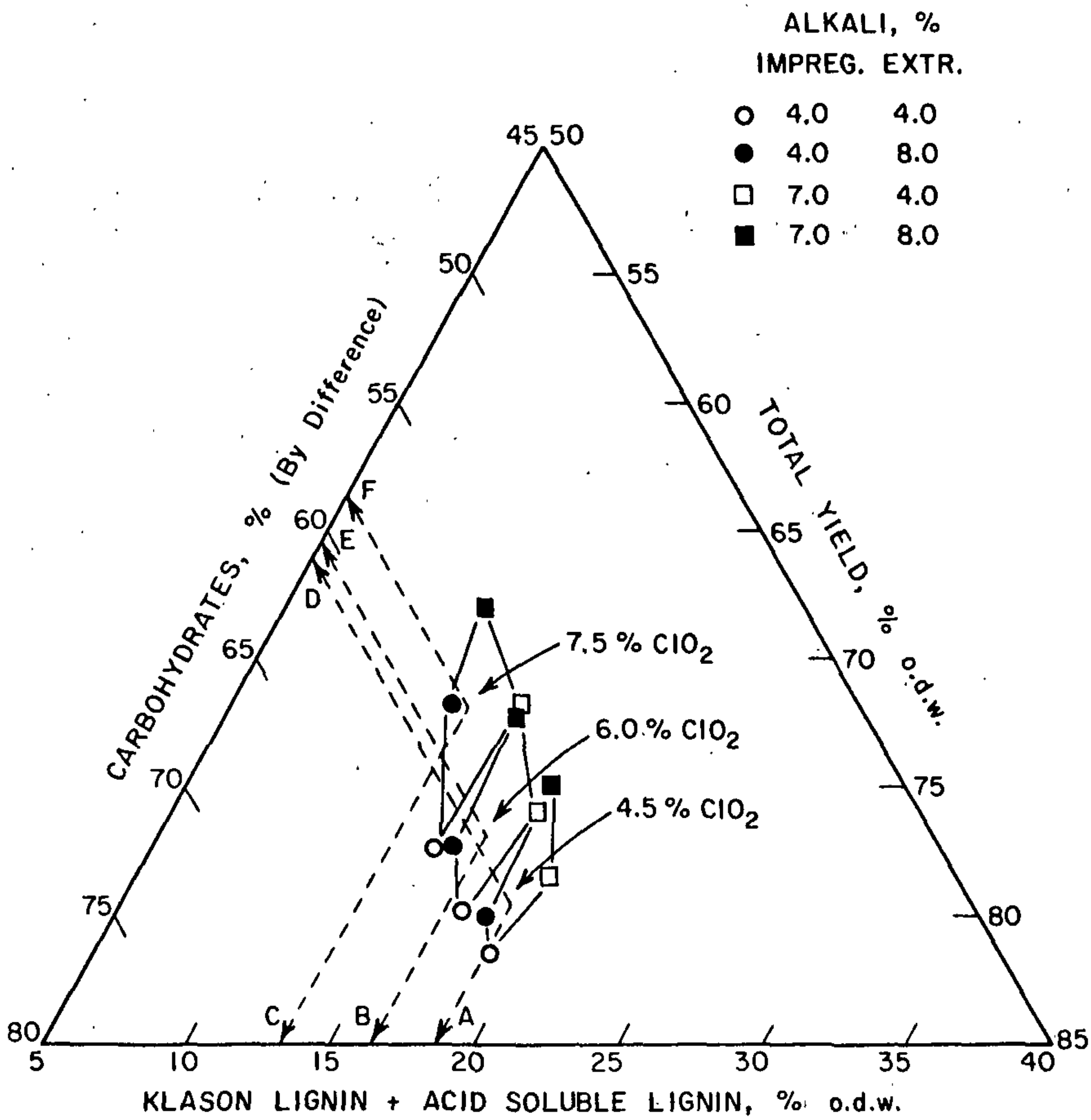

Figure 1. Plots Showing Changes in Yield and Chemical Composition of Pulps for Varying Amounts of Oxidant and the Same Set of Conditions for Alkali Impregnation and Extraction

PLAN

To bring the above work to a conclusion, the plan which was developed envisaged the production of pulps based on the essential steps as indicated above. After primary refining, tests would be made to determine the handsheet and hydrodynamic properties of the pulps using a high-yield kraft pulp for a basis of comparison.

It was planned that the process conditions would be designed to embrace, on the one hand, a pulp that should be at least comparable in strength to the high-yield kraft pulp and, on the other hand, a pulp that should be economically attractive. Earlier work had indicated that it may be necessary to use as much as 6 to 9% chlorine dioxide for the production of a pulp with the level of strength properties desired (Report Thirteen) and as little as about 4.5% chlorine dioxide in the production of a 75% yield pulp to achieve economic attractiveness (Report Eighteen). To embrace an area that would recognize both of these points, the detailed information on which Fig. 1 is based was used to set up process conditions and the salient points of these conditions can be conveniently outlined further with reference to Fig. 1.

It was decided to consider two levels of oxidant usage, namely 4.5 and 7.5% chlorine dioxide. In addition, it was decided to have two levels of alkali-impregnation of chips by using nominally the same conditions as employed to obtain the data in Fig. 1. On this point it is noted that use of more alkali in the impregnation (Fig. 1) had resulted in a lower yield pulp without there being any apparent additional removal of lignin which raises the question of whether or not a lower yield would be advantageous in terms of papermaking properties.

For the alkali extraction, it was decided to use only the higher amount of alkali applicable in Fig. 1, at least to begin with. This would mean producing a total of four pulps from alkali-impregnated chips.

It was also planned that each of these pulps would be primary refined with some variation in the plate gap since an indication had been obtained previously (Report Thirteen) that this could be a significant factor influencing sheet strength.

In addition, to cover the alternative of alkali treatment after fiberization, it was decided to fiberize some chips which had been impregnated with water.

PREPARATION OF PULPS

Impregnation/Fiberization

Loblolly pine chips were impregnated and fiberized in a Bauer No. 418 pressurized refiner system as described in the experimental part. Although chip impregnation with alkali was carried out using nominally the same conditions which gave alkali uptakes of 4.0 and 7.0%, respectively, in preliminary work (Appendix I), the apparent alkali uptake under pilot conditions was 5.3 and 11.7%. The latter figures are based on the amount and analysis of recovered impregnating liquor. They represent maximum figures and are probably higher than the actual uptake.

Obtaining yield data after chip fiberization in the pilot system is made difficult by the fact that all of the chips put into the system are not usually turned out as fiberized product. For example, a significant amount becomes hung-up in the casing of the refiner, and although much of this can be blown out after a run, no provision was made to collect such material in separate containers during this work.

Determination of the soluble solids content in fiberized chips impregnated with 11.7% alkali (o.d. chips basis) gave a value of 16.6% (total solids basis) and after allowing for the apparent alkali content, the implied yield of fiberized chips would be 93% (o.d. chip basis). Since the data on experiments carried out as in Appendix I are more accurate, the more conservative figure of 86.7% yield (Appendix I) was used when proceeding with the production of pulps. A similar approach was used for chips impregnated with the lesser amount of alkali.

Fiberized chips were characterized by Bauer McNett classification and the results are included in the experimental part.

Delignification

Delignification of alkali-impregnated and fiberized chips with chlorine dioxide-alkali was carried out using the process conditions included in Table II. The range of yields is 72 to 86%, which is significantly above the usual yield level of about 55 to 60% for high-yield kraft linerboard pulps. It is noted that when more alkali was used in the chip impregnation, the yield is lower without there being a marked change in the amount of lignin removed, which is supported by the data in Fig. 1. The use of more oxidant resulted in the removal of significantly more lignin, as expected.

It is also noted that the relationship between Kappa number and lignin content is influenced by the process conditions, so that Kappa number cannot be used as a reliable indicator of lignin content. This is illustrated in Fig. 2 which is based on data included in Appendix I.

TABLE II

DELIGNIFICATION OF ALKALI IMPREGNATED LOBLOLLY PINE CHIPS

Code	A-51		A-53	
Impregnation/fiberization: NaOH uptake, %	5.3		11.7	
Assumed yield, %	93.0[a]		86.7[a,b]	
Lignin modification: 25 to 35°C. in 60 min., 8% consistency				
ClO_2, %	4.5	7.5	4.5	7.5
Time, min.	25	50	30	55
Final pH	2.0	1.7	2.1	1.5
Yield, %	--	--	--	--
Alkali extraction: 60 min., 90°C., 12% consistency				
NaOH, %	8.0	8.0	8.0	8.0
Final pH	11.6	11.4	11.4	11.3
Yield, %	86	77	80	72
Kappa no.	105.5	79.3	116	78.0
Klason lignin, % o.d. pulp	22.5	16.7	22.6	16.0
Acid sol. lignin, % o.d. pulp	1.4	1.9	1.4	1.9
Code	5.3/4.5/86	5.3/7.5/77	11.7/4.5/80	11.7/7.5/72

[a]These yields were assumed on the basis of data in Appendix I in which similar concentrations of alkali, etc., were used for impregnation, etc.

[b]Soluble solids in fiberized chips were 16.6%, and after allowing for inorganic content (11.7/111.7 or 10.5 g./100 g.o.d.) this gives 83.4/89.5 or a 93% yield of fiberized chips, hence the more conservative figures of 93.0 and 86.7% were used in calculating pulp yields.

To determine the influence of omitting alkali in the chip impregnation, delignification of water-impregnated and fiberized chips was carried out using the process conditions in Table III. In this it can be seen that when 11.7% sodium hydroxide was used in the pretreatment, the pulp yield was a relatively low 66%. For the other example in Table III where 5.3% sodium hydroxide was used in the pretreatment to give an 86% yield before lignin modification, the pulp yield was 70%. This pulp yield ties-in reasonably well with the value of 68% obtained in Appendix I for the similar delignification of the 87% yield product before lignin modification where 7.0% alkali was used in chip impregnation. It is not surprising that the greater degree of subdivision applicable in Table III compared with Appendix I results in less alkali (5.3%) being needed in the pretreatment to reach about the same yield level before lignin modification (also see footnote).

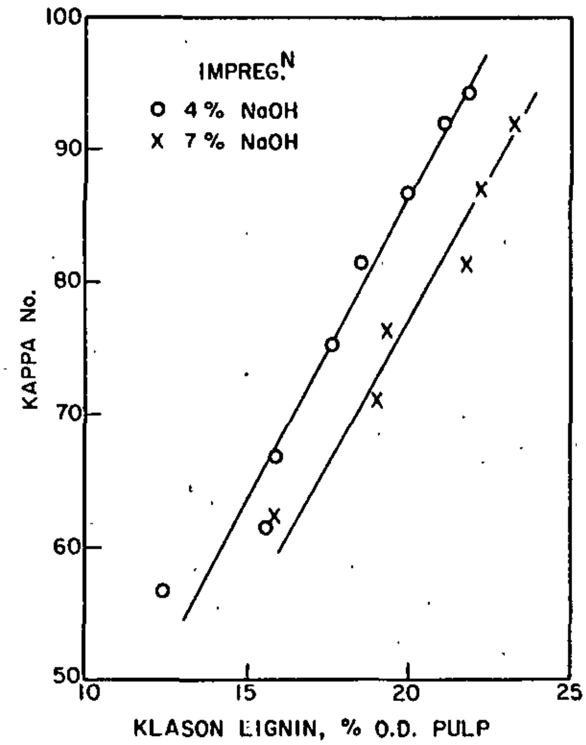

Figure 2. Plots of Kappa No. vs. Klason Lignin in Pulps with 4 and 7% Sodium Hydroxide Used in Impregnation (Table I).

Primary Refining

Primary refining is the expression used in this report to refer to the mechanical action needed to achieve fiber separation. This is necessary for the products of delignification in the 72 to 86% yield range as in Table II because the point of fiber liberation as discussed recently by McGovern (1) has not been reached.

It is considered that Pulp 0-5.3/7.5/70 (Table III) should be compared with Pulp 11.7/7.5/72 (Table II) (rather than with Pulp 5.3/7.5/77) on the basis of known and assumed yield levels of 86-87%, before lignin modification. The apparent discrepancy in the yields for the case of Pulp 0-5.3/7.5/70 compared with Pulp 5.3/7.5/77 (both of which were produced using similar chemical process conditions) is believed to reflect a difference in the degree of subdivision during alkali pretreatment plus the liklihood of the related amount of alkali being inflated for the latter because of the method of determination.

TABLE III

DELIGNIFICATION OF WATER IMPREGNATED AND FIBERIZED LOBLOLLY PINE CHIPS

Code	A-52	
Alkali Pretreatment		
Sodium hydroxide, %	11.7	5.3
Consistency, %	37	37
Pressure, p.s.i.g.	75[b]	75[a]
Time at pressure, min.	5	5
Final pH	12.1	--
Yield, %	75	86
Lignin modification: 25 to 35°C. in 60 min., 8% consistency		
ClO_2, %	4.5	7.5
Time, min.	40	55
Final pH	1.9	1.7
Alkali extraction: 60 min., 90°C., 12% consistency, 8% sodium hydroxide		
Final pH	11.2	11.2
Yield, %	66	70
Kappa no.	102	77.5
Klason lignin, % o.d. pulp	19.7	15.8
Acid sol. lignin, % o.d. pulp	1.4	0.96
Code	0-11.7/4.5/66	0-5.3/7.5/70

[a]Time to 75 p.s.i.g. by direct steaming was 1 min.
[b]Estimated time to 75 p.s.i.g.:-1 min.
[c]Steamed previously for 2 min. at 15 p.s.i. then pressure was relieved to 1 atm. and this operation was repeated before increasing the pressure to 75 p.s.i.g.

A Sprout-Waldron machine illustrated in Report Sixteen, was used for primary refining and the procedure followed is described in the Experimental part. A high-yield kraft pulp obtained in 56% yield (Pulp HYK/56) was made (see Experimental) to provide a reference pulp for a basis of comparison.

About four times as much power was required when primary refining kraft cooked chips compared with fiberized chips for the same conditions of temperature, consistency, feed rate, and plate gap. This is illustrated in Fig. 3.

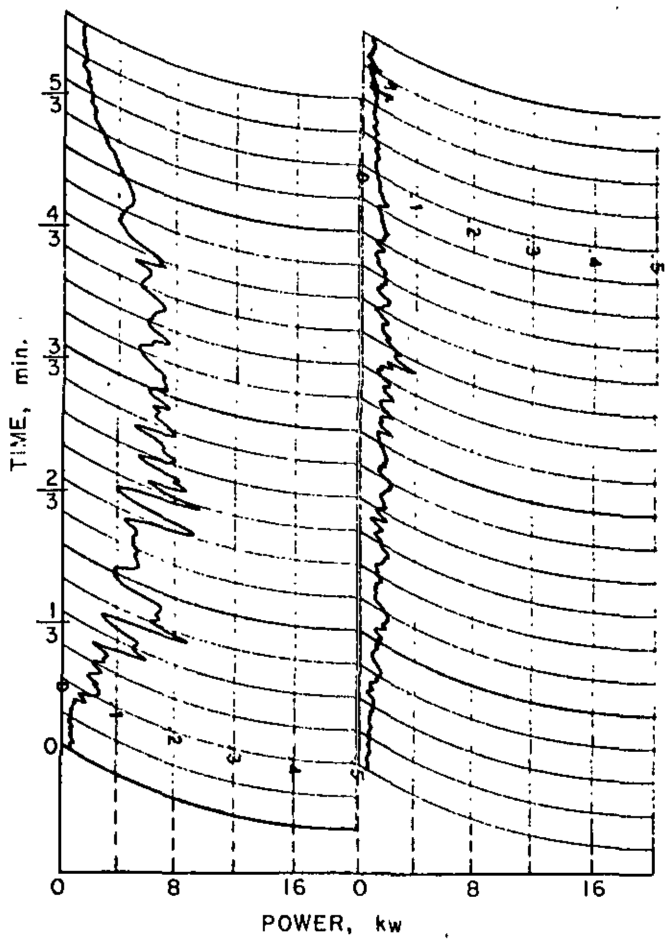

Figure 3. Typical Chart Strips from Watt-Hour Meter Showing Readings for 56% Yield Kraft Pulp (Left) and 80% Yield Chlorine Dioxide-Alkali Pulp (Right) During Primary Refining Under Similar Conditions. Chart Speed: 3 in./min.; Plate Gap: 0.018 in.

