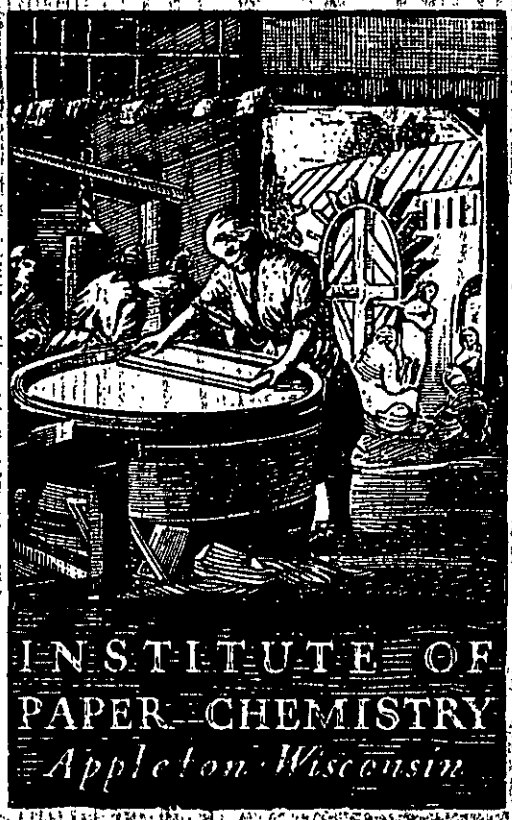

CONFIDENTIAL

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS:

AN INTERIM REPORT ON PROCESS STUDIES AND PAPERMAKING CHARACTERISTICS

Research Grant

Project 2500

Report Sixteen

A Progress Report

to

THE GRANTORS

August 7, 1972

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS: AN INTERIM REPORT ON PROCESS STUDIES AND PAPERMAKING CHARACTERISTICS

SUMMARY

As part of a plan to investigate the chlorine dioxide-alkali semichemical pulping of softwoods using chip impregnation with alkali before fiberization, a basis has been established to permit selection of the process conditions to produce 65-85% yield pulps. This basis is for an oxidant addition of 4.5-9.0% in a lignin modification step after fiberization and followed by alkali extraction. Pulps produced with the same Kappa number using less oxidant but more alkali had a spread of up to 5% yield level.

As a part of activities aimed at reducing the amount of chlorine dioxide needed to produce pulps from hardwoods, the use of 4.0-7.0% oxidant in a one-step lignin modification gave pulps with Kappa number 75-25 and 76-64% yield. For pulps of the same Kappa number, relationships to oxidant addition, alkali usage, and yields resembled those for softwoods, and there are indications that papermaking pulps can be made with 4.0% oxidant addition.

To pursue investigations on the papermaking behavior of holopulps, a clean, shive-free bleached red maple pulp with a relatively stable 88 TAPPI brightness has been prepared in 57-60% yield. The unbeaten pulp was bleached at high consistency in three stages, namely, chlorine dioxide/chlorine, alkali extraction, and chlorine dioxide.

As a part of investigations on the papermaking characteristics of a bleached red maple holopulp, data on wet web moisture content and wet pressing pressures have been compared with similar values for the corresponding kraft pulp.

Wet web moisture contents were found to be lower for the holopulp in comparisons at equal dry sheet density. Comparison of the same two pulps at similar handsheet drainage times showed comparable trends in sheet properties after pressing at 10 p.s.i.g. instead of 50 p.s.i.g. except that smoothness decreased less and tear factor became relatively greater for the holopulp. This holopulp when unbeaten had hydrodynamic properties similar to the appreciably beaten kraft pulp.

In another part of the investigations on papermaking characteristics, mixed furnishes have been examined to a limited extent. It was found that 5, 10, and 20% filler-grade clay was about 88% retained in furnishes containing holopulp whereas retention fell from 82 to 72% for the addition of up to 20% clay in furnishes with the corresponding hardwood kraft pulp. Similar results were not obtained with titanium dioxide. For the case of clay filler with comparison at the same specific scattering coefficient, sheet density and strength properties were quite similar for clay additions of 20% compared with 6% for the furnish containing holopulp compared to kraft pulp respectively. Therefore, in sheets containing hardwood holopulp instead of hardwood kraft pulp, 10% more clay filler was present in the former, which would be an advantageous cost factor.

INTRODUCTION

At an earlier date, promising results were reported on investigations into producing very high-yield unbleached chlorine dioxide-alkali pulps from softwoods. On the basis of the results obtained, it was proposed to continue studies in this area to define whether acceptable unbleached semichemical pulps can be made at more favorable cost, with particular reference to linerboard. Previously, the process steps included alkali conditioning after chip fiberization. This progress report includes the most recent work which is concerned with whether the alternative of chip impregnation with alkali could allow simplification of the process and cost advantages. Experiments so far have been designed to enable process conditions to be chosen with alkali impregnation before chip fiberization and chlorine dioxide-alkali delignification.

It is apparent from previous consideration of holopulp costs that reduction in oxidant usage is a key factor, and for this reason it was proposed to continue studies aimed at reducing the amount needed by varying the pulping conditions. This progress report also includes the results to date on a hardwood, showing the inter-relationship of oxidant-alkali consumption, degree of delignification, and pulp bleachability. These results were taken into account when preparing the bleached pulp needed to study papermaking behavior.

To further evaluate holopulp, it was proposed to study properties and behavior, and for that purpose a dirt-free, fully bleached hardwood pulp has been prepared. This report presents the current results obtained from experiments with this pulp, involving wet pressing at different pressures and three-component furnishes with two different mineral fillers as one component of the furnish.

PULPING

SOFTWOODS – UNBLEACHED, VERY HIGH-YIELD HOLOPULPS

In earlier work on softwoods, particularly as described in Progress Report Thirteen, it was demonstrated that fiberization at a temperature corresponding to steam pressures above atmospheric resulted in less fiber damage and that in delignification with chlorine dioxide-alkali, pretreatment with alkali was advantageous since it resulted in greater lignin removal for the addition of a certain amount of oxidant. As a continuation of this work, the alternative of chip impregnation with alkali instead of water and omission of alkali pretreatment after fiberization will be considered.

In this plan, the fiberization temperature and consistency will be left unchanged at 158°C. and about 45%, respectively, which means that the chips have to be impregnated with the amount of alkali needed in this step of the process. The amount of alkali needed is related to the extent to which extractives and substances such as hemicelluloses are to be dissolved. For example, in earlier work on fiberized chips it was found that at 90°C. about 10% of the wood substance was removable by alkali as long as the reaction proceeded for at least 15 min. with not less than 4% sodium hydroxide. As a sequel, it appeared that chips should be heated long enough at 158°C. after impregnation with alkali to reduce the yield level to about 90%.

On this basis, two experimental objectives to be adopted were:

to determine the alkali uptake for chip impregnation with aqueous sodium hydroxide of different concentrations, and

to determine the yield level after pretreatment of chips impregnated with at least two levels of alkali for different times.

Previous work has also shown that pulps of a particular yield can be obtained under oxidant-alkali delignification conditions different enough to influence costs, and that the lignin content of pulps obtained at the same yield may vary enough to influence pulp quality. Furthermore, pulps with papermaking properties can be obtained for a significantly different range of yields from 65% up to at least 80%.

On this basis, two additional experimental objectives to be adopted were:

> to determine the combination of oxidation and alkali extraction conditions capable of giving pulp yields of about 65-85%, and
>
> to determine the relative extent of lignin removal in the pulps obtained as above.

With these results in hand, it seemed that it would be possible to select process conditions to prepare a representative range of products in greater quantity for mechanical separation into individual fibers and evaluation as unbleached semi-chemical pulps.

Results and Discussion

The alkali uptake on impregnation of loblolly and black spruce chips with aqueous sodium hydroxide of different concentrations is illustrated in Fig. 1, and the yield levels for loblolly after pretreatment are shown in Fig. 2. Pretreatment consisted of heating 2.9, 4.0, and 7% alkali-impregnated loblolly chips for different times and then fiberizing. Corresponding practical details are given in Appendix I.

On the basis of these results, chip pretreatments chosen for further experiments were 2.9 and 7.1% sodium hydroxide followed by heating 2.5 and 5.0 min. at 75 p.s.i.g., respectively. Using earlier work as a guide, 4.5% and 9.0% were

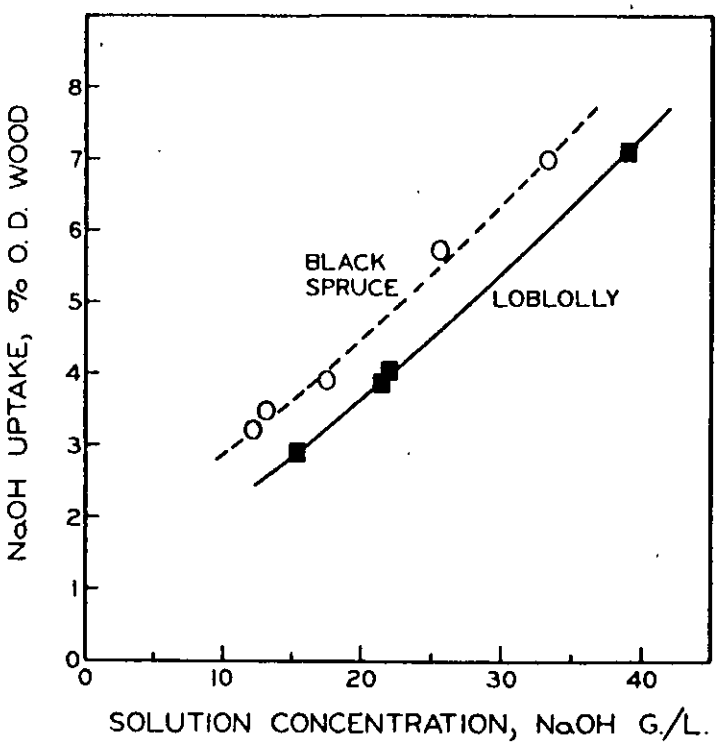

Figure 1. Impregnating Solution Concentration and Corresponding Alkali Uptake by Chips