The freeness values obtained for various pulps after primary refining at different plate gaps prior to evaluation by handsheet testing and determination of hydrodynamic properties are presented in Table IV. From this, it can be seen that the freeness levels of the chlorine dioxide-alkali pulps made using alkali-impregnated chips were at least as high as for a high-yield kraft pulp.

TABLE IV

CANADIAN FREENESS AFTER PRIMARY REFINING

Consistency, 5.0%; water temp., 190-200°F.;
feed rate, approx. 300 g. o.d./min.

Code		Plate gap, 0.001 in. 18 Canadian Freeness, ml.	5
HYK/56		720	705
0-5.3/7.5/70	Water-Impregnated Chips	745	600
0-11.7/4.5/66	Water-Impregnated Chips	730	--
5.3/4.5/86	Alkali-Impregnated Chips	740	725
5.3/7.5/77	Alkali-Impregnated Chips	735	720
11.7/4.5/80	Alkali-Impregnated Chips	740	725
11.7/7.5/72	Alkali-Impregnated Chips	740	730

PAPERMAKING PROPERTIES

Handsheet Evaluation

For handsheet evaluation, the pulps were beaten in a PFI mill and tested using the procedures as indicated in the Experimental part. The results obtained for the pulps produced as in Table II are summarized in Table V. More complete test data on which this table is based are given in Appendix II.

From Table V it will be seen that burst factor, breaking length, stretch, tensile stiffness, ring crush, and degrees-to-crack (see footnote) all tend to have more favorable values as yield decreases. Sheet density does not appear to follow the same trend so clearly; in fact, it seems to be more related to the amount of oxidant used during delignification. It is also noted that most properties of pulps with about equal lignin content are more favorable at the lower yield level achieved by using more alkali during the impregnation of chips.

The test results obtained for pulps produced as in Table III without alkali impregnation of chips, are summarized in Table VI which includes some results from Table V for comparison. More complete test data on pulps produced as in Table III are given in Appendix III.

From Table VI it will be seen that the pulp produced at 70% yield without alkali-impregnation of chips has essentially comparable properties to that produced at 72% yield with alkali-impregnation of chips and using the same amount of oxidant. This lends support to the basis for calculating yield in the case of the latter pulp. At the same time this pulp does have somewhat better properties, which is what would be expected if there was less chip damage when using alkali-impregnation.

Degrees-to-crack are determined by the liner cracking test. This is a measure of the rupture angle associated with the first appearance of a crack in the linerboard surface when a clamped specimen of linerboard is folded over an anvil of small diameter in a Linerboard Cracking Tester. Good correlations have been found between linerboard cracking angle and the cracking of combined board, especially for linerboard with a basis weight of 69 and 90 lb. per 1000 sq. ft. An earlier investigation on the subject of linerboard cracking which describes the tester and results obtained is covered in a summary report (2).

TABLE V

SUMMARY OF HANDSHEET TEST RESULTS FOR PULPS PRODUCED AS IN TABLE II

Pulp Code	5.3/4.5/86	11.7/4.5/80	5.3/7.5/77	11.7/7.5/72
Pulp yield, %	86	80	77	72
Kappa no.	106	116	79	78
Handsheet density, g./cc.	0.39-0.51	0.38-0.51	0.47-0.57	0.44-0.54
Burst factor	18-27	22-35	30-40	39-50
Breaking length, km.	3.5-5.1	3.9-6.3	5.0-6.7	5.8-7.5
Stretch, %	1.8-2.0	1.9-2.4	2.3-2.7	2.5-2.8
Tear factor (Elmendorf)	72-57	106-76	81-65	116-90
Tensile stiffness, Et, kg./cm.	286-371	296-424	340-424	380-438
Modified ring crush, lb./in.	4.7-5.7	4.7-5.8	5.2-6.0	5.4-6.6
Degrees-to-crack	40-36	46-43	50-44	52-47

TABLE VI

SUMMARY OF HANDSHEET TEST RESULTS FOR PULPS PRODUCED AS IN TABLE III

Pulp Code	0-5.3/7.5/70	11.7/7.5/72	0-11.7/4.5/66	11.7/4.5/80
Pulp yield, %	70	72	66	80
Kappa no.	78	78	102	116
Handsheet density, g./cc.	0.46-0.55	0.44-0.54	0.42-0.55	0.38-0.51
Burst factor	35-45	39-50	28-44	22-35
Breaking length, km.	5.5-7.2	5.8-7.5	4.8-7.3	3.9-6.3
Stretch, %	2.3-2.7	2.5-2.8	2.1-2.8	1.9-2.4
Tear factor (Elmendorf)	104-83	116-90	118-89	106-76
Tensile stiffness, Et, kg./cm.	379-442	380-438	348-442	296-424
Modified ring crush, lb./in.	5.0-5.6	5.4-6.6	5.0-6.6	4.7-5.8
Degrees-to-crack	48-46	52-47	43-47	46-43

Results for the pulp produced at 66% yield as in Table III are also included in Table VI. In spite of its relatively low yield, this pulp did not have properties as favorable as those with 70 and 72% yields, as discussed in the above paragraph, which were produced using a greater amount of oxidant. This illustrates that lower yield does not necessarily imply higher strength properties. The use of less oxidant in producing this 66% yield pulp gives strength properties overlapping those of an 80% yield pulp produced using the same amount of oxidant and included in Table VI for comparison.

The results, as summarized in Table V, have been compared graphically with those obtained for the high-yield kraft reference pulp for which more complete test data are given in Appendix IV. Figure 4 illustrates this comparison for the case of burst factor.

In the primary refining step of pulp production, different plate gaps were used. This had an influence on the level of strength properties reached when beating for the same amount in a PFI mill and full details on the differences observed are covered in the relevant Appendices. Pulps produced under different process conditions or at different yield levels appear to respond differently to changes in plate gap. For example, when the plate gap was decreased from 0.018 in. to 0.005 in. for the 86% yield chlorine dioxide-alkali pulp, a higher level of burst was achieved whereas with the same change for the 56% yield kraft pulp, a lower level of burst was achieved. Hence, the results associated with using plate gaps of 0.005 and 0.018 in., respectively, for the 86 and 56% yield pulps were selected when drawing curves to make comparisons as in Fig. 4. On the other hand, with the same change in plate gap for the case of the 72% yield chlorine dioxide-alkali pulp, no change in the level of burst was observed, compared with a significant change for the

56% yield kraft reference pulp. This situation is illustrated in Fig. 4 by the inclusion of a second set of points for these two pulps. In subsequent figures, second sets of points have been included only for the 72% yield pulp.

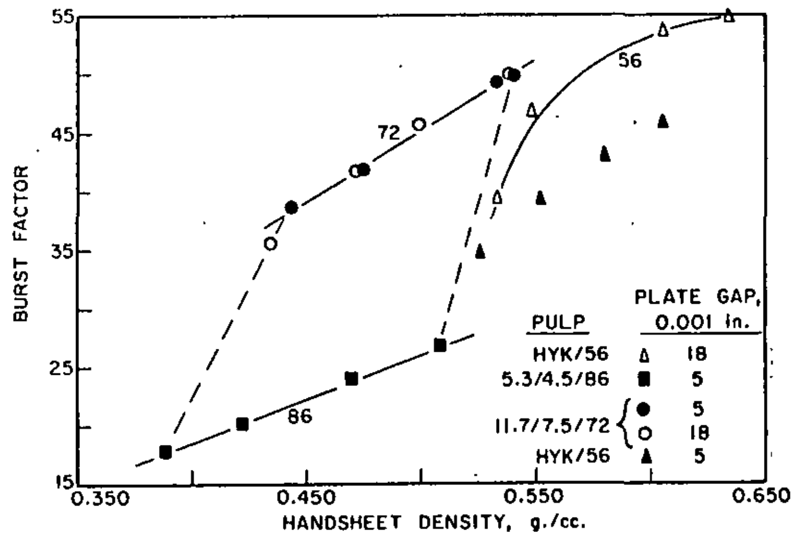

Figure 4. Plots of Burst Factor vs. Handsheet Density for 72 and 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulps Compared with a 56% Yield Loblolly Pine Kraft Pulp

Comparisons analogous to that in Fig. 4 are shown in Fig. 5-8 for breaking length, tear factor, tensile stiffness, and degrees-to-crack data. In Fig. 4-8, the overall pattern of results is similar in that the 72% yield chlorine dioxide-alkali pulp is essentially equal to the 56% yield kraft reference pulp except that the sheet densities of the former are lower. The tendency for sheet properties of this softwood chlorine dioxide-alkali pulp to be comparable to the kraft reference pulp at lower density has not been observed so far in work on hardwoods.

The curves for the 72 and 86% yield pulps in Fig. 4-8 bracket an area within which the corresponding test data for the 80 and 77% yield pulps also fit. As yield decreases, more favorable values tend to be realized within the quadrilateral areas marked in the figures.

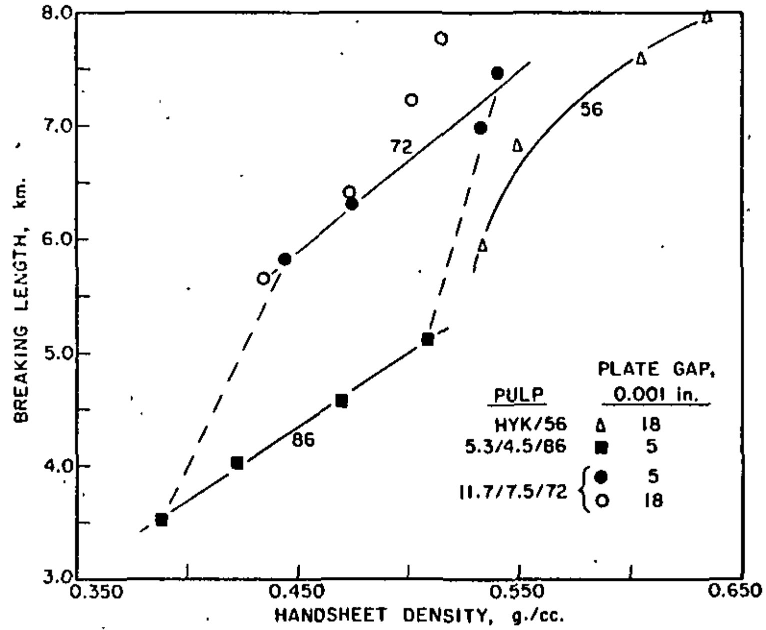

Figure 5.- Plots of Breaking Length vs. Handsheet Density for 72 and 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulps Compared with a 56% Yield Loblolly Pine Kraft Pulp

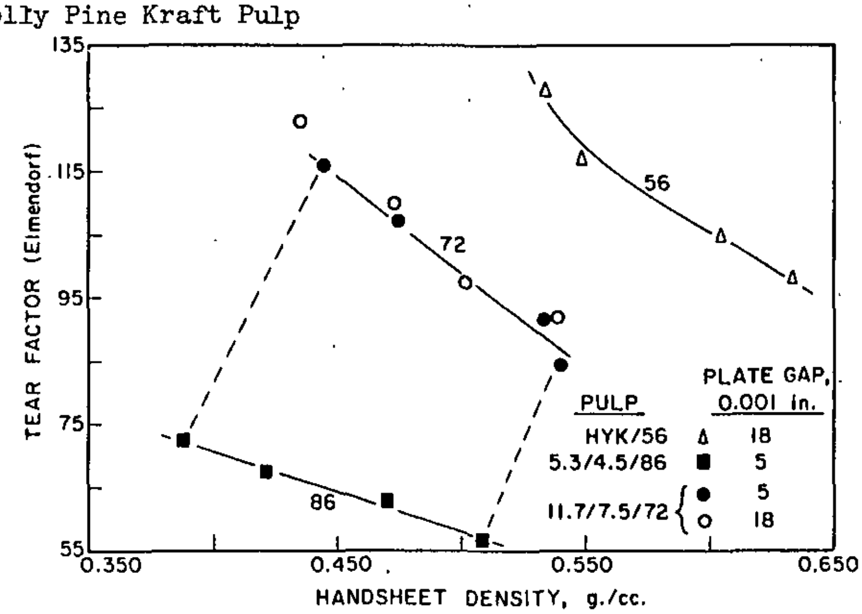

Figure 6. Plots of Elmendorf Tear Factor vs. Handsheet Density for 72 and 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulps Compared with a 56% Yield Loblolly Pine Kraft Pulp

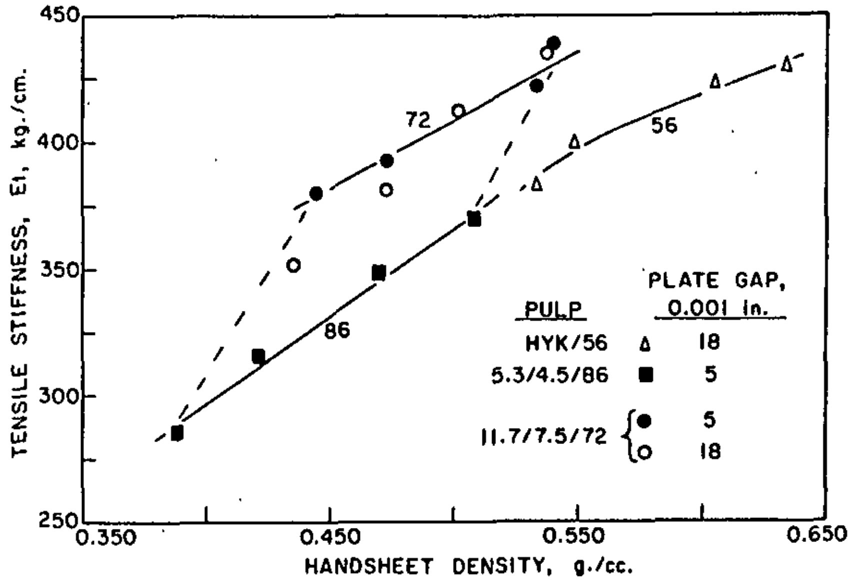

Figure 7. Plots of Tensile Stiffness vs. Handsheet Density for 72 and 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulps Compared with a 56% Yield Loblolly Pine Kraft Pulp

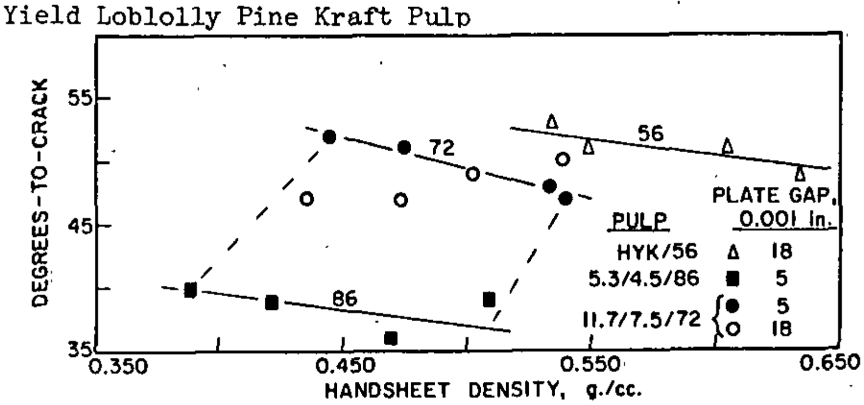

Figure 8. Plots of Degrees-to-Crack vs. Handsheet Density for 72 and 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulps Compared with a 56% Yield Loblolly Pine Kraft Pulp

For the case of ring crush tests, less separation of the values for 72 and 86% pulps was found as shown in Fig. 9. This shows that the range of values for the 86% yield pulp reached the lower end of the range for the kraft reference pulp.

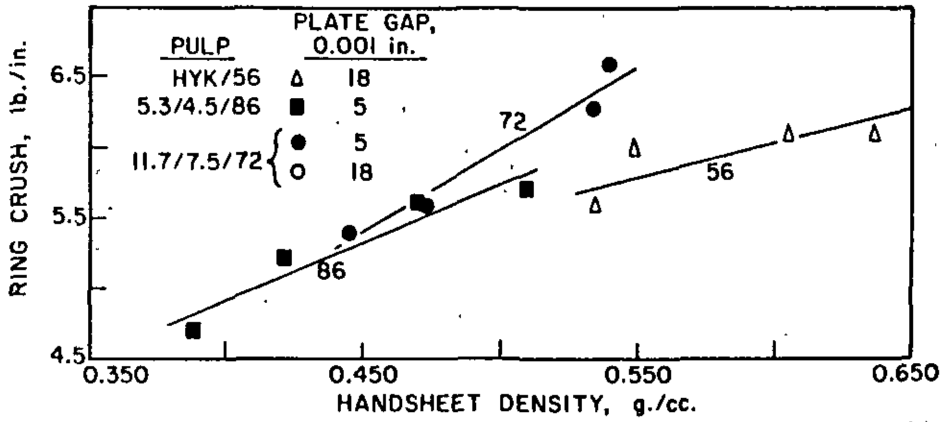

Figure 9. Plots of Ring Crush vs. Handsheet Density for 72 and 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulps Compared with a 56% Yield Loblolly Pine Kraft Pulp

It is apparent from the above that a loblolly pine chlorine dioxide-alkali pulp can be produced at about 70% yield with papermaking strength properties about comparable to a 56% yield kraft pulp from the same chip supply. In addition, it is obvious that the 72% yield pulp produced using 7.5% oxidant would cost appreciably more than the 86% yield pulp produced using 4.5% oxidant. From the indications on cost referred to above, it appears an economically attractive situation might lie somewhere between these two. While it appears unlikely that papermaking strength properties comparable to those of the 72% yield pulp would be realized, one question that arises concerns whether it is necessary to achieve that level of strength and, if not, whether this class of pulps might have some other possible advantages.

Regarding this last point, there are two observations which it seems appropriate to note. These relate to color and shives. The color of the chlorine dioxide-alkali pulps even at the 86% yield level is not markedly different from that of a high-yield kraft pulp. In addition, all of these pulps in the 72-86% yield range were relatively shive-free including the 86% yield pulp, as illustrated in Fig. 10.

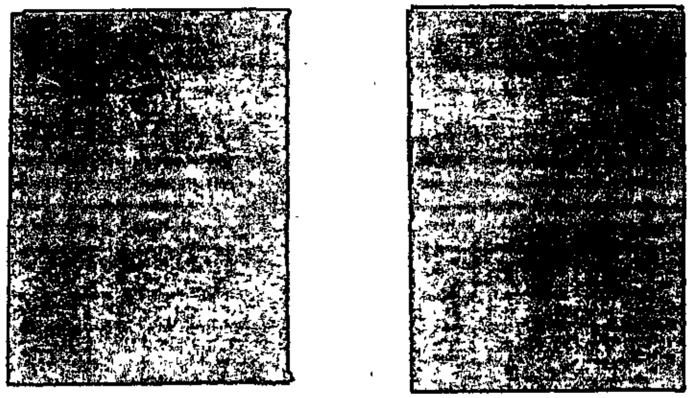

Figure 10. Handsheet Tabs from 86% Yield Loblolly Pine Chlorine Dioxide-Alkali Pulp Beaten in PFI Mill for 450 (Left) and 1650 (Right) Counter Revolutions

Hydrodynamic Properties

Filtration resistance data were obtained as described in the experimental part on samples of pulps used for providing the handsheet test results discussed above. The general trends of filtration resistance measurements are illustrated in Fig. 11, which is for pulps that were all primary refined using nominally the same conditions before beating in a PFI mill. Complete filtration resistance data are included in Appendix V.

Figure 11 shows that the 70% yield chlorine dioxide-alkali pulp made without alkali-impregnation of chips tended to have significantly higher filtration resistance values than found for either a comparable pulp made from alkali-impregnated chips or the high-yield kraft reference pulp. This demonstrates an advantage of alkali-impregnation before chip fiberization. Figure 11 also shows that the chlorine dioxide-alkali pulps when compared with the kraft reference pulp tend to have a similar rate of increase in filtration resistance during the early and intermediate stages of beating. For the later stages of beating, the rate of increase becomes relatively slower for the chlorine dioxide-alkali pulps.

These differences in the rate of increase in filtration resistance appear to be mainly derived from differences in the development of specific surface on beating, as illustrated in Fig. 12. This figure is based on more complete data on hydrodynamic properties which are included in Appendix V.

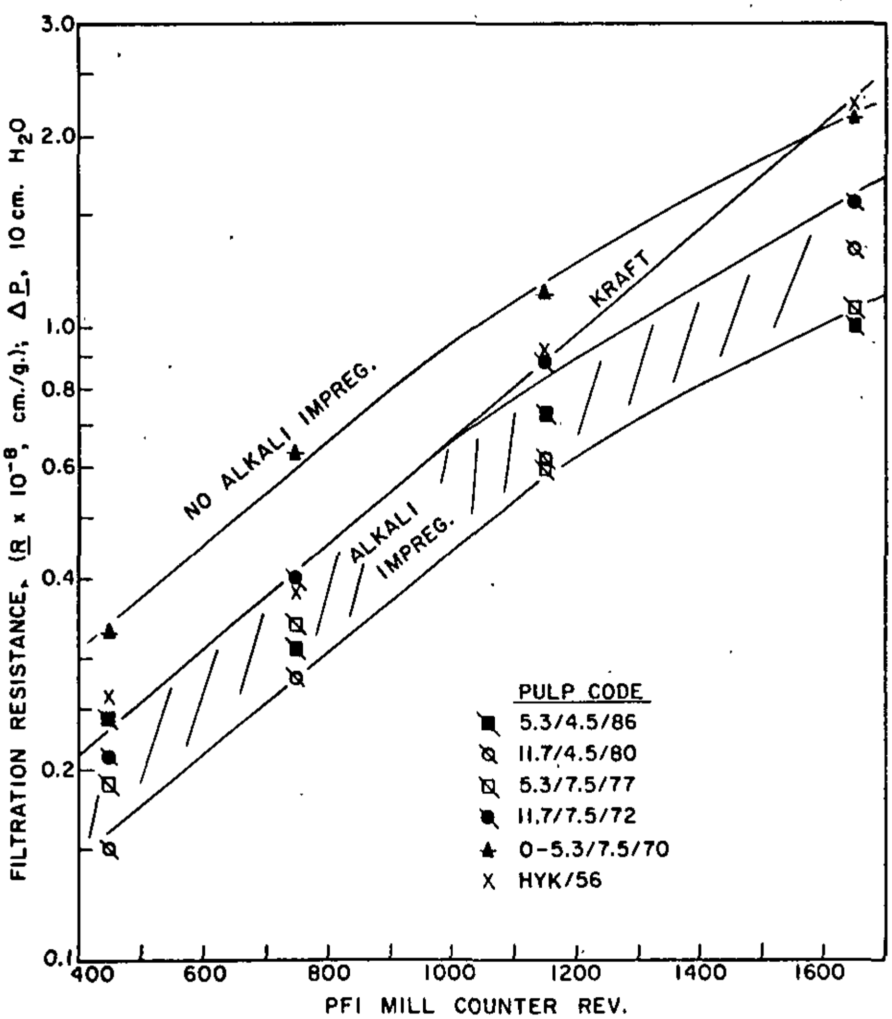

Figure 11. Plots of Filtration Resistance ($\underline{R} \times 10^{-8}$, cm./g.) at $\Delta\underline{P}$ = 10 cm. H_2O vs. PFI Mill Counter Revolutions for Pulps Primary Refined Under the Same Conditions with 0.018 in. Plate Gap

The relative strength of handsheets made from pulps with different filtration resistance values as in Fig. 11 can be illustrated by plotting burst factor, for example, vs. filtration resistance as presented in Fig. 13.

This figure also includes points without slashes which are for pulps that were primary refined with a plate gap of 0.005 in. It will be noted that for each pulp, the curves associated with the use of two different plate gaps, namely, 0.005 and 0.018 in., tend to overlap except for the 80% yield pulp. Thus, as a general rule, it appears that at least within this range of plate gaps, although variation in gap may change the strength properties obtained after a given amount of subsequent beating, there is no marked change in the relationship between filtration resistance and burst factor.

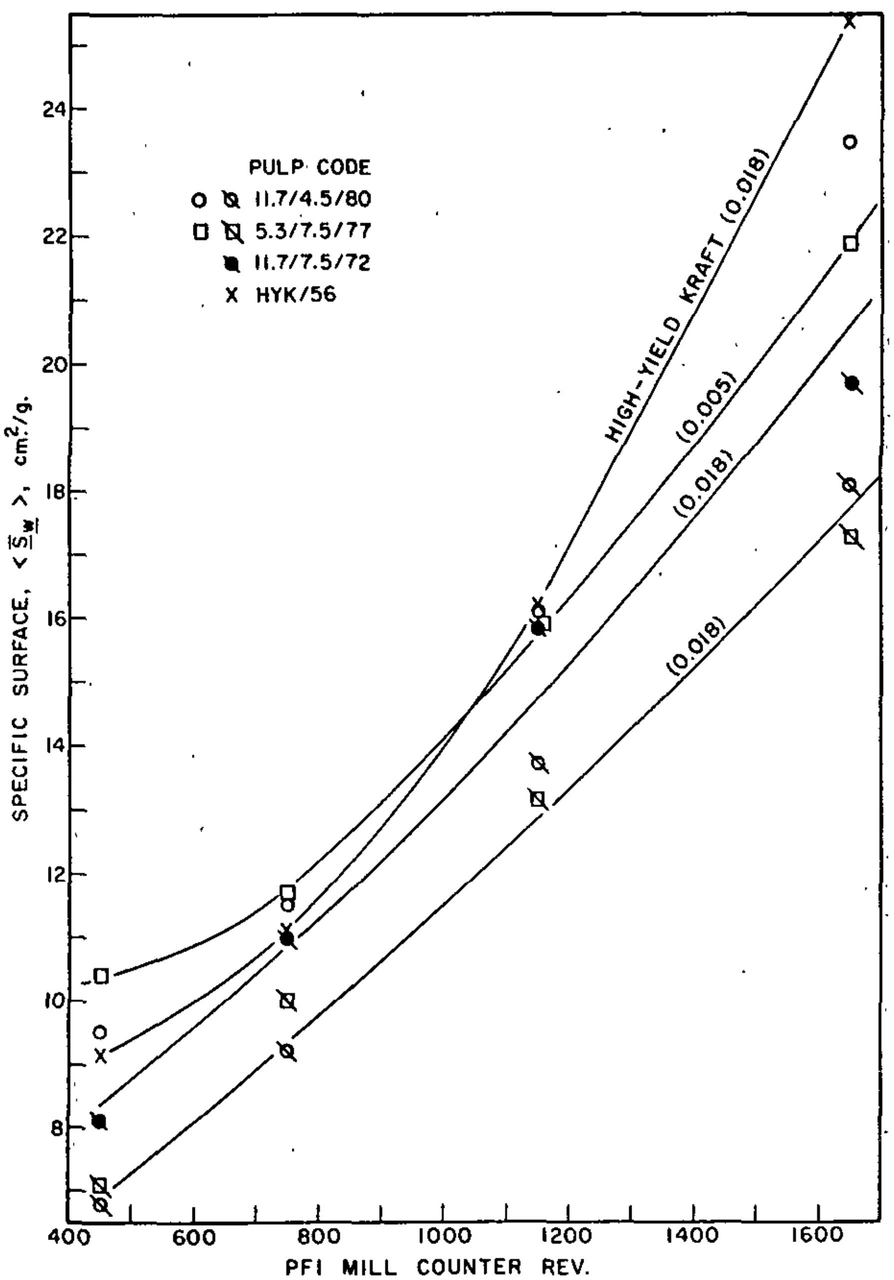

Figure 12. Plots of Specific Surface vs. PFI Mill Counter Revolutions for Chlorine Dioxide-Alkali Pulps and a Kraft Reference Pulp

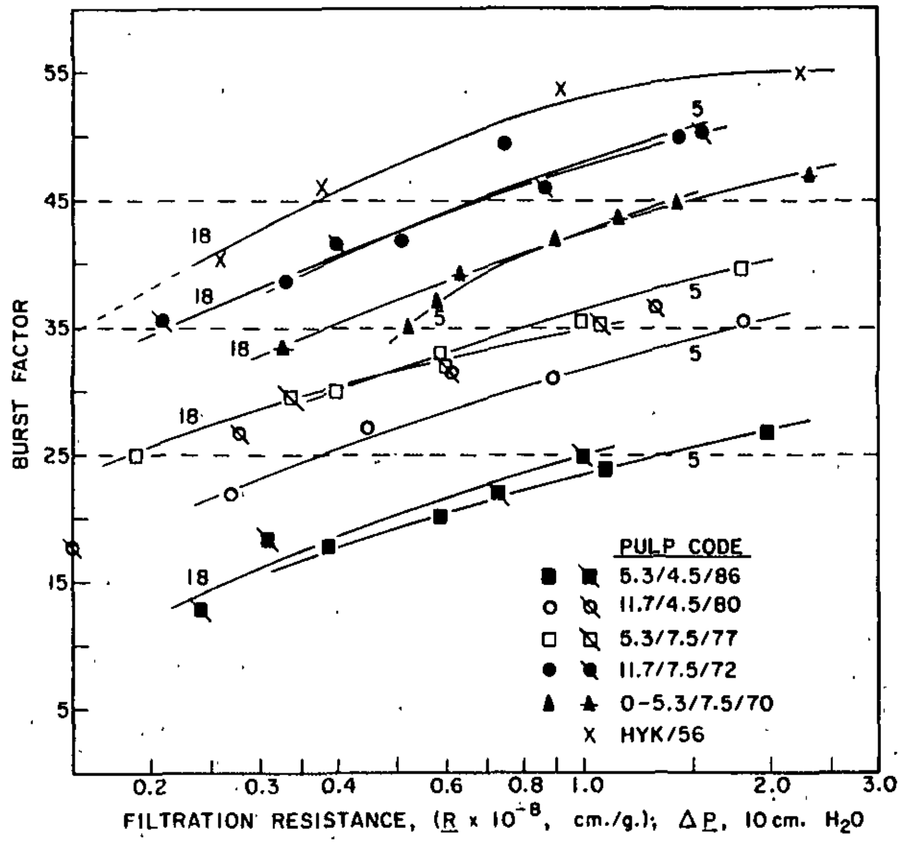

Figure 13. Plots of Burst Factor vs. Filtration Resistance ($\underline{R} \times 10^{-8}$, cm./g.) at $\overline{\Delta P}$ = 10 cm. H_2O for Loblolly Pine Chlorine Dioxide-Alkali and High-Yield Kraft Pulps

Considering burst factor levels of say 25, 35, and 45 and excepting the 70% yield chlorine dioxide-alkali pulp, which was produced without alkali-impregnation of chips, it is clear that the benefits of higher pulp yield applicable to any of these levels is associated with greater filtration resistance. The intermediate level of burst, which is reached in the early stages of beating the high-yield kraft reference pulp is reached by all except the highest yield chlorine dioxide-alkali pulp. On the basis of previous considerations (Report Eighteen) the 80% yield pulp, for example, which was produced using 4.5% oxidant, is regarded as economically attractive. The acceptability of such a pulp would appear dependent upon this intermediate level of burst being adequate, consideration of other properties, and upon accommodation of the increased filtration resistance.