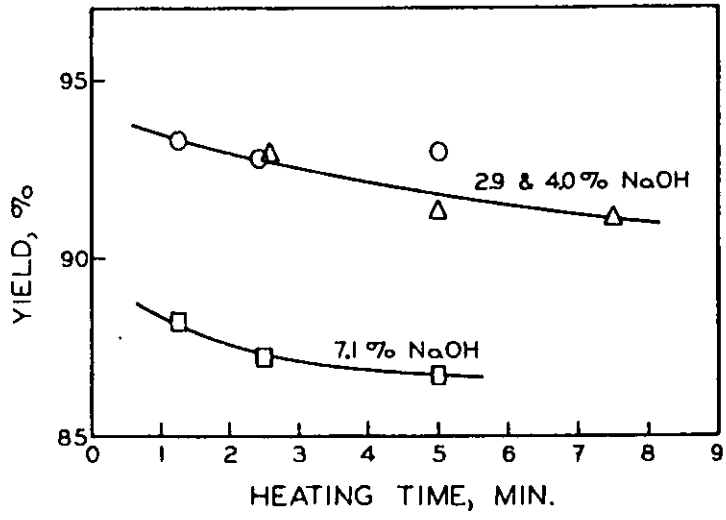

Figure 2. Time of Heating Impregnated Loblolly Chips at 75 p.s.i.g. and Corresponding Yield Levels After Pretreatment

chosen as the upper and lower levels of oxidant to be investigated; then a check was run to determine whether the mildest and severest combinations of pretreatment and lignin modification gave yields in the 65 to 85% range after chlorine dioxide-alkali delignification. The results for loblolly as presented in Fig. 3 confirmed that by appropriate choice of alkali extraction conditions after oxidation the desired yield range could be bracketed.

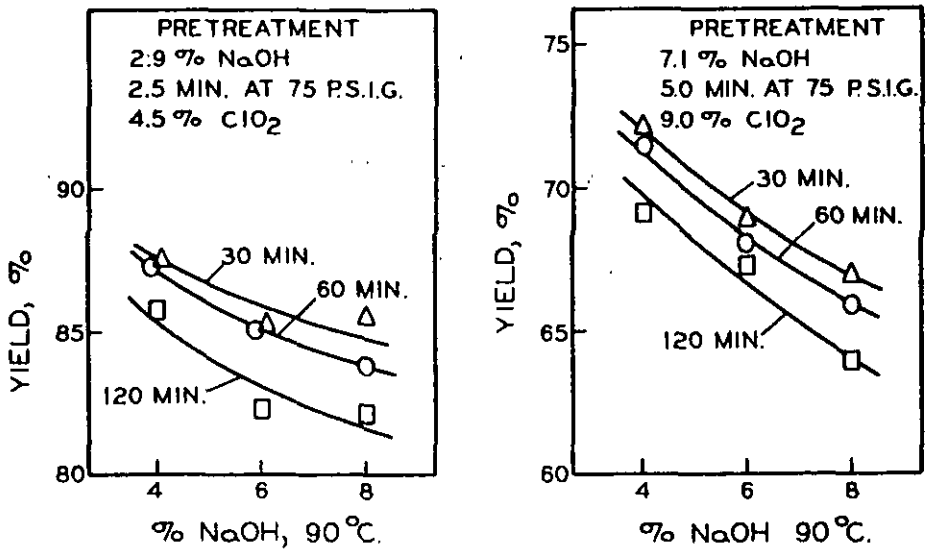

Figure 3. Amount of Alkali Used in Extraction After Using Mildest (A) and Severest (B) Combinations of Pretreatment and Lignin Modification, with Corresponding Yield Levels for Loblolly

In the experiments carried out to obtain the results in Fig. 3, an extraction temperature of 90°C. was chosen on the basis of previous work. Final pH data, as included in Fig. 4 for loblolly, reveal that for the case of pretreatment with 7.1% alkali and oxidation with 9.0% oxidant, the final pH was essentially

dependent on the amount of alkali added for extraction times of 30-120 min. For the same set of pulps, Kappa number data as also included in Fig. 4 reveal that Kappa number tended to be more dependent on the amount of alkali added than extraction time for 60-120 min.

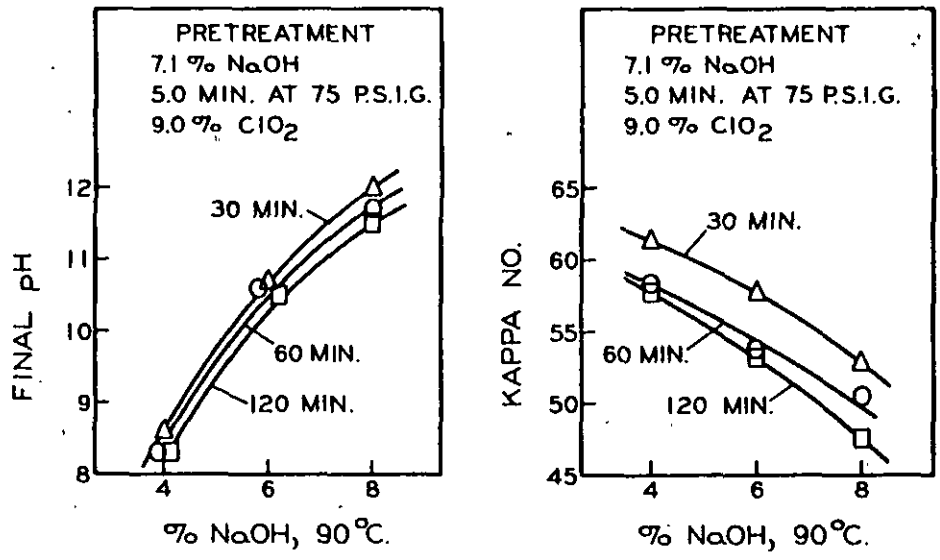

Figure 4. Amount of Alkali Used in Extraction After Severest Pretreatment and Lignin Modification of Loblolly, Showing Corresponding Final pH (A) and Kappa Number (B)

For the mildest conditions of pretreatment and lignin modification, final pH and Kappa number showed less dependence on the amount of alkali used in the extraction. This can be seen from the results presented in Table I, where in calculating Klason lignin removed and carbohydrate lost it has been assumed that Klason lignin is equal to 0.15 Kappa number on a pulp basis. As a first approximation, these values although not absolute are believed to provide a guide to apparent trends in lignin removal and carbohydrate loss. Thus it can be seen for each set of results that the level of lignin removal is determined mainly by oxidant addition and is changed by only 1-2% as a consequence of varying the

extraction conditions. On the other hand, the corresponding change in yield level is 5-9%, indicating about a fourfold loss of material other than permanganate-reactive lignin as a consequence of varying the extraction conditions. Further, this loss of material is greatest in the set of results having the lower lignin level.

TABLE I

RELATIVE LIGNIN REMOVAL IN 65-85% YIELD RANGE FOR 4.5 AND 9.0% OXIDANT AFTER LOBLOLLY CHIP PRETREATMENT WITH 2.9 AND 7.1% ALKALI RESPECTIVELY

Alkali impregnation: steamed twice at 15 p.s.i.g. for 2 min., then covered with NaOH solution for 30 min. at 100 p.s.i.g. over pressure.		
NaOH concn., g./l.: initial	15.4	39.0
final	13.0	33.2
NaOH uptake, %[a]	2.9	7.1
Steaming, 75 p.s.i.g.		
Min.	2.5	5.0
Condensate pH	10.4	12.3
Fiberization: 12-in. Sprout-Waldron refiner; first pass 0.065-in. gap, second pass 0.015-in. gap.		
Yield, %	92.9	86.7
Lignin modification: 25 → 35°C. in 60 min.; 8% consistency.		
ClO_2, %	4.5	9.0
Time, min.	45	60
Final pH	1.6	1.8
Yield, %	91.9	82.7
Kappa no.	90.1	81.4

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

NaOH, %	4.0			6.0			8.0			4.0			6.0			8.0		
Time, min.	30	60	120	30	60	120	30	60	120	30	60	120	30	60	120	30	60	120
Final pH	11.8	11.5	10.2	11.9	11.9	11.7	12.5	12.2	12.0	8.6	8.3	8.3	10.7	10.6	10.5	12.0	11.7	11.5
Yield, %	87.2	87.4	85.8	85.2	85.0	82.2	85.5	83.7	82.1	72.1	71.6	69.1	68.9	68.0	67.2	66.9	65.9	63.9
Kappa no.	86.5	88.6	85.5	91.1	86.8	86.5	88.8	83.8	85.7	61.3	58.2	57.8	57.8	55.8	53.2	52.8	50.5	47.5
Klason lignin, %[b]	11.3	11.6	11.0	11.6	11.1	10.6	11.4	10.5	10.6	6.6	6.3	6.0	6.0	5.5	5.4	5.3	5.0	4.6
K. lignin removed, %	17.3	17.0	17.6	17.0	17.5	18.0	17.2	18.1	18.0	22.0	22.3	22.6	22.6	23.1	23.2	23.3	23.6	24.0
Cabohydrate loss, %[d]	-4.5	-4.4	-3.4	-2.2	-2.5	-0.2	-2.7	-1.8	-0.1	5.9	6.1	8.3	8.5	8.9	9.6	9.8	10.5	12.1

[a] All percentages are on the original o.d. chips.

[b] Calculated: Klason lignin = 0.15 Kappa no. × yield.

[c] Assuming original wood contained 28.6% Klason lignin.

[d] Calculated: 100 - (yield + Klason lignin removed).