The relationships between the curves in Fig. 13 show that for a particular filtration resistance as the yield level of chlorine dioxide-alkali pulps (produced using the same process steps) is decreased, there is an increase in burst factor which reflects a separation in the burst factor vs. filtration resistance curves. In another study (3) on high-yield southern pine kraft pulps with Kappa number 53-116 which corresponds to about 50-60% yield, no such separation in similarly plotted data was found. This is shown in Fig. 14. The reason for this observed divergence in behavior of these two different kinds of pulp is not apparent.

It is noted that relationships similar to those discussed above for Fig. 13 are observed when burst factor is plotted as a function of Canadian freeness which is shown in Fig. 15. Thus, it appears that Canadian freeness can be used as an alternative to filtration resistance for the pulps refined and beaten to the extent applicable to the data in Fig. 15.

LOWER CHLORINE DIOXIDE USAGE

To determine the feasibility of partial substitution of chlorine dioxide by chlorine, four different ratios of chlorine dioxide and chlorine with 85 to 35% chlorine dioxide by weight were investigated using similar chemical process conditions. These ratios bracket the composition of the gas stream from a chlorine dioxide generator, as discussed further in the part of this report on hardwoods.

The results obtained are presented in Table VII and the process conditions used are essentially the same as for Pulp 11.7/7.5/72 prepared as in Table II. In Table VII the Kappa numbers are consistently higher than found

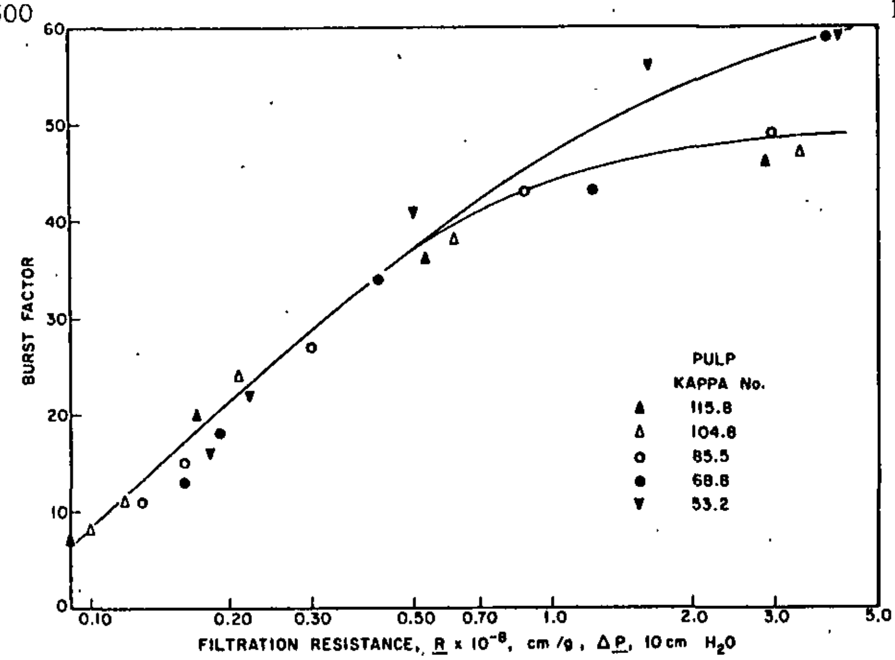

Figure 14. Plots of Burst Factor vs. Filtration Resistance ($\underline{R} \times 10^{-8}$, cm./g.) at $\underline{\Delta P}$ = 10 cm. H_2O for Southern Pine High-Yield Kraft Pulps

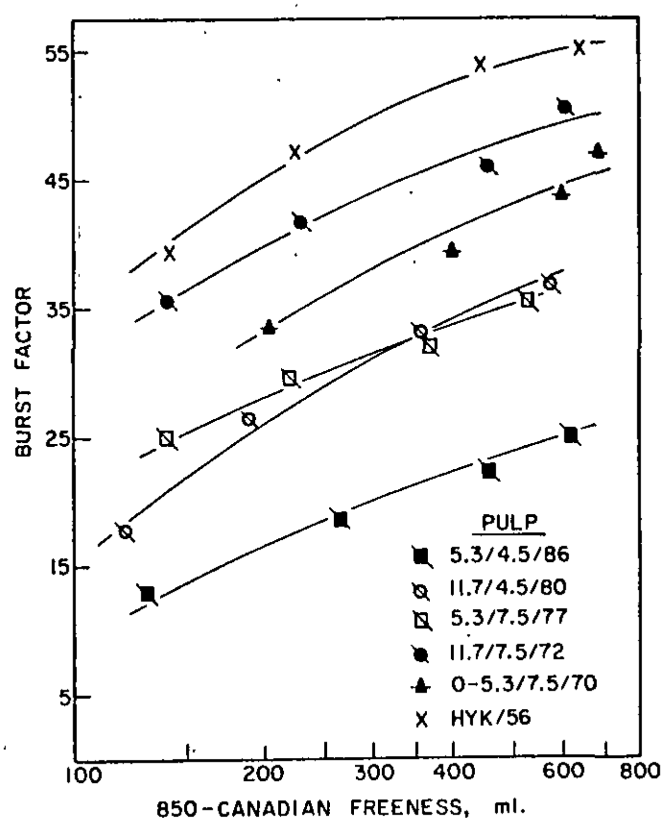

Figure 15. Plots of Burst Factor vs. 850-Canadian Freeness, ml. for Loblolly Pine Chlorine Dioxide-Alkali and High-Yield Kraft Pulps

for the pulp in Table II, and it is believed this may be related to the lower final pH after alkali extraction for the case of the results in Table VII.

TABLE VII

CHLORINE DIOXIDE/CHLORINE-ALKALI PULPING OF LOBLOLLY PINE

Impregnation/fiberization as in Table II

Lignin modification: 25 to 35°C. in 60 min., 7.5% ClO_2 on chemical equiv. basis

ClO_2:Cl_2 (w:w)	100	85:15	65:35	55:45	35:65
Chlorine dioxide, %	7.5	7.0	6.2	5.7	4.4
Chlorine, %	0	1.2	3.4	4.7	8.1
Consistency, %	8.0	8.0,8.0[a]	7.9	6.9,8.0[a]	5.3,6.2[a]
Time, min.	70	65,65	60	50,50	45,45
Final pH	1.4	1.6,1.3	1.3	1.3,1.2	1.2,1.2

Alkali extraction: 8.0% sodium hydroxide, 12% consistency, 90°C., 60 min.

Final pH	10.8	10.8,10.8	10.8	10.7,10.7	10.7,10.8
Yield, %	73.4	72.5,72.6	73.7	70.9,74.1	71.0,72.0
Kappa no.	86.5	83.6,89.8	85.6	83.6,91.9	86.2,89.9

Primary refining: as in Table IV, except with 0.010 in. gap

Pulp codes:	11.7/7.5(100)	11.7/7.5(85:15)	--	11.7/7.5(55:45)	--

[a]Duplicate runs.

Evaluation data were obtained by beating in a PFI mill and handsheet testing, for those pulps prepared using 100:0, 85:15, and 55:45 chlorine dioxide: chlorine as indicated in Table VII. No significant differences were observed in the evaluation data which are given in Appendix VI. Thus, it is concluded that in the production of loblolly pine pulps as described in this report, the chlorine dioxide used for lignin modifications can be substituted by the chemical equivalent amount of chlorine dioxide and chlorine containing up to at least 45% chlorine by weight. This means the oxidant could consist of a mixture of chlorine dioxide and chlorine as in the gas stream from a chlorine dioxide generator.

EXPERIMENTAL

Raw Materials

The loblolly pine (*Pinus taeda* L.) consisted of the other half of the bolts (ex-Union Camp) previously used, as described in Progress Report Sixteen, plus about an equal quantity of loblolly pine from another source (Kimberly-Clark).

Alkali Impregnation of Chips

Screened chips were presteamed and impregnated with aqueous sodium hydroxide in two lots in a digester at Bauer Bros., Springfield, Ohio. Different alkali concentrations were used in each impregnation as detailed in Table VIII and based on preliminary studies described in Progress Report Sixteen.

Water Impregnation of Chips

Chips were steamed in a 2-cu. ft. digester in a basket for 2 min. at 15 p.s.i.g., the pressure released to atmosphere, the chips steamed for a further 2 min. at 15 p.s.i.g., then covered with water at ambient temp. with a nitrogen overpressure of 100 p.s.i.g. for 30 min. Water-impregnated chips were allowed to drain for 30 min. before removing them from the digester; chip code A-52. The procedure was repeated as necessary.

Fiberization of Impregnated Chips

Alkali and water impregnated chips were fiberized in the Bauer machine described in Progress Report Thirteen and related data are given in Table IX.

TABLE VIII

ALKALI IMPREGNATION OF LOBLOLLY PINE CHIPS

Code	A-51	A-53
Chips		
Wet weight of chips, lb.	121	121
O.d. weight, lb.	75	75
Alkali		
Sodium hydroxide, lb. + water, gal.	15.1 + 79.4	26.5 + 79.4
g.p.l. (sp.gr.)	22.0 (1.010)	39.6 (1.020)
Presteam Digester		
Two min. at 15 p.s.i.g. to give temp. 165-170°F.		
Chip Charging and Presteaming		
Time to charge, min.	14	16
Presteam 2 min. at 15 p.s.i.g.		
Temp., °F.	165	157
Blow, drain condensate and repeat		
Temp., °F.	225	195
Liquor Charging and Impregnating		
Temp., °F.	220	200
Impregnation time, min.	30	30
press, p.s.i.g.	100	100
Liquor and Chip Discharge		
Recovered liquor, gal. (lb.)	69.6 (588)	70.5 (605)
pH	13.4	13.5
g.p.l.	18.2	29.6
sp. gr.	1.015	1.030
Sodium hydroxide applied, % o.d. chips	5.3	11.7
Wet weight of chips, lb.	206.25	222.8
O.d. weight of chips, lb.	76.3	83.6

TABLE IX

FIBERIZATION DATA FOR LOBLOLLY PINE CHIPS

Refiner	No. 418 Pressurized Bauer		
Plates (0.010 in. taper)	1 set 36325/1 set 36325		
Code	A-52	A-51	A-53
Weight used for run, lb. o.d.	64	70.9	75.7
Moisture content, %	61	63	63
Steam pressure, p.s.i.g.	75	75	75
Steaming time, min.	5.0	5.0	5.0
Plate clearance, 0.001 in.	35	35	35
Run time, min.	7.4	7.0	7.5
Feed rate, o.d. tons/day	6.2	7.3	7.3
Load, brake h.p. days/o.d. ton	3.1[a]	2.5[a]	2.7[a]

[a]Value should be increased 20% to obtain the estimated total, including allowances for no-load powers and motor efficiency.

Bauer McNett Classification

Fiberized chips were characterized by Bauer McNett classification carried out in accordance with TAPPI Standard Method T 233 su-64. The screens used and the classification data from a single run are given in Table X.

Delignification and Primary Refining

Alkali pretreatment (when included), lignin modification and alkali extraction were carried out under the conditions set out in Tables II and III. After each process step in which chemicals were added, the product was separated from spent liquor and water washed in a centrifuge with recycling to avoid loss of fines.

TABLE X

BAUER McNETT CLASSIFICATION DATA[a]

Code	A-52	A-51	A-53
On-6-mesh, %	27.4	12.5	15.9
On-12-mesh, %	21.6	26.4	29.2
On-35-mesh, %	36.8	45.3	39.0
On-65-mesh, %	5.3	7.8	6.7
Through-65-mesh (by diff.), %	8.9	8.0	9.2

[a]Water temperature 6.5°C.

Primary refining was carried out using a Sprout-Waldron machine with a 0.018-in. plate gap under the conditions described below for the case of the high-yield kraft reference pulp.

<u>High-Yield Kraft Reference Pulp</u>

Loblolly pine chips, as used in the above chip fiberization, were cooked under the conditions given in Table XI. The cooked chips, which partly hung in the digester after blowing, were centrifuged, washed with hot water, soaked overnight, centrifuged, then soaked again in hot water (45-50°C.) for about 1 hr., centrifuged and the last wash repeated before sampling for yield. The wash waters were recycled until free of fines.

<u>Primary Refining for High-Yield Kraft Pulp</u>

Washed, blown chips (Table XI), which had appreciably disintegrated on blowing, were processed into fiber in a 12-in. Model No. 105-A Sprout-Waldron refiner illustrated in Progress Report Sixteen and fitted with an Esterline Angus Model AW recording watt-hour meter. No. 17,804 plates had been fitted to the refiner and preliminary tests were made to give results as shown in Table XII. The cooked chips were steamed for 5 min. at atmospheric pressure before refining.

TABLE XI

HIGH-YIELD KRAFT PULP

Liquor:wood	3.5:1
Active alk., %	14.4
Sulfidity, %	30
Max. temp., °C.	172
Time to 172°C.	85 min.
Time at 172°C.	33 min.
Blowdown to 85 p.s.i.	5 min.
Kappa no.[a]	85.6
Klason lignin, % o.d.p.	12.5
Acid sol. lignin, % o.d.p.	0.9
Yield, %	55.6
Code	HYK/56

[a]Obtained on sample of chips which had been fiberized in Sprout-Waldron refiner.

TABLE XII

PRELIMINARY PRIMARY REFINING

Water temp., 190-200°F.; feed rate, approx. 300 g.o.d.p./min.

	Consistency, %	
	3.5	5.0
Plate Gap, 0.001 in.	Canadian Freeness, ml.	
22	740,745	740
20	735,740	725
18	720,725	720
16	720,720	710,710
14	710	--

Pulp Evaluation (Handsheets)

The pulps were beaten in 40 g.o.d. lots at 10% consistency in a PFI mill having a 3.4-kg. load. Handsheets of 60 g./sq. m. (1.2-g. sheets) were prepared according to TAPPI Standard Method T 205 m-58. For the degrees-to-crack test, two 6.28-g. sheets (i.e., 69 lb./1000 sq. ft.) were made in a British handsheet mold, pressed for 5 min. at 50 p.s.i.g. and dried on a steam drum with a surface temperature of 230-235°F. Most sheet testing procedures are described in Progress Reports Eight and Twelve.

The degrees-to-crack test was carried out at 73°F. and 10% relative humidity using a Linerboard Cracking Tester. The specimen size tested was 1.5 in. x 6 in. and the test area was sprayed with Rust Oleum flat black no. 412 to facilitate the detection of cracking. Each reported value is the mean of six tests.

At each beating level the pulp not needed for handsheets was put aside for determination of filtration resistance, etc., as reported below. The results obtained from handsheet testing are presented in Tables V-VI and in Appendices II and III.

Hydrodynamic Properties

The filtration resistance of various pulps prepared as described above was determined using a research model constant-rate filtration apparatus described previously (4). Relevant techniques also have been described previously (5-7).

Apparent wet mat density as a function of compacting pressure was measured by the procedure reported at an earlier date (8).

Specific surfaces and volumes were calculated from plots of time-pressure drop values from filtration resistance measurements and correlated values of wet mat density which are applicable to a modified Kozeny-Carman equation as already discussed (6).

CONCLUSIONS

Unbleached loblolly pine chlorine dioxide-alkali pulps that are relatively shive-free and similar in color to a corresponding high-yield kraft pulp can be produced from alkali-impregnated chips in 70-85% yield.

An advantage of using alkali-impregnated chips is that pulps tend to have relatively lower filtration resistance values.

The chlorine dioxide used for lignin modification can be substituted on a chemical equivalent basis by chlorine dioxide and chlorine with an amount of chlorine at least equal to that present in the gas stream from a chlorine dioxide generator.

During primary refining, about four times as much power is required for a high-yield kraft pulp compared with the chlorine dioxide-alkali pulps.

Compared with a 56% yield kraft pulp, papermaking strength properties including burst factor, breaking length, stretch, tensile stiffness, ring crush, and degrees-to-crack, tended to be very similar at about 70% yield for a chlorine dioxide-alkali pulp, in spite of relatively lower sheet densities. At higher yield levels these strength properties and sheet densities decreased.

An intermediate level of burst, which is reached in the early stages of beating the high-yield kraft pulp, is reached by the chlorine dioxide-alkali pulps with up to about 80% yield. The benefit of higher yield is associated with greater filtration resistance or lower Canadian freeness. On the basis of previous indications on cost, pulps capable of developing an intermediate level of bursting strength fall into an economically attractive category.

HARDWOODS — RED MAPLE

BACKGROUND

In previous work on hardwoods, the point had been reached where a clean, shive-free bleached red maple pulp with a relatively stable 88 TAPPI brightness had been produced in 57-60% yield for investigations on its papermaking characteristics. The bulk of the results obtained on these were described in Progress Report Sixteen. It included the finding that wet web moisture contents were lower for this holopulp than for the corresponding red maple kraft pulp in comparisons at equal dry sheet density.

It was also found that filler-grade clay was retained to a greater extent in furnishes containing holopulp compared with the corresponding hardwood kraft pulp. For comparison at the same specific scattering coefficient, sheet density and strength properties were quite similar for clay additions of 20% for the furnish containing holopulps compared with 6% for the case of the hardwood kraft pulp. Thus, in sheets containing hardwood holopulp instead of hardwood kraft pulp, more clay filter was present in the former, which would be an advantageous cost factor.

These test results were subsequently further substantiated by a small papermaking trial using the Institute web former. No disadvantages were observed when using the furnish containing holopulp and data related to that trial are included in Table XIII.

To prepare the unbleached red maple holopulp in the work just described the amount of oxidant needed for lignin modification was chemically equivalent to 8% chlorine dioxide and was added as chlorine dioxide and chlorine

TABLE XIII

WEB FORMER RESULTS FOR FURNISHES WITH HUBER SSW CLAY FILLER

Fiber furnish: 30% bleached softwood kraft
70% bleached red maple as shown

	Holopulp	Kraft
Clay added, % o.d. fiber	30	15
Furnish:		
Canadian freeness, ml.	400	380
Filtration resistance, $\underline{R} \times 10^{-8}$, cm./g.; $\Delta\underline{P}$ = 10 cm. H_2O	1.66[a]	1.53[a]
Filler content, % o.d. sheet	14	8
Basis weight, a.d. g./m.^{2}	46	44
Sheet density, g./cc.	0.50	0.48
TAPPI brightness	83	83
Spec. scattering coeff., 650 nm.	397	416
Breaking length, km. (MD)	4.8	4.6
Stretch, % (MD)	1.2	2.0
Tensile stiffness, Et, kg./cm. (MD)	330	263
Tear factor (Elmendorf) (MD)	88	86

[a]Further details in Appendix VII.

on an 85:15 w/w basis. The plan in the present work was to substitute chlorine dioxide to an increasing degree by the chemical equivalent amount of chlorine. If this could be done without adverse effect at least to the extent of showing that the oxidant could consist of a mixture of chlorine dioxide and chlorine such as occurs in the gas stream from a chlorine dioxide generator, this would mean a lower cost basis through lower chemical cost. For a case in which sodium chlorate is converted to chlorine dioxide in 97% yield, as in the SVP plant at Franklin, Virginia, chlorine dioxide:chlorine in the generator gas stream is 65:35 (9).

LOWER CHLORINE DIOXIDE USAGE

Preparation of Pulps

Six different ratios of chlorine dioxide and chlorine with 85 down to 15% chlorine dioxide by weight including the 65:35 ratio as noted above, were investigated using similar chemical process conditions for the delignification of red maple fiberized chips. The amount of lignin removed, as indicated by Kappa number, was less after the chlorine dioxide content was decreased below about 55% as shown in Fig. 16.

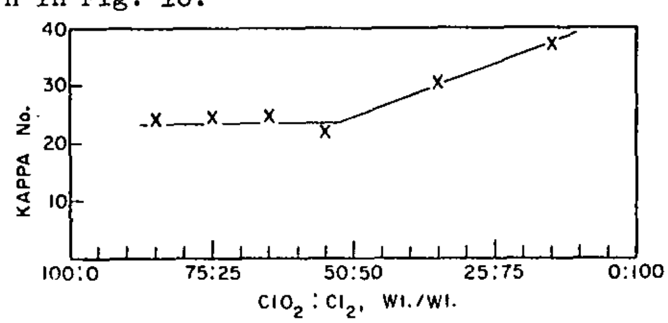

Figure 16. Plot of Kappa Number vs. Chlorine Dioxide:Chlorine in the Lignin Modification Step of Red Maple Delignification

The delignification conditions used in obtaining the results in Fig. 16 are summarized in Table XIV. This is derived from the more extensive results given in Appendix VIII. In Table XIV the chemical process conditions are based on those used previously to produce the bleached pulp required for the investigations on papermaking characteristics as referred to above. However, in the present work the pulps were passed through the Sprout Waldron refiner used in the loblolly pine experiments before screening. Tests showed that without this action a significant percentage of screen rejects would have been obtained.

The occurrence of a significant percentage of screen rejects before refining is in contrast to a negligible amount of screen rejects found at the same point when producing pulp for the investigations on papermaking characteristics (Report Sixteen). It is believed that this difference arises from between-batch changes in the classification characteristics of the fiberized red maple chips. Support for this is provided by the classifications included in Table XV. This illustrates the very close similarity in process conditions with the exception that much less power was used in October, 1972 to produce the fiberized chips needed for the work described in this report and presumably as a consequence the product had coarser classification characteristics. The reason why there was a greater power input in March, 1972 is not known.

It can be seen from Table XIV that as the relative amount of chlorine was increased, the final pH fell in the alkali extraction. Conceivably, further work might show that by increasing the amount of alkali used for the extraction when chlorine content is increased during lignin modification yield and Kappa number would fall to levels comparable to those observed in the example where chlorine content was 45%.

TABLE XIV

CHLORINE DIOXIDE/CHLORINE-ALKALI DELIGNIFICATION OF FIBERIZED RED MAPLE

Process Step	Process Conditions					
Alkali pretreatment:	3% NaOH, 10% consistency, 80°C., 15 min.					
Lignin modification:	25→35°C. in 60 min.					
	ClO_2:Cl_2 (w/w)	85:15	65:35	55:45	35:65	15:85
	Chlorine dioxide, %	7.5	6.6	6.1	4.7	2.5
	Chlorine, %	1.3	3.6	5.0	8.7	14.4
	Consistency, %	8.0	8.0	7.3	6.3	4.0
	Time, min.	140	113	108	65	65
Alkali extraction:	7.5% NaOH, 15% consistency, 80°C., 120 min.					
	Final pH	10.8	10.7	10.6	9.7	8.3
	Yield, %	66	67	67	69	71
	Kappa no.	24	25	22	31	37
	Klason lignin, % o.d.p.	3.9	4.2	3.8	5.9	7.2
Primary refining:	3.5% consistency, 195°F. feed water, 0.008 in. plate gap					
	Screen rejects, % o.d.p.	0.1	0.1	0.1	--	--
	Material loss, % o.d.p.[a]	2.7	2.2	2.1	--	--

[a]With water recycling.

TABLE XV

COMPARISON OF DATA FOR DIFFERENT LOTS OF FIBERIZED RED MAPLE CHIPS

Refiner: No. 418 Pressurized Bauer
Plates: Two Sets of Pattern No. 36326

Date	October, 1972	March, 1972
Code	A-54	A-41
Chip treatment	--water impregnation--	
Chip moisture content, % wet basis	58	60
Weight used for run, lb. o.d.	95	83
Conditions:		
Steam pressure, p.s.i.g. (°C.)	80 (163)	80 (163)
Steaming time, min.	3.0	3.0
Plate clearance, 0.001 in.	30	30
Run time, min.	10.3	8.8
Feed rate, o.d. tons/day	6.62	6.81
Load, brake h.p. days/o.d. ton[a]	3.2	10.2
Bauer-McNett classification:		
On-6-mesh, %	19.9	0.3
On-12-mesh, %	20.1	0.5
On-35-mesh, %	25.3	17.3
On-65-mesh, %	17.0	39.7
Through-65-mesh (by diff.), %	17.7	42.2

[a]This value should be increased 20% to obtain the estimated total, including allowances for no-load powers and motor efficiency.

To determine whether this level of chlorine addition can be used without detrimental effect on bleached pulp properties, unbleached pulps were bleached as set out in Table XVI. The process conditions are based on those used at an earlier date (Report Sixteen).

TAPPI brightnesses in Table XVI are about 2-3 points lower and yield is higher than in previous work (Report Sixteen). This probably reflects the coarser character of the fiberized chips in the present work as referred to already. A significant aspect of Table XVI is that the unbleached pulps prepared with chlorine dioxide:chlorine equal to 55:45 in the lignin modification had at least comparable bleachability to pulps prepared using chlorine dioxide with only 15% chlorine content.

Evaluation of Pulps

The bleached pulps prepared as indicated in Tables XIV and XVI were evaluated by beating in a Valley beater, and by determination of filtration resistance and handsheet properties. Evaluation data are presented in Table XVII. More extensive values on which Table XVII is based are given in Appendix IX. Table XVII shows no significant difference in bleached pulp properties when the chemical equivalent of 8.0% chlorine dioxide used for lignin modification is substituted by chlorine dioxide and chlorine with up to at least 45% chlorine. At this point the amount of chlorine dioxide is reduced to about 6.0% for lignin modification.

The average values for various properties in Table XVII have been plotted as a function of handsheet density in Fig. 17 and 18. These figures also include similar data for a bleached kraft pulp used for comparison, and the evaluation data for this pulp are given in Appendix IX.

TABLE XVI

BLEACHING CHLORINE DIOXIDE/CHLORINE-ALKALI RED MAPLE PULPS
(PREPARED AS IN TABLES XIV AND XV)

I. Chlorine Dioxide/Chlorine (same for all pulps)

Chlorine dioxide, %	0.77	Consistency, %	10
Chlorine, %	0.38	Temp., °C.	60
Time, min.	60	Final pH	2.3

II. Alkali Extraction (same for all pulps)

Sodium hydroxide, %	1.4	Consistency, %	15
Time, min.	90	Temp., °C.	70
Final pH	10.9-11.1		

III. Chlorine Dioxide (same for all pulps)

Chlorine dioxide, %	0.5	Consistency, %	10
Time, min.	80-90	Temp., °C.	70
Final pH	3.3-3.6	Residual ClO_2	trace

	Pulp ClO_2:Cl_2		
	85:15	65:35	55:45
Yield, %[a]	59.0, 59.0	59.9, 59.9	59.6, 59.1
TAPPI brightness, %	85.0, 84.6	84.1, 84.0[b]	85.6, 86.0
after 1% SO_2	85.7, 86.0	85.5, 85.0	86.7, 87.0
Steam-aged brightness, %	74.4, 73.9	74.5, 73.1	75.4, 77.4
after 1% SO_2	77.4, 77.9	78.3, 77.0	79.6, 79.8

[a]Determination includes subtraction for material loss on screening.
[b]For "unbonded" sheet (ethanol) brightness was 89.0%.

TABLE XVII

EVALUATION DATA: BLEACHED CHLORINE DIOXIDE/CHLORINE-ALKALI RED MAPLE PULPS (TABLE XVI)

Test	Pulp	Valley Beating Time, min. 0	3	7	13
Canadian freeness, ml.	85:15	240	215	175	120
	65:35	250	205	170	130
	55:45	245	220	180	125
Filtration resistance,[a] 10^{-8} cm./g. ($\Delta \underline{P}$ = 10 cm. H_2O)	85:15	2.0	2.4	2.8	4.8
	65:35	1.9	2.0	2.7	4.4
	55:45	1.7	1.9	2.6	4.3
Handsheet density, g./cc.	85:15	0.70	0.71	0.72	0.75
	65:35	0.70	0.71	0.73	0.76
	55:45	0.70	0.72	0.74	0.76
Breaking length, km.	85:15	8.1	8.5	9.1	9.4
	65:35	7.0	7.6	8.7	9.4
	55:45	7.9	8.0	8.8	9.5
Tensile energy abs., g. cm./cm.^{2}	85:15	119	130	146	152
	65:35	82	91	138	152
	55:45	112	114	141	152
Tensile stiffness, Et, kg./cm.	85:15	517	528	548	551
	65:35	487	517	526	558
	55:45	495	509	527	554
Tear factor (Elmendorf)	85:15	80	80	77	73
	65:35	72	74	74	69
	55:45	78	75	75	72
MIT fold	85:15	209	212	395	1006
	65:35	190	257	418	897
	55:45	166	238	391	878
Spec. scatt. coeff., 650 nm.	85:15	253	248	235	202
	65:35	252	248	242	202
	55:45	258	249	238	200

[a]Further data in Appendix IX.