The results obtained above were used in planning experiments to more completely show the relative extent of lignin removal as a function of oxidant addition with bracketed conditions for alkali extraction, as in Appendix II which incorporates the results given in Table I. From this appendix, oxidant addition and Kappa number as related to different process conditions are depicted in Fig. 5.

In this figure it can be seen that there is a spread of Kappa numbers corresponding to each level of oxidant addition. This spread reflects the amount of alkali in the impregnation of loblolly chips and the extraction after lignin modification.

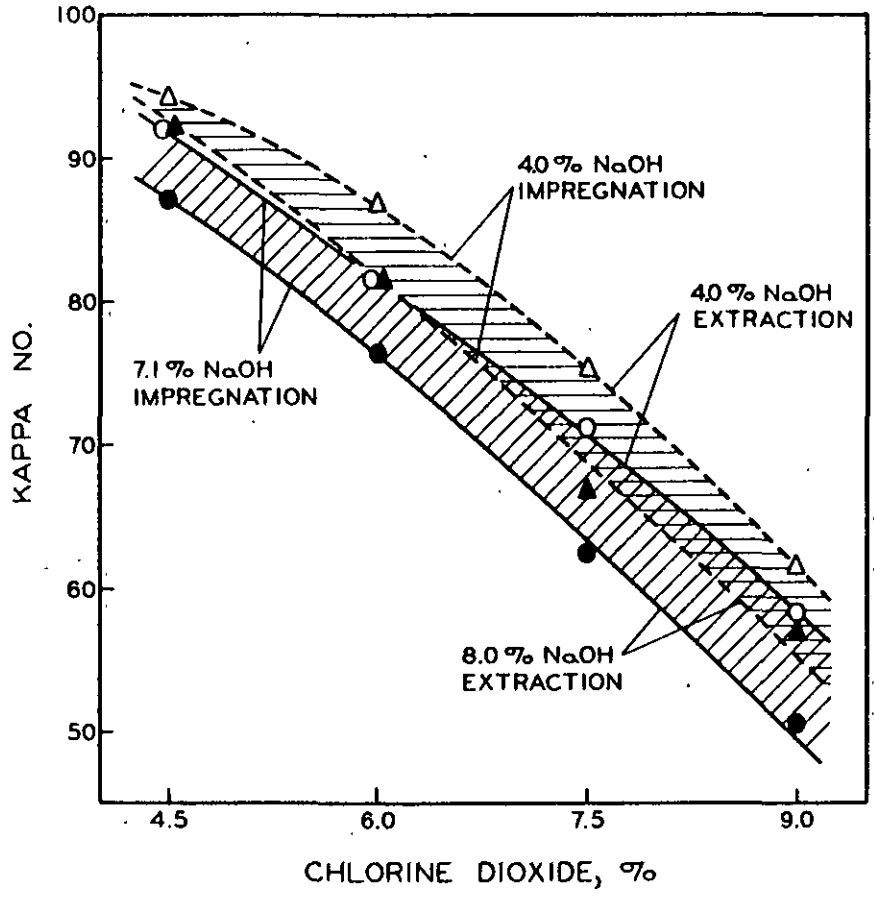

Figure 5. Amount of Oxidant Used (After Loblolly Chip Impregnation with 4.0 and 7.1% NaOH) and Corresponding Kappa Number (After Alkali Extraction with 4.0 and 8.0% NaOH)

Along with the spread of Kappa numbers shown in Fig. 5, for each level of oxidant addition there is a spread in yield level. For example, from Appendix II the spread in yield level for 4.5% oxidant is from 74.8 to 87.4%, while the corresponding apparent Klason lignin content varies only from 9.8 to 11.6%, depending upon the process conditions and particularly on the amount of alkali used. When taking pulp costs and quality into account, it is evident that pulps

obtained at different yield levels for a given level of oxidant addition should be tested.

It is also evident from Fig. 5 that pulps with the same Kappa number can be obtained under significantly different process conditions. In addition, there are significant differences in yield as seen by reference to Appendix II and illustrated by example in Table II. From this it is clear that pulps can be produced with the same Kappa number using less oxidant but with more alkali and at a lower yield. Thus when taking pulp costs and quality into account, it is evident that pulps obtained at a given Kappa number level using different process conditions should be considered.

TABLE II

ILLUSTRATION OF VARIATION IN YIELD AND CHEMICALS NEEDED FOR THREE LEVELS OF KAPPA NUMBER (LOBLOLLY)

Kappa number	87.0	86.6	76.3	75.2	62.3	61.4
Yield, %	75	80	72	78	68	73
Oxidant, % ClO_2	4.5	6.0	6.0	7.5	7.5	9.0
Alkali, % NaOH	15	8	15	8	15	8

It is interesting to note that there is no analogy to the above situation in kraft pulping, for example, since differences of 5% in yield level are not obtained in the normal way at the same Kappa number level. This relates to the two-step mechanism of chlorine dioxide-alkali delignification being basically different with material removal in alkali, complicated by the presence of hemicelluloses. The outcome is that it is possible to obtain pulps with the same Kappa number or calculated lignin:yield ratio at significantly different yields as in Table II.

The equipment needed to refine partially delignified fiber bundles into individual fibers to provide pulps required as a part of this study has now been installed and is shown in Fig. 6.

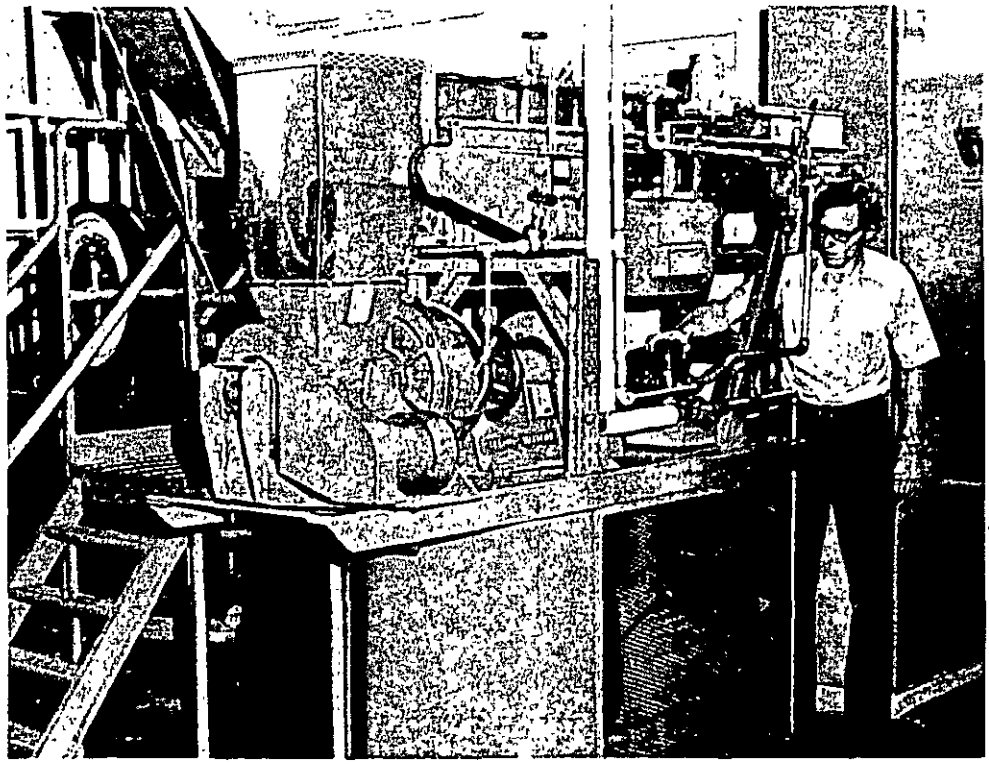

Figure 6. Refiner System to Be Used for Treating Partially Delignified Fiber Bundles

Thus, for the evaluation of unbleached, very high-yield holopulp from softwoods using chip impregnation with alkali before fiberization, a basis has been established to permit selection of the process conditions. This basis confirms that pulps should be obtained at different yield levels for a given level of oxidant addition, and using different process conditions for a given Kappa number level for the determination of papermaking properties after disk refining.

HARDWOODS – OXIDANT CONSUMPTION

There has been only limited additional activity to date in the area of reducing oxidant usage and this has not included giving further consideration to mixtures of chlorine dioxide plus chlorine. The results that have been obtained so far are presented and discussed below.

Results and Discussion

The situation concerning the influence of oxidant usage and process conditions on the delignification of a hardwood is essentially analogous to that discussed in the previous part of this report which was concerned with softwoods. That is, Kappa number and yield are both influenced by the amount of oxidant added and the condition of the alkaline process steps. The amount of oxidant added and the corresponding Kappa number range for red maple pulps arising from the use of different alkali extraction conditions are illustrated in Fig. 7. From this it can be seen that for the addition of 4.0-7.0% oxidant the Kappa number level is at least 10 units higher when the mildest conditions of alkali extraction were used. Further details of the process conditions are included in Table III.

Like loblolly, red maple chlorine dioxide-alkali pulps can be produced with the same Kappa number using less oxidant but with more alkali and at a lower yield. However, there are quantitative differences so that data cannot be taken directly from Table III as data in Table II were taken from Appendix II. When results from Table III are considered as in Fig. 8, this provides an alternative basis for illustrating the situation for red maple, and the following points are of particular interest.