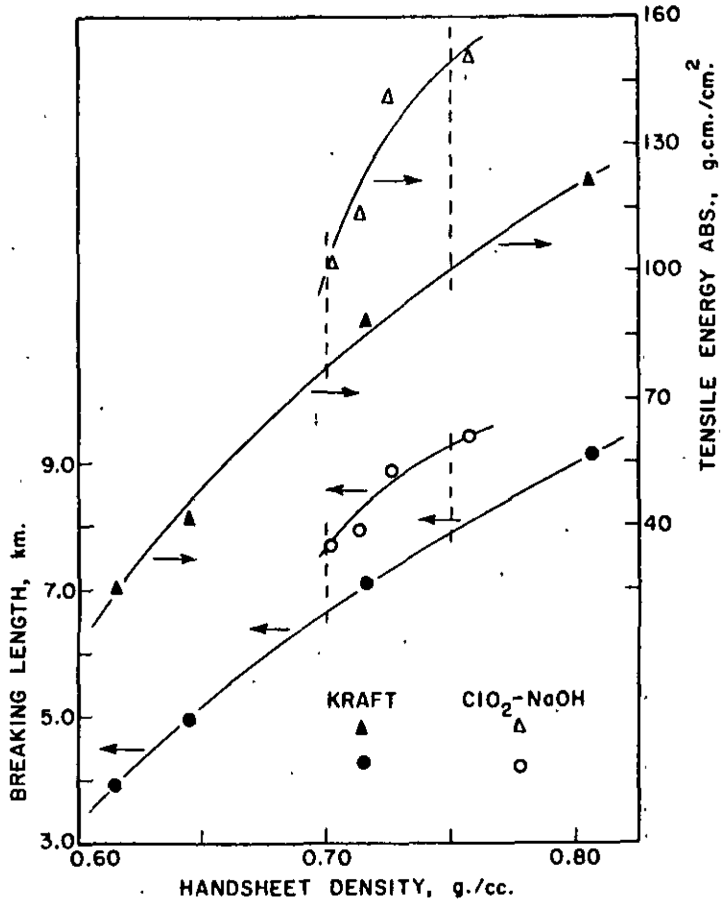

Figure 17. Plots of Breaking Length and Tensile Energy Absorption vs. Handsheet Density for Bleached Red Maple Chlorine Dioxide/Chlorine-Alkali and Kraft Pulps

Figures 17 and 18 show that, although the kraft pulp is characterized by providing sheets with a greater handsheet density range, these holopulps have significantly higher breaking length, tensile energy absorption, tensile stiffness and MIT fold when compared at similar sheet densities with the kraft pulp.

When Elmendorf tear factor and specific scattering coefficient are plotted as a function of breaking length as in Fig. 19, it will be seen that these holopulps have a tear factor about comparable to kraft and a specific scattering coefficient slightlv less than for the kraft pulp.

A numerical comparison of bleached red maple chlorine dioxide-alkali and kraft pulps is given in Table XVIII. This provides a more extensive basis for comparison than is covered by Fig. 17, 18, and 19.

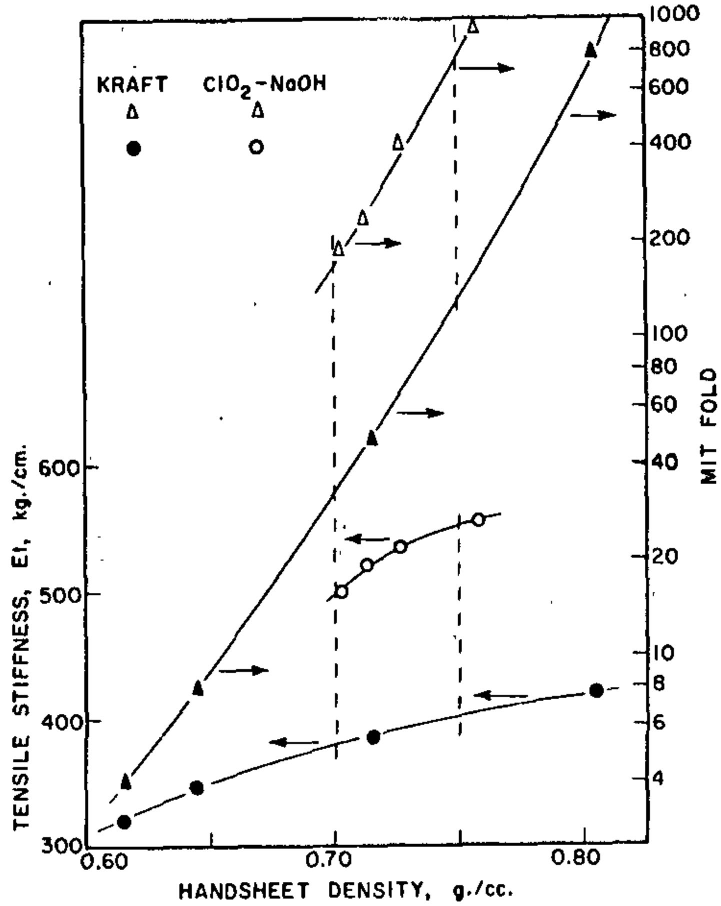

Figure 18. Plots of Tensile Stiffness and MIT Fold *vs*. Handsheet Density for Bleached Red Maple Chlorine Dioxide/Chlorine-Alkali and Kraft Pulps

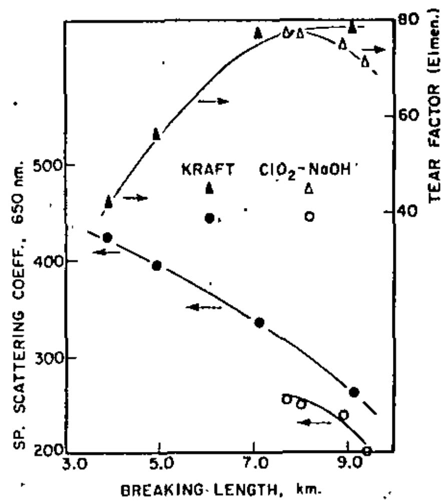

Figure 19. Plots of Specific Scattering Coefficient and Elmendorf Tear Factor *vs*. Breaking Length for Bleached Red Maple Chlorine Dioxide/Chlorine-Alkali and Kraft Pulps

EXPERIMENTAL

Raw Materials

The red maple (*Acer rubrum* L.) chips used for the work described below were produced from fourteen logs with underbark diameters ranging from 4.25 to 8.5 in., and received from Northern Wisconsin during March, 1972. After being debarked, the logs were chipped in a 4-knife, 38-in. diameter Carthage chipper to give a nominal 5/8-in. chip. The chips were screened on a 24-in. Sweco Dynoscreen. Chip moisture content on a wet basis was 31%; specific gravity, 0.463 (dry weight/green vol.).

Fiberization

Screened chips for fiberization were impregnated with water as described in Progress Report Sixteen. The impregnated chips were fiberized in the Bauer machine used to fiberize the loblolly pine chips as described in this report, except that a different plate combination was used. Fiberization and classification data are given in Table XV.

TABLE XVIII

COMPARISON OF BLEACHED RED MAPLE KRAFT AND CHLORINE DIOXIDE-ALKALI PULPS

	Pulp	
	ClO_2/Cl_2-NaOH	Kraft
Handsheet density, g./cc.	0.70-0.75	0.70-0.75
Beating time, min.	0-12[a]	11-17[b]
Canadian freeness, ml.	250-135	400-310
Filtration resistance, $\underline{R} \times 10^{-8}$, cm./g.[c]	1.7-4.8	0.95-3.85
Handsheet drainage time, sec.	5.3-10.5	5.8-7.5
Breaking length, km.	7.7-9.3	6.7-7.9
Tensile energy absorp., g. cm./cm.^{2}	100-151	78-100
Tensile stiffness, Et, kg./cm.	498-552	380-402
Tear factor (Elmendorf)	77-72	73-78
MIT fold	165-770	33-135
Spec. scattering coeff., 650 nm.	256-210	350-310

[a] 2.0-Kg. bedplate load.
[b] 5.5-Kg. bedplate load.
[c] $\Delta \underline{P}$ = 10 cm. H_2O.

Delignification

Alkali pretreatment, lignin modification and alkali extraction were carried out essentially as described in previous reports. The chlorine dioxide and chlorine were added as separate solutions in amounts calculated from analyses and based on the relevant ovendry weight of fiberized chips. After each process step the product was separated from spent liquor and washed in a centrifuge with recycling to avoid loss of fines.

Bleaching

The three stages of bleaching were carried out in plastic bags. For those stages in which chlorine dioxide was added the bags were heat-sealed after which the contents were rapidly heated to near reaction temperature in a microwave oven. Tests were made near the end of the recorded reaction times to ensure the amount of residual oxidant was not significant.

Evaluation

Pulps were beaten in a 1.5-lb. Valley beater according to TAPPI Standard Method T 200 ts-66 except that the weight on the end of the bedplate lever was 2.0 kg. for the holopulps. At each beating interval, stock (2.64 l) was withdrawn to prepare handsheets and to determine freeness and filtration resistance. Details on handsheet forming and testing are given in Reports Eight and Twelve. Filtration resistance was measured as described in this report for the loblolly pine pulps.

CONCLUSIONS

Red maple holopulps can be prepared with the same lignin content when the chlorine dioxide used for lignin modification is substituted by the chemical equivalent amount of chlorine dioxide and chlorine with up to at least 45% chlorine by weight. This reduces the amount of chlorine dioxide to about 6.0% for lignin modification for a high brightness pulp and demonstrates that the oxidant could consist of a mixture of chlorine dioxide and chlorine as in the gas stream from a chlorine dioxide generator.

Pulp bleachability and bleached pulp strength properties are not significantly influenced when the chlorine content is increased up to at least 45% in the chlorine dioxide and chlorine mixture. At comparable sheet density the strength properties of these red maple holopulps were generally better than those of a red maple bleached kraft reference pulp.

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THE INSTITUTE OF PAPER CHEMISTRY

G. A. Nicholls

G. A. Nicholls
Senior Research Associate

V J Van Drunen

V. J. Van Drunen
Research Assistant
Division of Materials
Engineering & Processes

APPENDIX I

PRELIMINARY DATA USED IN DEVELOPING EXPERIMENTAL PLAN

TABLE XIX

RELATIVE LIGNIN REMOVAL ABOVE 65% YIELD FOR 4.5, 6.0, 7.5, AND 9.0% OXIDANT
AFTER LOBLOLLY CHIP PRETREATMENT WITH ALKALI

Alkali impregnation: steamed twice at 15 p.s.i. for 2 min., then covered with NaOH solution for 30 min. with 100 p.s.i g. nitrogen over pressure, drained for 30 min.

NaOH concn., g./l. initial	22.1	39.0
final	19.0	33.2
NaOH uptake, %[a]	4.0	7.0
Steaming at 75 p.s.i.g.		
Min.	5.0	5.0
pH condensate	11.8	12.3
Fiberization: 12 in. laboratory Sprout-Waldron refiner, first pass at 0.065 in., second pass at 0.015 in.		
Yield, %	93.0	86.7

Lignin modification: 25°C. to 35°C. in 60 min., 8% consistency

ClO_2, %	4.5	6.0	7.5	9.0	4.5	6.0	7.5	9.0
Time, min.	60	75	90	105	50	60	75	80
Final pH	1.9	1.7	1.6	1.5	1.8	1.5	1.2	1.8
Yield, %	89.3	89.0	88.4	88.0	84.1	83.8	83.2	82.7
Kappa no.	106.3	101.1	94.5	84.7	100.4	94.5	84.3	81.4

Alkali extraction: 60 min., 90°C., 12% consistency

NaOH, %	4.0	8.0	4.0	8.0	4.0	8.0	4.0	8.0	4.0	8.0	4.0	8.0	4.0	8.0	4.0	8.0
Final pH	9.8	11.4	9.4	11.5	8.6	11.2	8.3	11.3	10.8	12.0	9.9	12.0	9.4	11.8	8.3	11.7
Yield, %	81.5	80.1	79.9	77.4	77.5	71.8	72.7	69.6	78.4	74.8	76.1	72.2	71.9	68.1	71.6	65.9
Kappa no.	94.1	92.1	86.6	81.4	75.2	66.7	61.4	56.8	91.9	87.0	81.4	76.3	71.1	62.3	58.2	50.5
Klason lignin, % o.d.p.	21.8	21.0	19.9	18.5	17.6	15.9	15.6	12.4	23.2	22.1	21.7	19.3	19.0	15.8	--	--
Klason lignin, %	17.8	16.8	15.9	14.3	13.6	11.4	11.3	8.6	18.2	16.5	16.5	13.9	13.7	10.8	--	--
Acid sol. lignin, %	1.1	1.1	1.2	1.2	1.4	1.3	1.7	1.5	1.2	1.1	1.3	1.2	1.4	1.2	--	--

APPENDIX II

HANDSHEET DATA FOR PULPS MADE FROM ALKALI IMPREGNATED CHIPS

TABLE XX

EVALUATION DATA: 86% YIELD LOBLOLLY CHLORINE DIOXIDE-ALKALI PULP (5.3/4.5/86)

	Primary Refining Gap, 0.001 in.							
	18				5			
	PFI Mill, counter revs.							
Property	450	750	1150	1650	450	750	1150	1650
Canadian freeness, ml.	715	575	400	210	610	460	325	220
	720	595	375	245	595	435	260	185
Handsheet drainage time, sec.	4.4	4.8	5.0	5.8	4.8	5.0	5.2	5.7
	4.5	4.8	5.0	5.5	4.8	5.0	5.2	6.4
Handsheet density, g./cc.	0.348	0.415	0.451	0.508	0.372	0.411	0.465	0.492
	0.388	0.422	0.470	0.495	0.405	0.434	0.475	0.523
Bendtsen smoothness, ml./min.	3130	2710	2160	2100	2770	2600	2280	2250
	2940	2490	2260	2300	2650	2430	2340	2260
Burst factor	13.8	18.6	22.9	25.9	18.1	20.0	23.7	26.1
	11.9	18.1	21.2	24.0	17.5	20.3	24.3	27.5
Breaking length, km.	2.86	3.83	4.38	5.21	3.48	3.95	4.58	4.98
	2.79	3.65	4.33	4.61	3.56	4.06	4.54	5.23
Stretch, %	1.5	1.9	1.9	2.2	1.8	1.9	2.1	2.1
	1.4	1.6	1.9	2.0	1.8	1.9	2.0	1.9
Tensile stiffness, Et, kg./cm.	233	291	315	372	273	303	347	362
	234	265	290	312	300	328	350	380
Tear factor (Elmendorf)	62.8	81.7	65.3	61.3	75.3	70.5	65.3	60.1
	68.9	65.9	61.7	56.2	69.3	64.3	60.9	53.5
Modified ring crush, lb./in.	4.1	4.7	5.3	6.3	5.1	5.3	5.6	6.0
	4.1	4.9	5.7	5.8	4.2	5.1	5.5	5.4
Degrees-to-crack	34	34	38	38	38	36	36	39
	43	45	31	31	41	42	36	38

TABLE XXI

EVALUATION DATA: 80% YIELD LOBLOLLY CHLORINE DIOXIDE-ALKALI PULP (11.7/4.5/80)