1. The results are related to three distinct curves corresponding to the addition of 4.0, 5.5, and 7.0% oxidant.

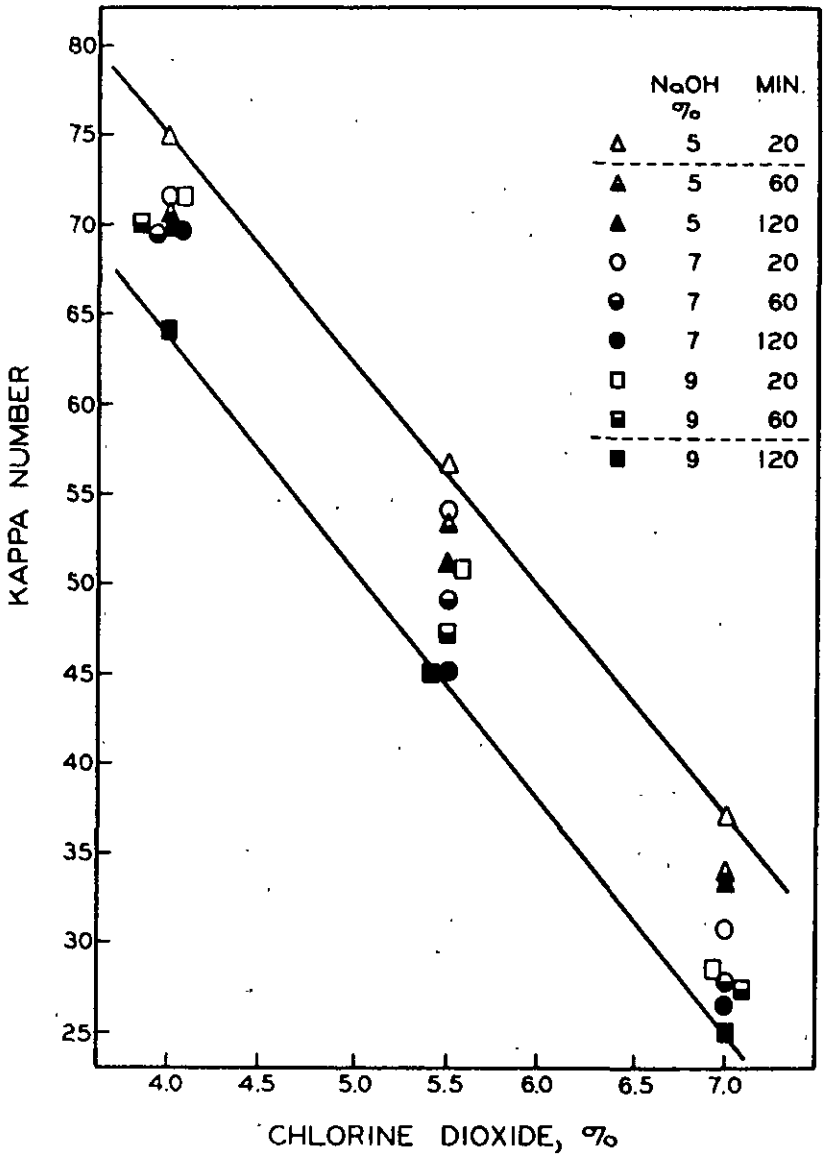

Figure 7. Amount of Oxidant Added and Corresponding Kappa Numbers for Red Maple Pulps Obtained Using Different Alkali Extraction Conditions

TABLE III

DATA FOR DIFFERENT OXIDANT ADDITIONS IN FIBERIZED RED MAPLE DELIGNIFICATION

Alkali conditioning, 3.0% NaOH, 10% consistency, 70°C., 15 min.

pH after mixing	n.d.
Final pH	9.1
Yield, %	n.d.

Lignin modification: 25 to 35°C. in 60 min., 12% consistency.

ClO_2, %	4.0	5.5	7.0
Time, min.	35	45	60
Final pH	2.1	1.9	1.8
Yield, %	90.8	91.0	90.1

Alkali extraction: 80°C., 15% consistency.

NaOH, %	5.0			7.0			9.0		
Time, min.	20	60	120	20	60	120	20	60	120
4.0% ClO_2									
Final pH	10.8	10.4	10.1	11.5	11.2	11.1	11.8	11.6	11.5
Yield, %	76.6	73.9	73.3	74.0	72.3	70.9	72.9	71.5	69.3
Kappa no.	74.8	70.5	69.6	71.5	69.4	69.6	71.5	70.0	64.1
Klason lignin, %[a]	8.6	7.8	7.7	7.9	7.5	7.4	7.8	7.5	6.7
5.5% ClO_2									
Final pH	10.4	9.9	9.4	11.2	11.1	10.8	11.5	11.3	11.2
Yield, %	72.9	71.6	71.0	70.4	68.8	67.9	69.3	68.1	67.0
Kappa no.	56.5	53.2	51.0	54.0	49.0	45.1	50.7	47.2	45.0
Klason lignin, %[a]	6.2	5.7	5.4	5.7	5.1	4.6	5.3	4.8	4.5
7.0% ClO_2									
Final pH	9.9	9.1	8.9	10.9	10.7	10.7	11.2	11.0	11.1
Yield, %	71.7	69.7	69.1	67.4	66.1	65.1	65.7	65.0	63.8
Kappa no.	37.0	33.9	33.3	30.8	27.9	26.5	28.6	27.4	25.0
Klason lignin, %[a]	4.0	3.6	3.5	3.1	2.8	2.6	2.8	2.7	2.4

[a] Klason lignin = 0.15 x Kappa no. x yield.

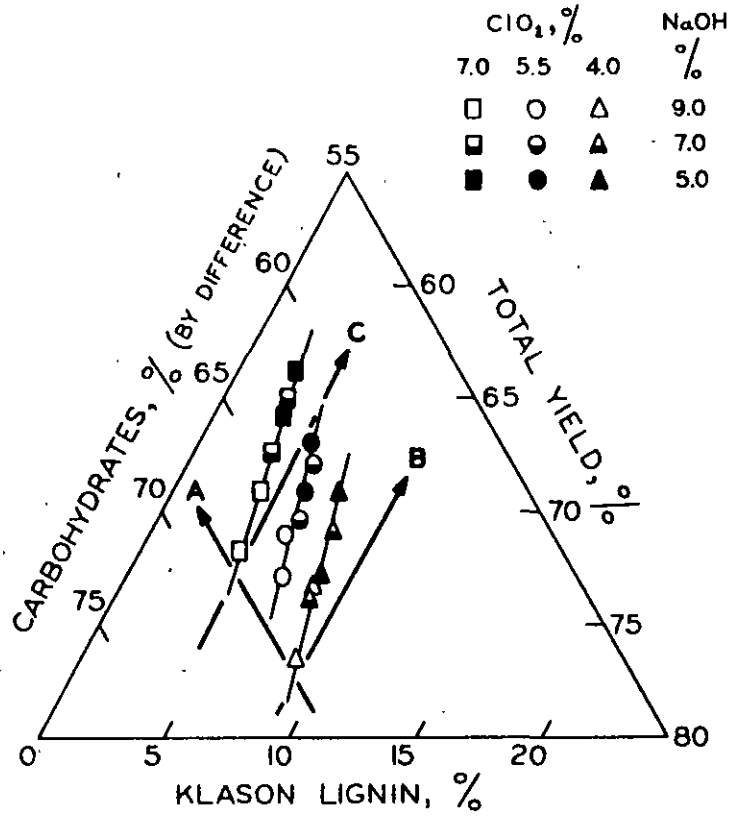

Figure 8. Yield and Calculated Lignin and Carbohydrate Values for Red Maple Pulps as Discussed in Text

2. The curves are separated in the direction of selective delignification as indicated by Arrow A.

3. The extension of each curve to lower yield levels corresponds with the use of more severe alkali extraction conditions.

4. The extension of each curve to lower yield levels approximates the direction of selective carbohydrate removal as indicated by Arrow B.

5. The curves are intersected by lines of constant calculated lignin: yield ratio or Kappa number as indicated by Arrow C.

6. The intercepts of Arrow C indicate a yield level difference of about 8.0% at a constant Kappa number for the addition of 7.0 and 5.5% chlorine dioxide and imply different conditions of alkali extraction.

The spread in Kappa number seen in Fig. 7 is accompanied by a corresponding spread in yield of almost 10%, as shown in Fig. 9. In previous activities on this project, the occurrence of screen rejects and pulp shives has impeded consideration of pulps obtained at yield levels above the fiber liberation point which is near 65% yield. The best result obtained so far for oxidant consumption without resorting to mechanical defibration to eliminate screen rejects required the addition of 7.5% chlorine dioxide. When oxidant consumption was reduced to 6.0% chlorine dioxide, mechanical defibration was needed to reduce the amount of screen rejects. In essence, Fig. 9 confirms that for hardwood pulps obtained at yield levels near the fiber liberation point, about 6.0-7.5% chlorine dioxide is apparently needed. If mechanical defibration is used to obtain a shive-free pulp, this removes the need for using as much as 6.0-7.5% chlorine dioxide. Preliminary tests have clearly indicated that pulps made with 4% chlorine dioxide have significant papermaking potential. The equipment now available as illustrated in Fig. 6 will facilitate the gathering of more specific information in this area.