Property	Primary Refining Gap, 0.001 in.							
	18				5			
	PFI Mill, counter revs.							
	450	750	1150	1650	450	750	1150	1650
Canadian freeness, ml.	725	640	475	270	675	570	410	240
	730	675	500	280	685	595	400	210
Handsheet drainage time, sec.	4.5	4.8	5.1	5.7	4.7	4.8	5.0	5.7
	4.5	4.8	5.0	5.9	4.7	4.9	5.1	6.0
Handsheet density, g./cc.	0.366	0.408	0.468	0.511	0.386	0.435	0.477	0.522
	0.346	0.409	0.468	0.494	0.371	0.407	0.452	0.506
Bendsten smoothness, ml./min. (backside of sheet)	3090	2730	2310	2300	3000	2470	2470	2310
	3170	2830	2610	2230	3010	2830	2610	2360
Burst factor	19.2	27.4	34.0	36.1	23.6	27.0	31.6	35.2
	16.3	25.3	32.3	37.0	20.2	26.9	29.9	35.6
Breaking length, km.	3.83	4.89	5.63	6.44	4.14	4.60	5.54	6.38
	2.88	4.28	5.44	6.08	3.70	4.26	4.98	6.30
Stretch, %	1.6	1.9	2.2	2.3	2.0	2.0	2.2	2.3
	1.1	1.7	2.2	2.1	1.7	1.8	1.9	2.5
Tensile stiffness, Et, kg./cm.	311	353	373	412	302	358	408	448
	256	318	340	381	290	319	358	399
Tear factor (Elmendorf)	118	104	85.5	75.5	106	91.6	82.5	77.4
	117	99.5	87.7	79.1	106	96.2	83.7	74.4
Modified ring crush, lb./in.	4.6	5.1	5.7	6.0	4.8	5.1	6.2	6.2
	4.0	4.9	5.5	6.5	4.6	4.9	5.2	5.4
Degrees-to-crack	40	39	46	48	44	49	48	44
	43	42	59	51	45	43	43	41

TABLE XXII

EVALUATION DATA: 77% YIELD LOBLOLLY CHLORINE DIOXIDE-ALKALI PULP (5.3/7.5/77)

Property	Primary Refining Gap, 0.001 in.							
	18				5			
	PFI Mill, counter revs.							
	450	750	1150	1650	450	750	1150	1650
Canadian freeness, ml.	710	620	490	390	620	430	325	210
	705	640	470	250	580	440	290	180
Handsheet drainage time, sec.	4.5	4.8	5.1	5.3	4.8	5.0	5.3	5.6
	4.6	4.8	5.2	5.6	4.8	4.9	5.5	7.4
Handsheet density, g./cc.	0.404	0.426	0.501	0.507	0.463	0.493	0.526	0.560
	0.424	0.490	0.513	0.556	0.476	0.505	0.547	0.586
Bendtsen smoothness, ml./min.	2820	2700	2240	2230	2360	2240	2180	2020
	2850	2450	2110	2090	2460	2340	2240	2330
Burst factor	25.3	28.4	32.3	34.6	30.4	33.5	34.5	39.5
	24.6	30.6	31.6	36.0	29.5	32.6	36.9	39.7
Breaking length, km.	4.21	4.82	5.78	5.91	5.16	5.66	6.07	6.70
	3.94	4.98	5.60	6.15	4.91	5.41	6.27	6.66
Stretch, %	2.0	2.3	2.4	2.2	2.5	2.5	2.5	2.8
	1.9	2.2	2.4	2.6	2.1	2.2	2.5	2.5
Tensile stiffness, Et, kg./cm.	290	290	332	362	360	381	417	429
	271	305	336	368	319	347	393	418
Tear factor (Elmendorf)	92.0	83.9	75.8	72.9	82.1	78.2	74.2	69.0
	84.3	73.6	73.2	67.8	79.2	71.6	68.5	60.8
Modified ring crush, lb./in.	4.8	4.4	5.0	4.9	5.1	5.8	6.0	5.9
	4.3	5.2	6.0	6.2	5.3	5.3	6.1	6.0
Degrees-to-crack	39	38	46	43	50	48	46	48
	54	55	49	52	49	44	42	44

TABLE XXIII

EVALUATION DATA: 72% YIELD LOBLOLLY CHLORINE DIOXIDE-ALKALI PULP (11.7/7.5/72)

	Primary Refining Gap, 0.001 in. — 18				5			
	PFI Mill, counter revs.							
Property	450	750	1150	1650	450	750	1150	1650
Canadian freeness, ml.	705	615	370	230	650	575	390	245
	710	625	410	250	--	530	--	220
Handsheet drainage time, sec.	4.5	4.8	5.2	6.1	4.7	4.9	5.3	5.9
	4.6	4.8	5.1	5.7	--	5.0	--	6.0
Handsheet density, g./cc.	0.430	0.477	0.504	0.540	0.445	0.478	0.533	0.535
	0.439	0.469	0.499	0.537	--	0.472	--	0.545
Bendtsen smoothness, ml./min.	2620	2470	2320	2220	2580	2580	2410	2350
(backside of sheet)	2810	2530	2420	2370	--	2490	--	2490
Burst factor	35.9	43.1	47.4	50.3	38.7	43.7	49.3	51.0
	35.3	40.2	44.2	50.1	--	39.8	--	48.6
Breaking length, km.	5.60	6.47	7.19	7.92	5.82	6.37	6.98	7.40
	5.70	6.37	7.25	7.62	--	6.24	--	7.53
Stretch, %	2.4	2.5	2.6	2.9	2.5	2.6	2.8	2.8
	2.3	2.5	2.8	2.7	--	2.5	--	2.8
Tensile stiffness, Et, kg./cm.	356	396	420	441	380	403	423	441
	347	368	406	432	--	381	--	434
ear factor (Elmendorf)	121	110	98.5	90 2	116	110	91.5	90.9
	125	110	96.3	93.8	--	104	--	88.3
odified ring crush, lb./in.	4.9	5.5	6.2	5.6	5.4	6.2	6.3	6.7
	6.0	5.9	6.3	6.6	--	5.0	--	5.5
egrees-to-crack	44	45	43	44	52	49	48	46
	49	48	52	56	--	52	--	48

APPENDIX III

HANDSHEET DATA FOR PULPS MADE WITHOUT ALKALI
IMPREGNATION OF CHIPS AS IN TABLE III

TABLE XXIV

EVALUATION DATA: 66% YIELD LOBLOLLY
CHLORINE DIOXIDE-ALKALI PULP (0-11.7/4.5/66)

Property	Primary Refining Gap, 0.018 in. — PFI Mill, counter rev. 450	750	1150	1650
Canadian freeness, ml.	705 700	625 635	380 410	200 225
Handsheet drainage time, sec.	4.6 4.6	4.8 4.8	5.2 5.2	6.2 6.3
Handsheet density, g./cc.	0.414 0.427	0.463 0.468	0.525 0.510	0.568 0.539
Bendtsen smoothness, ml./min. (backside of sheet)	2670 2640	2450 2420	2150 2060	2200 2190
Burst factor	27.8 27.5	33.9 33.0	39.6 39.0	44.9 43.7
Breaking length, km.	4.76 4.90	5.73 5.85	5.09 6.59	7.44 7.22
Stretch, %	2.1 2.1	2.5 2.5	2.6 2.5	2.7 2.8
Tensile stiffness, Et, kg./cm.	342 353	386 401	423 420	452 431
Tear factor	121 114	107 108	92.8 92.6	87.8 90.9
Modified ring crush, lb./in.	4.9 5.0	5.7 5.5	5.9 6.0	6.4 6.8
Degrees-to-crack	40 46	45 45	39 46	42 51

TABLE XXV

EVALUATION DATA: 70% YIELD LOBLOLLY CHLORINE DIOXIDE-ALKALI PULP (0-5.3/7.5/70)

	Primary Refining Gap, 0.001 in.							
	18				5			
	PFI Mill, counter revs.							
Property	450	750	1150	1650	50	150	450	750
ian freeness, ml.	645	450	260	160	525 540	440 475	310 320	205 215
heet drainage time, sec.	4.8	5.0	5.8	8.0	4.9 4.8	5.0 5.0	5.5 5.3	6.4 6.3
heet density, g./cc.	0.445	0.505	0.553	0.579	0.470 0.458	0.486 0.501	0.522 0.528	0.544 0.546
en smoothness, ml./min. ackside of sheet)	2620	2410	2370	2360	2500 2530	2750 2350	2810 2280	2420 2380
factor	33.5	39.3	43.6	46.9	36.6 33.3	38.2 36.6	42.4 41.3	43.9 45.6
ing length, km.	5.70	6.63	7.34	7.71	5.65 5.26	6.22 5.59	6.68 6.68	7.24 7.20
h, %	2.3	2.6	2.7	2.7	2.4 2.2	2.6 2.3	2.8 2.5	2.7 2.7
le stiffness, Et, kg./cm.	382	401	439	460	376 381	385 387	402 418	446 437
actor (Elmendorf)	104	90.2	82.9	76.4	99.7 108	96.2 98.0	91.0 89.0	84.8 81.7
ed ring crush, lb./in.	4.9	5.6	6.1	6.2	4.6 5.4	5.1 5.4	5.4 5.7	5.1 6.0
e-to-crack	48	48	48	46	47 48	46 51	45 46	45 47

APPENDIX IV

HANDSHEET DATA FOR 56% YIELD KRAFT REFERENCE PULP

TABLE XXVI

EVALUATION DATA: 55.6% YIELD LOBLOLLY KRAFT (HYK/56)

	Primary Refining Gap, 0.001 in.							
	18				5			
	PFI Mill, counter revs.							
Property	450	750	1150	1650	150	450	750	1150
Canadian freeness, ml.	710 705	620 630	385 420	205 --	615 625	505 450	360 385	230 240
Handsheet drainage time, sec.	4.3 4.4	4.8 4.7	5.3 5.2	7.1 --	4.7 4.7	4.8 5.0	5.2 5.3	6.1 5.9
Handsheet density, g./cc.	0.517 0.549	0.557 0.539	0.604 0.605	0.634 --	0.507 0.544	0.554 0.550	0.583 0.579	0.610 0.601
Bendtsen smoothness, ml./min. (backside of sheet)	1810 2030	1790 1780	1890 1700	1720 --	1790 1950	1610 1840	1530 1790	1630 1810
Burst factor	38.2 40.3	47.6 46.1	53.3 54.0	54.8 --	33.0 36.8	40.3 38.1	43.9 41.5	45.9 45.2
Breaking length, km.	5.87 6.01	6.75 6.87	7.54 7.69	7.97 --	5.49 5.91	6.04 6.13	7.03 6.73	7.22 6.94
Stretch, %	2.5 2.3	2.9 2.9	3.1 3.1	3.3 --	2.4 2.6	2.5 2.5	3.0 2.8	3.2 3.1
Tensile stiffness, Et, kg./cm.	379 388	399 402	420 427	431 --	383 414	409 417	443 442	443 449
Tear factor (Elmendorf)	126 130	115 119	104 105	98 --	117 113	105 102	99.7 100	92.4 96.5
Modified ring crush, lb./in.	5.4 5.7	5.9 6.1	6.0 6.1	6.1 --	5.5 5.7	5.7 5.6	6.1 5.7	6.0 5.5
Degrees-to-crack	58 48	51 51	48 54	49 --	53 57	57 54	59 56	60 55

APPENDIX V

FILTRATION RESISTANCE AND OTHER HYDRODYNAMIC DATA

TABLE XXVII

FILTRATION RESISTANCE DATA FOR PULP 5.3/4.5/86

Pressure Drop ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g.[a]			
	86-018-450	86-018-750	86-018-1150	86-018-1650
10	0.24	0.31	0.73	1.00
20	0.27	0.44	1.07	1.50
30	0.32	0.55	1.36	1.93
40	0.37	0.64	1.63	2.33
50	0.41	0.73	1.89	2.72
60	0.45	0.82	2.14	3.09
70	0.49	0.90	2.39	3.45
80	0.53	0.98	2.63	3.81
90	0.57	1.06	2.86	4.14

Pressure Drop ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g.[a]			
	86-005-450	86-005-750	86-005-1150	86-005-1650
10	0.39	0.59	1.09	1.98
20	0.55	0.85	1.62	2.98
30	0.68	1.08	2.10	3.87
40	0.79	1.29	2.53	4.67
50	0.91	1.49	2.95	5.45
60	1.02	1.67	3.35	6.30
70	1.12	1.86	3.75	6.96
80	1.23	2.04	4.13	7.69
90	1.33	2.22	4.50	8.36

[a] Mean of duplicates.

TABLE XXVIII

FILTRATION RESISTANCE DATA FOR PULP 11.7/4.5/80

Pressure Drop $\Delta \underline{P}$, cm. H_2O	Resistance $\underline{R} \times 10^{-8}$, cm./g.			
	80-018-450	80-018-750	80-018-1150	80-018-1650
10	0.15	0.29, 0.27	0.61, 0.62	1.35, 1.29
20	0.21	0.39, 0.38	0.91, 0.93	2.00, 2.01
30	0.25	0.49, 0.48	1.17, 1.21	2.61, 2.63
40	0.29	0.57, 0.57	1.47, 1.47	3.18, 3.22
50	0.33	0.66, 0.66	1.65, 1.71	3.74, 3.80
60	0.37	0.74, 0.74	1.88, 1.96	4.29, 4.35
70	0.40	0.82, 0.82	2.10, 2.19	4.81, 4.89
80	0.44	0.90, 0.90	2.32, 2.42	5.32, 5.42
90	0.47	0.97, 0.98	2.53, 2.64	5.82, 5.94

Pressure Drop $\Delta \underline{P}$, cm. H_2O	Resistance $\underline{R} \times 10^{-8}$, cm./g.[a]			
	80-005-450	80-005-750	80-005-1150	80-005-1650
10	0.27	0.45	0.90	1.81
20	0.38	0.65	1.37	2.79
30	0.48	0.82	1.78	3.68
40	0.57	0.98	2.16	4.50
50	0.65	1.14	2.53	5.27
60	0.73	1.29	2.88	6.05
70	0.81	1.44	3.24	6.80
80	0.88	1.58	3.57	7.53
90	0.96	1.71	3.91	8.26

[a]Mean of duplicates.

TABLE XXIX

FILTRATION RESISTANCE DATA FOR PULP 5.3/7.5/77

Pressure Drop $\underline{\Delta P}$, cm. H_2O	Resistance $\underline{R} \times 10^{-8}$, cm./g.[a] 77-018-450	77-018-750	77-018-1150	77-018-1650
10	0.19	0.34	0.60	1.06
20	0.24	0.49	0.92	1.66
30	0.31	0.63	1.20	2.19
40	0.37	0.75	1.45	2.68
50	0.43	0.87	1.69	3.14
60	0.48	0.98	1.92	3.59
70	0.53	1.09	2.14	4.02
80	0.58	1.20	2.38	4.47
90	0.64	1.31	2.59	4.88

Pressure Drop $\underline{\Delta P}$, cm. H_2O	Resistance $\underline{R} \times 10^{-8}$, cm./g.[a] 77-005-450	77-005-750	77-005-1150	77-005-1650
10	0.40	0.59	0.99	1.79
20	0.58	0.89	1.52	2.84
30	0.73	1.16	2.00	3.77
40	0.87	1.41	2.44	4.66
50	1.00	1.64	2.86	5.51
60	1.13	1.87	3.28	6.36
70	1.26	2.10	3.68	7.16
80	1.38	2.31	4.09	7.95
90	1.50	2.53	4.46	8.74

[a]Mean of duplicates.