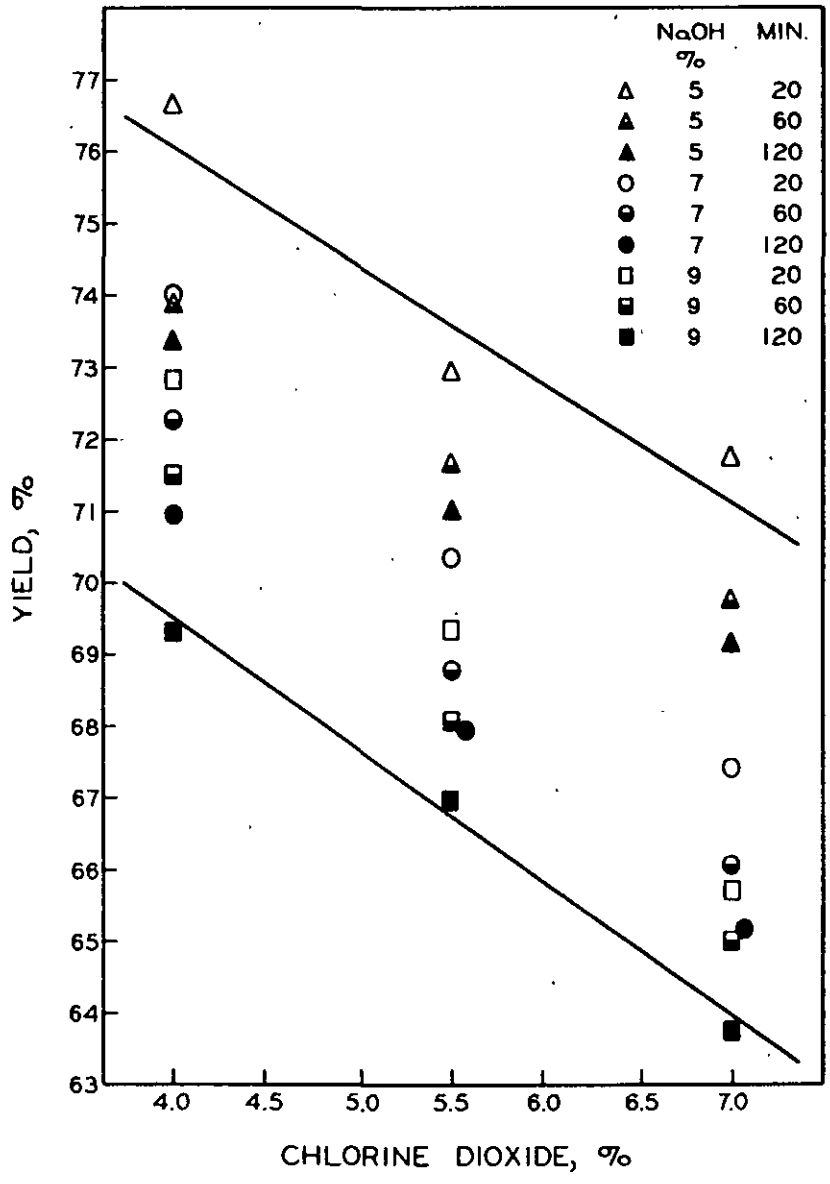

Figure 9. Amount of Oxidant Added and Corresponding Yields for Red Maple Pulps Obtained Using Different Alkali Extraction Conditions

PAPERMAKING BEHAVIOR

This part of the report is addressed to further characterizing holopulps in terms of properties and behavior.

The question of how to characterize a pulp is one on which there seems to be no consensus of expert opinion, as evident at a recent international conference devoted to pulp characterization (1).

Previously in this project, attention has been focused on handsheet properties of holopulps as 100% of the furnish. This has left mixed furnishes incorporating groundwood, chemical pulps, and fillers unstudied. Additionally, various factors such as wet sheet properties, filler retention, flocculation, and calendering, for example, have been left unstudied.

To attempt to cover all the factors which scientists, pulp manufacturers, and papermakers may want characterized is beyond the scope of this present project and therefore attention has been focused on certain aspects of characterization. These are wet pressing and filler retention using 100% bleached hardwood holopulp in the case of the former and a "wood-free" three-component furnish for the latter.

Before preparing the pulps for experiments in these areas, previous work was reviewed with the conclusion that if possible a bleached holopulp should meet two criteria not fully satisfied previously. These criteria are:

the pulp should be clean or shive free, and

the level of brightness should be high and relatively stable.

An additional criterion was that only a limited amount of time could be allowed for the efforts to meet these criteria, even if some compromise became necessary. Thus the next three bits of this report are devoted to:

the bleached pulp,

wet pressing, and

filler retention.

THE BLEACHED PULP

Since the amount of oxidant is a key factor in determining degree of delignification and costs, consideration was given to the unbleached Kappa number level and bleachability with hypochlorite. The choice of Kappa number levels was made on the basis of oxidant addition and independently of yield level associated with fiber liberation.

From Fig. 10 it can be seen that there are significant differences in the brightness levels attainable depending upon pulp Kappa number which is related in turn to oxidant addition, and as might be expected, lower brightness levels are associated with higher Kappa numbers. Using these and previous results, for example Table XIV in Progress Report Fourteen, as a guide, it was decided that a pulp with Kappa number about 20 would be made in order to meet the criterion of high brightness. By projection of the data on which Fig. 7 is based, it appeared that the chemical equivalent of 8.0% chlorine dioxide would be required for a Kappa number of 20.

The red maple chips for producing bleached pulp were fiberized in a Bauer pressurized refiner system using conditions included in Appendix III. As discussed with reference to evaluation data in Appendix III, the use of these fiberization conditions represents a compromise in terms of a narrowing of the handsheet density range achieved using a different machine.

From a practical viewpoint, the significant point at this time is that it has not been possible to obtain comparable chlorine dioxide-alkali pulps using a pressurized Asplund and a pressurized Bauer refiner. In other words, the conditions

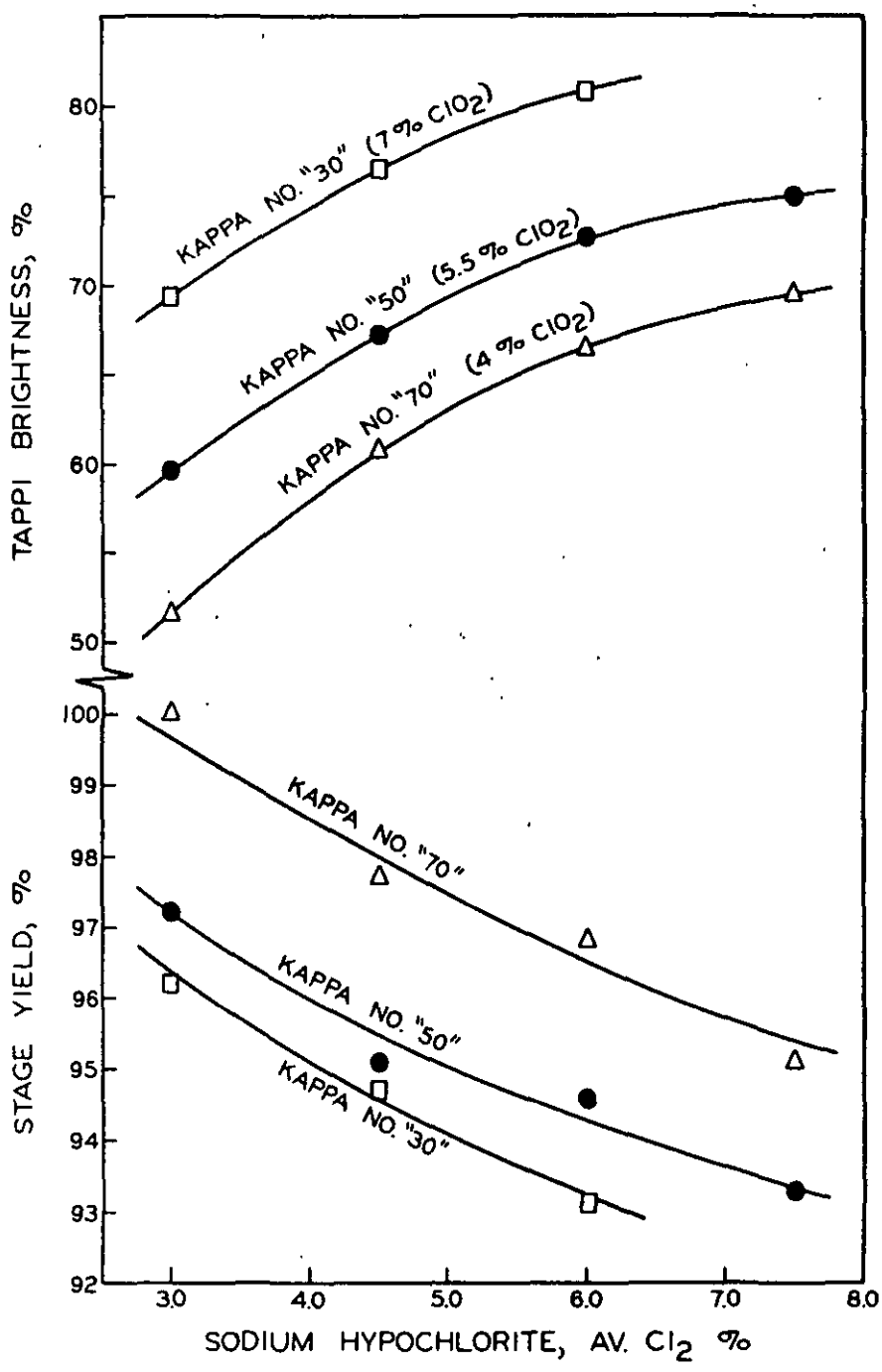

Figure 10. Amount of Hypochlorite with Corresponding Brightnesses and Stage Yields for Red Maple Pulps with Nominal Kappa Numbers as Shown. (For Origin of These Pulps, See the Experimental Part)

of fiberization that gave certain pulp properties when using the Asplund have not been successfully translated to the Bauer equipment which is more conveniently located. This is not new in that there have been similar situations in the past, but experience has also tended to demonstrate that what is achievable with single-disk machines is also feasible with double-disk machines. In a recent publication on changes in pulp character related to pressure refining conditions, Atack (2) has pointed out that the rate of shear will influence the glass transition temperature. It is conceivable that taking this kind of factor into account is important when switching from a single- to double-disk machine as was done in this project, in addition to which there was an appreciable diameter difference.

Process conditions used to delignify red maple fiberized chips are given in Table IV. In this, the amount of oxidant used is chemically equivalent to 8.0% chlorine dioxide as planned and consists of a mixture of chlorine dioxide and chlorine. The Kappa number is near the target level of 20 and screen rejects are negligible. Notes on the basis for using 3.0% sodium hydroxide in the alkali conditioning step and 80°C. in the alkali extraction are given in Appendix IV.

Pulp produced as in Table IV was readily bleached to a high brightness level by hypochlorite as shown in Table V. Previously, oven aging had been used as a method to test brightness stability, but on this occasion steam-aged brightnesses were obtained according to the work of Gullichsen (3) who has proposed such a method for the determination of color reversion of bleached pulps.

TABLE IV

CHLORINE DIOXIDE-ALKALI DELIGNIFICATION OF RED MAPLE FIBERIZED CHIPS

Alkali conditioning: 3% NaOH, 10% consistency, 70°C., 15 min.	
Final pH	9.0, 9.0
Lignin modification: 7.5% ClO_2, 1.33% Cl_2, 8% consistency, 25→35°C. in 60 min.	
Time to exhaustion, min.	95, 110
Final pH	1.7, 1.7
Alkali extraction: 7.5% NaOH, 15% consistency, 80°C., 120 min.	
Final pH	10.5, 10.8
Yield, %	65.4, 62.7
Kappa no.	23.3, 19.5
Rejects, % (0.006-in. slots)	0.1, 0.2
Accepts, % o.d. pulp	98.4, 98.2

TABLE V

HYPOCHLORITE-CHLORINE DIOXIDE BLEACHING OF PULP PREPARED AS IN TABLE IV

I. Hypochlorite: 20% consistency, 40°C.

Available chlorine, %[a]	2.0	3.0	4.0	5.0	3.0[b]
Time, min.	185	230	220	180	230
Final pH	8.1	8.1	8.2	8.2	8.3
Residual av. Cl_2, %	0.07	0.16	0.25	0.40	0.20
TAPPI brightness	76.1	83.6	84.1	85.0	81.0
Steam-aged brightness	54.1	60.1	59.2	60.0	57.6
Yield, %	n.d.	n.d.	n.d.	n.d.	63.0

II. Chlorine dioxide: 1% consistency, 70°C.

ClO_2, %	0.2	0.4	0.6
Time to exhaustion, min.	40	45	60
Final pH	3.1	3.4	3.5
TAPPI brightness	77.8	79.5	79.4
Steam-aged brightness	58.6	60.0	61.4

[a] Hypochlorite bleach contained 5% sulfamic acid on an available chlorine basis.

[b] This pulp was bleached with chlorine dioxide in Stage II. The pulps and chlorine dioxide solutions were mixed at room temperature, sealed in polyester film bags, heated rapidly in a microwave oven to 70°C., then placed in a water bath at 70°C. until it was considered that all the ClO_2 had been consumed.

Brightness loss on steam aging of bleached pulp as in Table V is compared with examples for bleached kraft hardwood pulps in Table VI. From this it can be seen that pulps as in Table V have relatively poor brightness stability on steam aging.

TABLE VI

COMPARISON OF HARDWOOD PULP BRIGHTNESSES

	Holopulp		Kraft Pulp	
Bleaching process	H		CEHD	CEDED
TAPPI brightness	76	85	87	89-90
Steam-aged brightness	54	60	79	86

There has been much study on brightness reversion and it is generally agreed that carbonyl groups can be the cause. Also, when pentosan contents are higher, brightness reversion is greater when hypochlorite is included in multistage bleaching, as shown for example in a relatively recent publication (4). Another study of relevance is more recent work on the oxidative degradation of holocellulose (5). This demonstrated that hemicellulose present in red pine holocellulose was degraded more rapidly by peracetic acid and hypochlorite than cellulose, and degradation was more pronounced with hypochlorite, as might be expected.

Degradation of holopulps by hypochlorite has been recognized as a possibility during this project, and handsheet data generally have been obtained as a means of determining whether there has been significant degradation. So far, there has been no general evidence obtained in this way that shows a significant lowering of fiber strength. However, while there may be no apparent degradation of the cellulosic skeletal material in fibers, there seems to be degradation of the hemicellulose that becomes especially evident in terms of steam-aged brightness

stability. For good brightness stability in a pulp containing significant amounts of hemicellulose, for example in a holopulp, the use of hypochlorite even with sulfamic acid (Table V) is apparently most undesirable.

To provide a pulp with a high level of brightness and with good brightness stability, a high-consistency bleaching experiment was designed, taking into account recent work by Kramer (6). This experiment excluded low-consistency chlorination, which is a disadvantageous process step when minimizing process water volume, and excluded the use of hypochlorite. The unbleached pulp was produced as in Table IV with 62.7% yield and the bleaching data are presented in Table VII.

TABLE VII

RED MAPLE CHLORINE DIOXIDE-ALKALI PULP HIGH-CONSISTENCY BLEACHING

I. Chlorine Dioxide-Chlorine: Consistency, 10%; temp., 60°C.

Chlorine dioxide, %	0.77	Time, min.	60
Chlorine, %	0.38	Final pH	2.5

II. Alkali Extraction: Consistency, 15%; temp., 70°C.

Sodium hydroxide, %	0.75	1.2	1.5	3.0
Time, min.	120	90	120	120
Final pH	10.1	10.8	11.3	11.8

III. Chlorine Dioxide: Consistency, 10%; temp., 70°C.

Chlorine dioxide, %	0.2	0.4	0.6	0.4	0.4	0.6	--
Time, min.	16	60	360	60	60	270	
Final pH	4.5	4.0	3.2	3.0	3.7	3.2	
Yield, %	n.d.	n.d.	n.d.	57	n.d.	n.d.	
TAPPI brightness	83.8	87.2	87.9	87.6	87.9	88.6	
Steam-aged brightness	73.0	79.6	79.6	79.8	81.0	82.3	

It can be seen from Table VII that red maple chlorine dioxide-alkali pulp is readily bleached at high consistency in three stages, namely D/C-E-D, to an 88 TAPPI brightness with good brightness stability. In addition, the pulp was essentially shive free. The bleached pulp yield was 57-60% on the basis of a yield range for unbleached pulp as in Table IV.

Bleached red maple chlorine dioxide-alkali pulp prepared as in Table VII at 57% yield was characterized by Valley beater evaluation, hydrodynamic properties, and determination of handsheet properties as part of the study on wet pressing that will be discussed next.

WET PRESSING

Wet web moisture content and the influence of wet pressing pressures on sheet properties are two significant factors in papermaking that relate to wet pressing.

An example of how pulp type can affect wet web moisture content, which relates to the cost of drying, is available from a recent study (7) using groundwood, glassine, and bleached kraft pulps. After pressing wet mats from each under similar conditions, paper web dryness was 63.3, 50.2, and 70.0%, respectively.

An example of how different wet pressing pressures can influence sheet properties is available from the work of Malmberg (8). From his work on bleached birch kraft pulp, it can be illustrated through Fig. 11 that unique relationships exist between different wet pressing pressures and sheet properties.

Because handsheet preparation procedures call for the use of a standardized wet pressing pressure, there is a tendency for sheet density to be thought of as a fundamental sheet property on which other sheet properties are dependent.

That this is untrue is well illustrated by Fig. 11. From this, it is apparent that if wet pressure is varied, the dependence of sheet properties on density is changed. When considering the papermaking behavior of a new class of pulp such as holopulp, a relevant question concerns the influence of pulp type on the kind of relationships shown in Fig. 11.

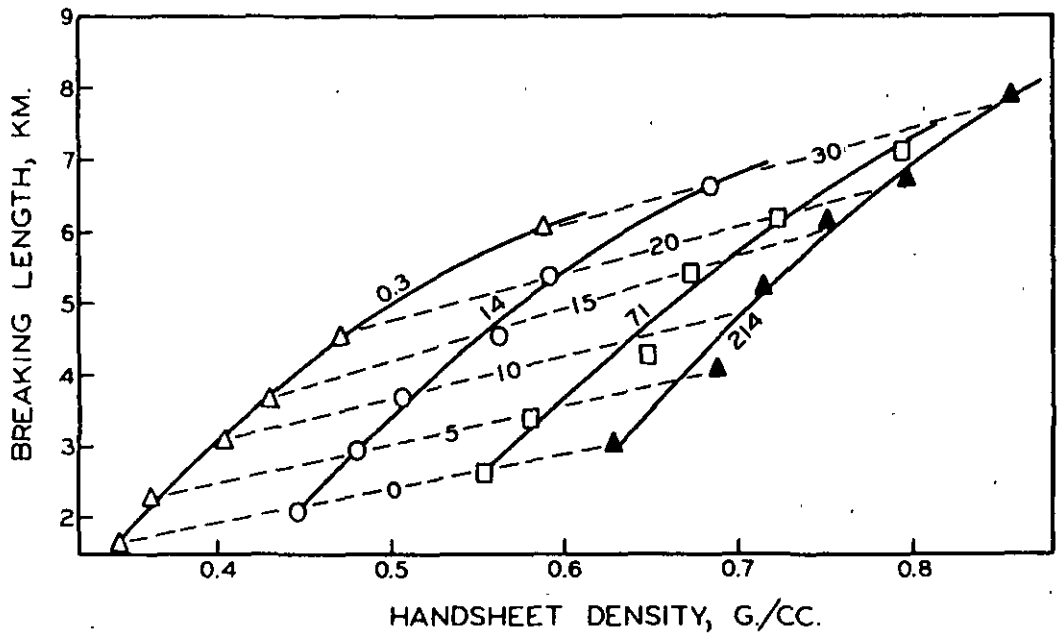

Figure 11. Handsheet Density and Corresponding Breaking Length for Wet Pressing Pressures of 0.3, 14, 71, and 214 p.s.i. on Handsheet (See Footnote) Based on Malmberg Data (8). Broken Lines Are for 0, 5, 10, 15, 20, and 30-min. Beating Times

Thus, on the subject of wet pressing, wet web moisture content and the influence of wet pressing pressures on sheet properties have been considered as part of this study on the properties and behavior of a bleached red maple chlorine dioxide-alkali pulp prepared as already described.

Note: In the TAPPI standard for handsheet preparation, the standard wet pressing gage pressure is 50 p.s.i. on the platen, which is 60.5 p.s.i. on handsheet.

To provide a basis for comparison, a bleached red maple kraft pulp was prepared as detailed in Appendix V.