TABLE XXX

FILTRATION RESISTANCE DATA FOR PULP 11.7/7.5/72

Pressure Drop ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g. 72-018-450	72-018-750	72-018-1150	72-018-1650
10	0.21, 0.22	0.40, 0.40	0.87, 0.87	1.57, 1.55
20	0.30, 0.30	0.59, 0.60	1.35, 1.33	2.46, 2.46
30	0.38, 0.37	0.76, 0.77	1.78, 1.74	3.26, 3.27
40	0.45, 0.43	0.92, 0.92	2.18, 2.13	4.03, 4.05
50	0.51, 0.49	1.07, 1.08	2.57, 2.51	4.77, 4.79
60	0.57, 0.55	1.21, 1.23	2.94, 2.87	5.49, 5.53
70	0.63, 0.59	1.35, 1.37	3.31, 3.23	6.20, 6.24
80	0.69, 0.67	1.49, 1.50	3.67, 3.57	6.89, 6.94
90	0.75, 0.71	1.62, 1.64	4.02, 3.91	7.57, 7.62

Pressure Drop ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g.[a] 72-005-450	72-005-750	72-005-1150	72-005-1650
10	0.33	0.51	0.75[b]	1.43[b]
20	0.48	0.77	1.14	2.22
30	0.61	0.99	1.48	2.91
40	0.72	1.20	1.81	3.57
50	0.84	1.40	2.12	4.19
60	0.94	1.59	2.41	4.83
70	1.05	1.77	2.72	5.43
80	1.15	1.96	3.01	6.02
90	1.25	2.13	3.29	6.58

[a]Mean of duplicates.

[b]Canadian freenesses higher than for corresponding results when plate gap was 0.018 in.

TABLE XXXI

FILTRATION RESISTANCE DATA FOR PULP 0-5.3/7.5/70

Pressure Drop $\Delta\underline{P}$, cm. H_2O	Resistance $\underline{R} \times 10^{-8}$, cm./g.[a]			
	70-018-450	70-018-750	70-018-1150	70-018-1650
10	0.33	0.63	1.13	2.17
20	0.48	0.95	1.76	3.43
30	0.61	1.24	2.32	4.52
40	0.72	1.50	2.85	5.57
50	0.83	1.76	3.36	6.59
60	0.95	2.00	3.85	7.56
70	1.05	2.24	4.33	8.47
80	1.15	2.47	4.78	9.39
90	1.25	2.71	5.28	10.28

Pressure Drop $\Delta\underline{P}$, cm. H_2O	Resistance $\underline{R} \times 10^{-8}$, cm./g.[a]			
	70-005-50	70-005-150	70-005-450	70-005-750
10	0.52	0.58	0.90	1.42
20	0.74	0.84	1.36	2.19
30	0.94	1.07	1.76	2.86
40	1.12	1.28	2.15	3.49
50	1.29	1.48	2.52	4.11
60	1.46	1.68	2.88	4.68
70	1.63	1.87	3.22	5.29
80	1.79	2.06	3.57	5.86
90	1.94	2.24	3.91	6.41

[a]Mean of duplicates.

TABLE XXXII

FILTRATION RESISTANCE DATA FOR PULP 0-11.7/4.5/66

Pressure Drop ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g.[a] 66-018-450	66-018-750	66-018-1150	66-018-1650
10	0.22	0.40	0.82	1.75
20	0.31	0.59	1.25	2.73
30	0.39	0.75	1.63	3.64
40	0.46	0.91	2.00	4.46
50	0.53	1.06	2.34	5.28
60	0.60	1.20	2.69	6.09
70	0.66	1.34	3.01	6.88
80	0.73	1.48	3.34	7.64
90	0.79	1.62	3.67	8.42

TABLE XXXIII

FILTRATION RESISTANCE DATA FOR PULP HYK/56

Pressure Drop ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g.[a] HYK/56-018-450	HYK/56-018-750	HYK/56-018-1150	HYK/56-018-1650
10	0.26	0.38	0.92	2.25
20	0.36	0.56	1.40	3.48
30	0.48	0.71	1.82	4.59
40	0.53	0.85	2.23	5.57
50	0.61	0.98	2.61	6.62
60	0.68	1.11	2.98	7.57
70	0.75	1.24	3.35	8.50
80	0.82	1.36	3.70	7.40
90	0.88	1.48	4.04	10.3

[a]Mean of duplicates.

TABLE XXXIV

HYDRODYNAMIC PROPERTIES OF PULPS

PFI Mill, counter rev.	HYK/56 (0.018)	11.7/4.5/80 (0.018)	11.7/4.5/80 (0.005)	5.3/7.5/77 (0.018)	5.3/7.5/77 (0.005)	11.7/7.5/72 (0.018)	0-11.7/4.5/66 (0.018)
Specific Surface, $\langle \bar{S}_w \rangle$, cm.^{2}/g.							
450	9,150	6,800	9,500	7,100	10,400	8,100	8,400
750	11,100	9,200	11,500	10,000	12,700	11,000	11,500
1150	16,700	13,700	16,100	13,150	16,400	15,860	15,300
1650	25,400	18,100	23,500	17,600	21,900	19,700	23,300
Specific Volume, $\langle \bar{V} \rangle$, cc./g.							
450	3.19	3.33	3.33	3.69	3.61	3.24	3.50
750	3.30	3.54	3.13	3.65	3.40	3.36	3.29
1150	3.48	3.37	3.67	3.62	3.43	3.53	3.60
1650	3.38	3.61	3.38	3.48	3.40	4.08	3.56
Compressibility Constant, M							
450	0.00121	0.00154	0.00155	0.00178	0.00197	0.00162	0.00134
750	0.00149	0.00152	0.00185	0.00169	0.00246	0.00150	0.00151
1150	0.00152	0.00215	0.00195	0.00203	0.00273	0.00225	0.00222
1650	0.00197	0.00282	0.00209	0.00205	0.00255	0.00236	0.00174
Compressibility Constant, N							
450	0.410	0.381	0.383	0.372	0.367	0.383	0.396
750	0.394	0.386	0.372	0.380	0.354	0.372	0.391
1150	0.396	0.359	0.372	0.372	0.344	0.362	0.362
1650	0.375	0.340	0.367	0.370	0.356	0.359	0.385

APPENDIX VI

HANDSHEET DATA FOR CHLORINE DIOXIDE/CHLORINE-ALKALI PULPS

TABLE XXXV

EVALUATION DATA: PFI MILL

	Pulp Code													
	11.7/7.5(100)				11.7/7.5(85:15)				11.7/7.5(55:45)					
	PFI Mill, counter rev.													
Property	450	750	1150	1650	250	450	750	1150	150	250	450	750	1150
Canadian freeness, ml.	630	425	250	160	680	575	325	230	690	590	535	280	--
									--	670	540	380	280
Handsheet drainage time, sec.	4.2	4.6	5.2	8.2	4.1	4.2	4.5	5.5	4.1	4.2	4.3	4.9	--
									--	4.1	4.3	4.7	5.3
Handsheet density, g./cc.	0.443	0.493	0.499	0.531	0.427	0.452	0.490	0.499	0.406	0.431	0.437	0.469	--
									--	0.385	0.424	0.457	0.480
Bendtsen smoothness, ml./min.	2720	2810	2910	2690	2504	2536	2408	2450	2762	2462	2418	2420	--
									--	2950	2770	2840	2690
Burst factor	37.8	43.1	45.5	45.3	34.1	36.6	41.5	44.6	29.3	33.5	36.4	41.0	--
									--	29.1	36.0	39.6	40.8
Breaking length, km.	6.51	7.70	7.76	8.41	5.38	6.31	6.94	7.60	4.72	5.66	5.81	6.91	--
									--	5.35	6.47	6.71	7.36
Stretch, %	2.5	2.8	2.7	2.7	2.2	2.6	2.7	2.8	2.3	2.5	2.6	2.6	--
									--	2.1	2.5	2.5	2.5
Tensile energy absorption, g.cm./cm.^{2}	65	89	88	94	44	67	77	88	45	60	64	78	--
									--	47	66	67	78
Tensile stiffness, Et, kg./cm.	404	449	461	492	350	391	425	442	342	384	379	424	--
									--	387	385	411	445
Tear factor (Elmendorf)	115	102	89	83	125	112	95	97	129	120	120	108	--
									--	129	114	108	98
Modified ring crush, lb./in.	5.9	7.5	6.1	6.4	4.6	4.6	5.0	5.0	4.4	4.8	4.9	4.9	--
									--	4.8	5.2	5.8	5.9

APPENDIX VII

FILTRATION RESISTANCE DATA (FURNISHES WITH CLAY FILLER)

TABLE XXXVI

FILTRATION RESISTANCE DATA FOR WEB FORMER FURNISHES WITH HUBER SSW CLAY FILLER

Fiber furnish: 30% bleached softwood kraft
70% bleached red maple as shown

Pressure Drop, cm. H_2O	Resistance, $\underline{R} \times 10^{-8}$, cm./g. Holopulp	Kraft
10	1.66	1.53
20	2.33	2.20
30	2.90	2.79
40	3.41	3.37
50	3.88	3.90
60	4.31	4.40
70	4.74	4.90
80	5.16	5.37
90	5.55	5.85

APPENDIX VIII

PROCESS CONDITIONS FOR RED MAPLE HOLOPULPS

TABLE XXXVII

CHLORINE DIOXIDE/CHLORINE-ALKALI PULPING OF RED MAPLE

Chip fiberization: As in Table III

Alkali pretreatment: 3% NaOH, 10% consistency, 80°C., 15 min.
Final pH 9.2, 9.3

Lignin modification: 25→35°C. in 60 min., 8% ClO_2 on chem. equiv. basis

ClO_2:Cl_2 (w:w)	85:15	75:25	65:35	55.45	35·65	15:85
Chlorine dioxide, %	7.5	7.1	6.6	6.1	4.7	2.5
Chlorine, %	1.3	2.4	3.6	5.0	8.7	14.4
Consistency, %	8.0	8.0	8.0	7.3	6.3	4.0
Time, min.	140	133	113	108	65	65
Final pH	1.5	1.3	1.2	1.2	1.1	1.0

Alkali extraction. 7.5% sodium hydroxide, 15% consistency, 80°C., 120 min.

Final pH	10.8	10.7	10.7	10.6	9.7	8.3
Yield, %	67.1,65.2	68.5,66.8	67.3,66.5	66.3,67.0	69.5,68.8	71.5,71.3
Kappa no.	27.1,20.9	27.7,21.2	26.2,23.6	20.8,23 4	30.8,30.2	37.7,36.7
Klason lignin, % o.d.p.	4.6,3.1	5.0,3.7	4.4,3.9	3.4,4 1	6.3,5.5	7.2,7.1
Acid sol. lignin, % o.d.p.	2.1,1.8	2.3,2.1	2.2,2 1	1.9,2.0	2.4,2.3	2.8,2.6

Primary refining (combined pulps). 3.5% consistency, 195°F. water feed, 200 g. o.d./min., 0.008 in. gap

Screen rejects, % o.d.p.	0.1	0.1	0 1	0.1	--	--
Material loss on screening, % o d.p.	2.7	2.3	2.2	2.1	--	--

APPENDIX IX

PULP EVALUATION DATA (RED MAPLE)

TABLE XXXVIII

VALLEY BEATER EVALUATION OF BLEACHED RED MAPLE CHLORINE DIOXIDE/CHLORINE-ALKALI PULPS

ClO_2 Cl_2	85 15				65 35				55 45			
Beating time, min	0	3	7	13	0	3	7	13	0	3	7	13
pH	4 8				4 6				4.6			
Canadian freeness, ml.	240	215	175	120	250	205	170	130	245	220	180	125
Handsheet drainage time, sec.	5 4	5.9	6 9	12 3	5 3	6.2	6 9	12.3	5 4	6.0	7.3	12.2
Handsheet density, g /cc	0 698	0.710	0.717	0 748	0 704	0.705	0.727	0 763	0.703	0.723	0.735	0.764
Bendtsen smoothness, ml /min.	516	449	454	516	647	599	488	507	470	425	497	502
Breaking length, km	8.1	8 5	9.1	9 4	7.0	7 6	8 7	9.4	7 9	8 0	8 8	9 5
Stretch, %	3 4	3 5	3 7	3 7	2 7	2 8	3 7	3 8	3.3	3 3	3 8	3.8
Tensile energy absorp , g cm /cm ²	119	130	146	152	82	91	138	152	112	114	141	152
Tensile stiffness, Et, kg /cm	517	528	548	551	487	517	526	558	495	509	527	554
Tear factor (Elmendorf)	80	80	77	73	72	74	74	69	78	75	75	72
MIT fold	209	212	395	1006	190	257	418	897	166	238	391	878
Spec scatt coeff , 650 nm	253	248	235	202	252	248	242	202	258	249	238	200
Spec absorp. coeff	1 49	1 40	1.41	1 50	1 28	1 49	1 20	1 50	1 10	1 11	1 18	1.28
Shive count, no./cm ²	0.50	0 21	0.11	0 06	0 67	0 32	0.18	0 14	0 42	0 32	0 26	0.08

TABLE XXXIX

VALLEY BEATER EVALUATION[a] OF BLEACHED RED MAPLE KRAFT PULP

Beating time, min.	0	4	12	24
Canadian freeness, ml.	555	495	375	205
Handsheet drainage time, sec.	4.9	5.2	6.0	12.8
Handsheet density, g./cc.	0.615	0.645	0.716	0.806
Bendtsen smoothness, ml./min.	360	370	300	280
Breaking length, km.	3.89	4.96	7.11	9.13
Stretch, %	1.6	2.1	3.0	3.5
T.E.A., g. cm./cm.^{2}	25.0	43.8	90.7	127
Tensile stiffness, kg./cm.	320	344	385	418
Tear factor (Elmendorf)	42	56	77	78
MIT fold	4	8	48	791
Spec. scatt. coeff., 650 nm.	423	395	337	262

[a]Data are the means from a duplicate evaluation and are from Report Sixteen.

TABLE XL

FILTRATION RESISTANCE DATA FOR BLEACHED RED MAPLE PULPS PREPARED AS IN TABLE XIV

Pressure Drop, ΔP, cm. H_2O	Resistance $R \times 10^{-8}$, cm./g.[a] Valley Beating Time, min. 0	3	7	13
	Pulp $ClO_2:Cl_2$ = 85:5			
10	2.0	2.4	2.8	4.8
20	2.9	3.4	4.2	7.4
30	3.7	4.4	5.5	9.6
40	4.4	5.3	6.6	11.8
50	5.0	6.3	7.8	13.9
60	5.7	6.9	8.8	16.0
70	6.4	7.8	9.8	18.0
80	7.0	8.6	10.9	19.8
90	7.6	9.4	11.9	21.8
	Pulp $ClO_2:Cl_2$ = 65:35			
10	1.9	2.0	2.7	4.4
20	2.6	2.9	4.0	6.8
30	3.3	3.7	5.1	8.9
40	3.9	4.5	6.2	10.9
50	4.5	5.2	7.2	12.9
60	5.0	5.8	8.2	14.8
70	5.6	6.5	9.2	16.6
80	6.2	7.1	10.0	18.3
90	6.7	7.8	11.0	20.1
	Pulp $ClO_2:Cl_2$ = 55:45			
10	1.7	1.9	2.6	4.3
20	2.5	2.8	3.9	6.6
30	3.2	3.6	5.1	8.6
40	3.8	4.3	6.2	10.5
50	4.4	5.0	7.2	12.3
60	5.0	5.7	8.2	14.1
70	5.5	6.4	9.2	15.9
80	6.1	7.0	10.1	17.4
90	6.6	7.6	11.1	19.2

[a]Mean of duplicates.