Results and Discussion

The results obtained on wet web moisture contents after pressing bleached red maple kraft and holopulp at 50 and 10 p.s.i.g. for different levels of beating are shown in Fig. 12. From this, it is apparent that wet web moisture contents are lower for holopulp than for kraft pulp for each wet pressing pressure tested when comparisons are made at equal dry handsheet density. In other words, there is no basis for the position that holopulp necessarily gives a "wet sheet" after wet pressing. Thus, the use of holopulp in papermaking should not adversely influence the cost of drying and could show a cost advantage.

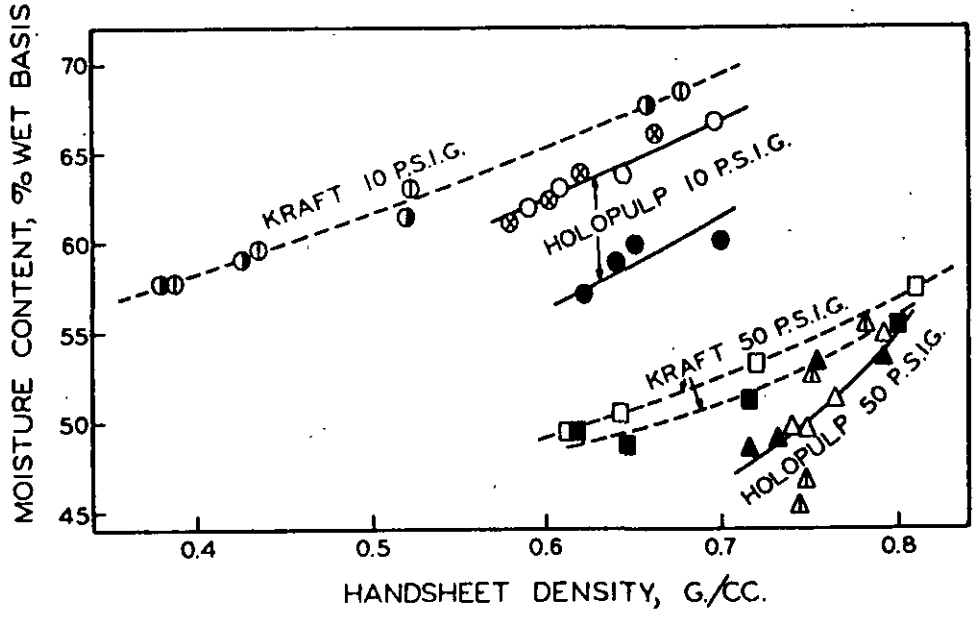

Figure 12. Handsheet Density and Moisture Content of Wet Mats from Bleached Holopulp and Kraft Pulp After Pressing at 10 and 50 p.s.i.g.

In considering what would be the effect of using holopulp instead of, say, a bleached kraft pulp on the relationship between different wet pressing pressures and breaking length, reference will be made to Fig. 13, which may be compared with Fig. 11 in the above discussion. From Fig. 13, it will be seen that the response to reducing the wet pressing pressure from 50 to 10 p.s.i.g. is about similar for both pulps, but the relative increase in bulk is possibly greater for the case of the kraft pulp.

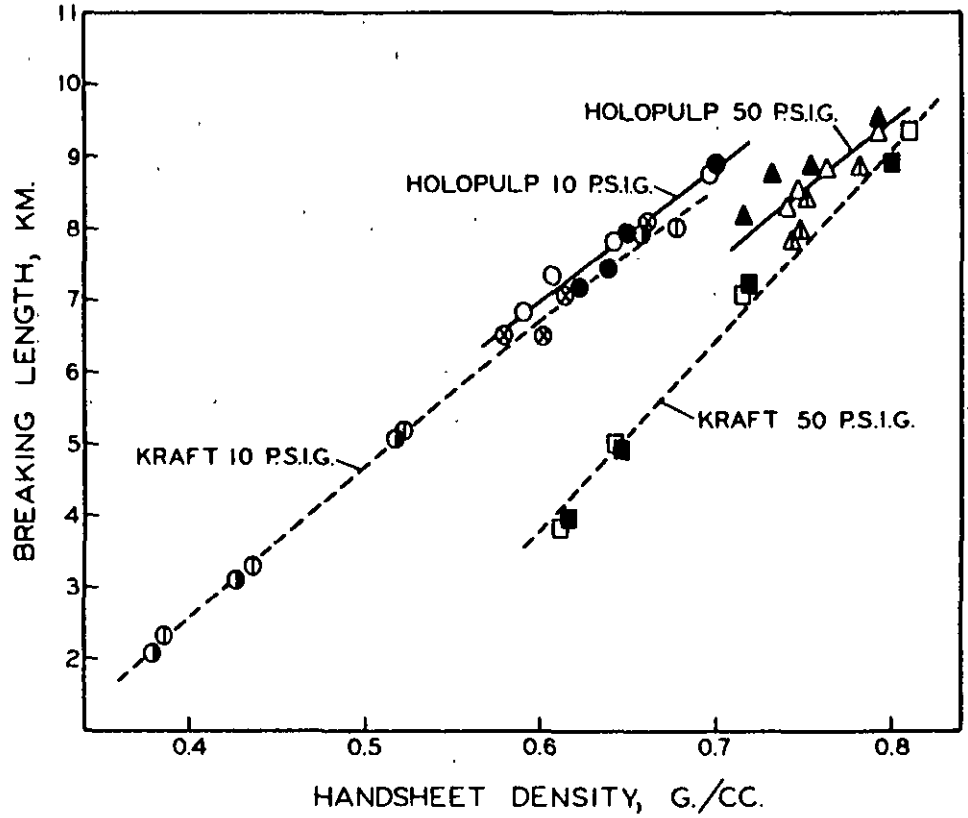

Figure 13. Handsheet Density and Breaking Length of Bleached Red Maple Holopulp and Kraft Pulp After Wet Pressing at 10 and 50 p.s.i.g.

A more extensive comparison showing the influence of wet pressing pressures on sheet properties of bleached red maple holopulp and kraft pulp is presented in Table VIII, on the basis of equal handsheet drainage times for the two pulps. As a general rule, decreasing the wet pressing pressures showed similar trends for both pulps and the holopulp had higher breaking length,

stretch, tensile energy absorption, tensile stiffness, and M.I.T. fold at both pressing pressures. Bendtsen smoothness showed a trend towards less decrease in smoothness at the lower pressure for the holopulp case. Surprisingly, tear factor became significantly higher with lower wet pressing pressure for the holopulp.

TABLE VIII

INFLUENCE OF WET PRESSING PRESSURES ON PAPERMAKING BEHAVIOR OF A HOLOPULP COMPARED WITH A KRAFT PULP[a]

	Holopulp (H)		Kraft (K)	
Handsheet drainage time, sec.	6.0		6.0	
Canadian freeness, ml.	210		375	
Beating time, min.	0		12	
	H	K	H	K
Wet pressing pressure, p.s.i.g.	50	50	10	10
Handsheet moisture content, % wet basis	48	52	60	62
Handsheet density, g./cc.	0.73	0.71	0.60	0.52
Breaking length, km.	8.1	7.1	6.8	5.1
Stretch, %	3.3	3.0	2.9	2.4
Tensile energy absorption, g.cm./cm.^{2}	119	91	90	53
Tensile stiffness, Et, kg./cm.	414	385	368	328
M.I.T. fold	134	48	40	10
Bendtsen smoothness (back), ml./min.	445	305	555	645
Tear factor	72	77	72	63
Spec. scattering coefficient, 650 mm.	246	337	339	441

[a] This table is based upon the more complete data in Appendix VI.

Thus, a bleached red maple chlorine dioxide-alkali pulp compared with the corresponding kraft pulp at similar handsheet density had a lower wet web moisture content after pressing at either 50 or 10 p.s.i.g. Comparison of the same two pulps at similar handsheet drainage times showed a comparable general trend in sheet properties when wet mats were pressed at lower pressures except that smoothness decreased less and tear factor became relatively greater for the holopulp.

These conclusions, with the bases on which they have been reached, raise questions related to the hydrodynamic characteristics of the pulps which are summarized in Table IX. From this it will be seen that this unbeaten bleached red maple holopulp has hydrodynamic properties similar to an appreciably beaten bleached red maple kraft pulp. This is substantiated in greater detail in Appendix VII where the complete sets of hydrodynamic data are presented.

TABLE IX

HYDRODYNAMIC PROPERTIES OF A HOLOPULP AND KRAFT COMPARED AS IN TABLE VIII

	Holopulp	Kraft
Handsheet drainage time, sec.	6.0	6.0
Canadian freeness, ml.	205	375
Beating time, min.	0	12
Filtration resistance, $\underline{R} \times 10^{-8}$, $\Delta\underline{P}$ = 10 cm. H_2O	2.56	1.69
Specific surface, $\underline{S}_w$, $cm.^2/g.$	27,800	21,700
Specific volume, $\underline{v}$, cc./g.	3.3	3.2
Compressibility constants, c.g.s. units:		
$\underline{M}$	0.00187	0.00220
$\underline{N}$	0.374	0.350

FURNISHES WITH FILLERS

As a general rule, bleached hardwood pulps are used in papermaking as one of a number of components in the furnish. Long-fiber pulp and fillers are frequently other components, and for convenience such mixed furnishes may be classified according to whether or not they also include a mechanical pulp.

In this part of the project concerned with the papermaking characteristics of a bleached hardwood holopulp, a three-component system was chosen for study, the components being bleached red maple holopulp, bleached softwood kraft pulp, and mineral filler, as might be used in making "wood-free" papers.

Pigments used for filling paper include barium sulfate, calcium carbonate, calcium silicates, calcium sulfate, clays, diatomaceous earth, titanium dioxide, and zinc sulfide. Of these fillers, substantial quantities of kaolin clays and titanium dioxide are used. A clay has been chosen as one filler, and because quite different results can be obtained with titanium dioxide, it has been chosen as a second filler.

Efficiency of filler retention during sheet formation and the influence of filler on paper properties have been chosen as the factors to be studied in determining the behavior of a bleached hardwood holopulp in a three-component furnish.

Although fillers are added to furnishes in amounts up to 40% of the basis weight, most filled papers contain up to 15% mineral filler. Addition of filler will particularly improve a paper's ink absorption, optical properties, and smoothness but reduce those strength properties dependent on fiber-to-fiber bonding. These adverse effects on strength and retention difficulties are two of the main characteristics associated with the use of fillers.

In a situation where alternative types of pulp were to be available as the main component of a papermaking furnish, a pulp giving better filler retention and showing less adverse effects on strength would be more desirable.

The plan developed for the initial part of this study was based on the use of a filler-grade clay at three levels of addition in pulp furnishes to consist of:

(a) 70% bleached red maple holopulp with 30% bleached softwood pulp, and

(b) 70% bleached red maple kraft pulp with 30% bleached softwood pulp to provide a basis for comparison.

Filler retention determinations for handsheets were planned on a single-pass basis and after the white water had reached equilibrium, which was assumed would exist when 20 sheets had been made.

To ensure proper evaluation of a furnish including filler, plans were made to flocculate the system to which rosin size had been previously added. Further details on the procedure are given in the Experimental part in Appendix VIII.

As a first step, it was planned that each bleached hardwood pulp would be considered as a furnish component at only one freeness level. After that, a similar set of results would be obtained using titanium dioxide as filler. Completion of the above would mark a review point and if significant differences were found in the sets of results for one or more fillers, then further work would be considered. The results in hand bring this part of the work to the review point already noted.

Results and Discussion

For this part of the present study in which bleached red maple kraft pulp was being used to provide a basis for comparison at only one freeness level with the

corresponding holopulp as a component of a mixed furnish, it was decided to use unbeaten holopulp. In view of previous observations on the drainage behavior of this pulp, it was also decided that the kraft pulp would be beaten for 20 min. which reduced the Canadian freeness to 350 ml. As may be seen from Appendix VII, this freeness would cause the kraft pulp to be closer to the holopulp in hydrodynamic properties than would have been the case if both pulps had been compared on an unbeaten basis.

It was found that Huber SSW filler-grade clay, chosen as an example of a papermaker's clay and added in amounts equal to 5, 10, and 20% of the total o.d. fiber, was retained significantly better by mixed furnishes containing bleached red maple holopulp compared with a similar kraft pulp. This was particularly apparent at the higher level of filler addition as shown in Fig. 14. The mixed furnish with holopulp appears to be exceptional in that the amount of clay retained in the sheet was 85-88% of the amounts added. Furthermore, there was little or no indication that this high retention value decreased as often happens when larger amounts of filler are added. Figure 14 is based on the more complete data presented in Appendix IX.

Titanium AWD was chosen as an example of a papermaker's titanium dioxide pigment and this was added in amounts equal to 2, 5, and 10% of the total o.d. fiber. The results which are presented in Appendix IX did not reveal a significantly different retention of titanium dioxide in mixed furnishes containing the holopulp as was observed for the case of a clay filler.

In view of the better clay filler retention observed in the mixed furnish containing a bleached holopulp compared with the corresponding bleached kraft pulp, the influence of filler addition on paper properties is of particular interest. An

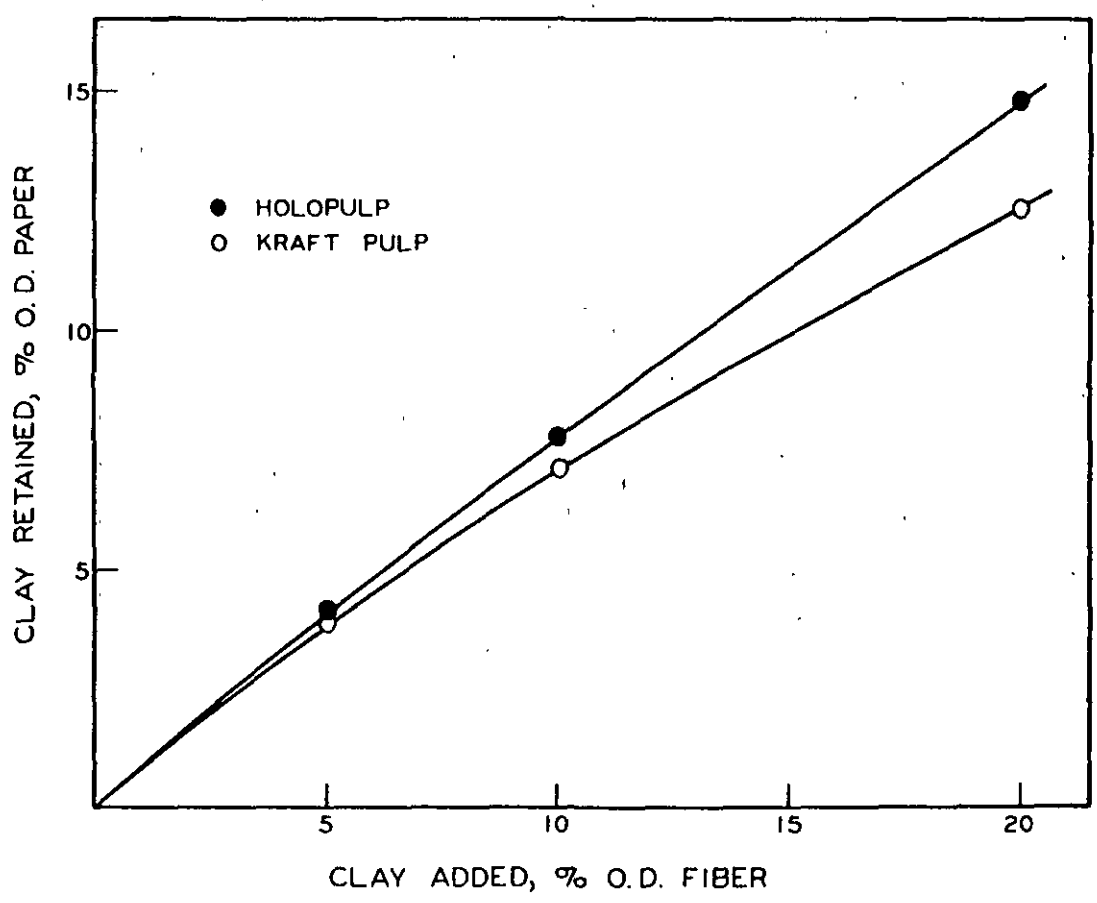

Figure 14. Filler Clay Addition with Corresponding Retention in Three-Component Furnishes Comparing Bleached Red Maple Holopulp and Kraft Pulp at One Freeness Level

outstanding feature of the results obtained is illustrated by means of an example presented in Table X. This is based on the detailed results of testing for both fillers considered and which are included in Appendix IX. In Table X, handsheet properties have been presented using equal specific scattering coefficient as a basis for comparing three-component furnishes including a bleached holopulp on the one hand and the corresponding kraft pulp on the other hand.

TABLE X

COMPARISON OF HANDSHEET PROPERTIES AT 435 SPECIFIC SCATTERING COEFFICIENT

Component alternative	Holopulp	Kraft
Huber SSW Clay, % added	20	6
Clay, % paper	15	4.3
TAPPI brightness	80	82
Sheet density, g./cc.	0.58	0.57
Breaking length, km.	4.0	4.3
Stretch, %	2.1	2.1
Tensile stiffness, Et, kg./cm.	340	360
Tear factor	94	99
M.I.T. fold	11	13
Titanox AWD, % added	2.4	0.4
TAPPI brightness	85	84
Sheet density, g./cc.	0.57	0.55
Breaking length, km.	5.7	4.7
Stretch, %	2.5	2.2
Tensile stiffness, Et, kg./cm.	390	350
Tear factor	102	109
M.I.T. fold	74	20

It will be seen for the case of furnishes with clay filler in Table X that optical properties, sheet density, and strength properties are quite similar, but this similarity corresponds to clay additions of 20% compared with 6% for the furnish containing holopulp as an alternative to kraft pulp. For the case of furnishes with titanium dioxide filler, there is a similar trend in the relative amounts of filler added, but in that case the bonding strength properties of the sheets containing holopulp are significantly higher. Perhaps the most important fact in Table X is that similar sheet properties were determined with a content of 10% more clay filler when a bleached holopulp was used as an alternative to the corresponding kraft pulp. This additional amount of clay would be an advantageous cost factor in the sum of raw material costs.

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THE INSTITUTE OF PAPER CHEMISTRY

R. G. Jamieson

R. G. Jamieson, Research Fellow, Division of Materials Engineering and Processes

G. A. Nicholls

G. A. Nicholls, Senior Research Associate
Division of Materials Engineering
and Processes

APPENDIX I

EXPERIMENTAL - SOFTWOODS

RAW MATERIALS

The loblolly pine (Pinus taeda L.) consisted of twelve 5-ft. bolts with under-bark diameters ranging from 4-1/2 to 7 inches. Half of each bolt was peeled, chipped in the Institute's 4-knife, 38-in. Carthage chipper to a nominal 5/8-in. chip size. Chips were screened in a 24-in. Sweco Dynoscreen with the through-1-in. and on-4-mesh fraction being retained. Moisture content was 49.4% wet basis.

The black spruce (Picea mariana) consisted of twelve 100-in. long bolts of fresh black spruce pulpwood with under-bark diameters varying from 4 to 6-1/2 inches. Part of each bolt was peeled, chipped, and screened as for the loblolly pine above. Moisture content was 41.7% wet basis.

ALKALI IMPREGNATION OF SCREENED CHIPS

The chips were steamed for 2 minutes at 15 p.s.i.g., the pressure released to atmospheric, steamed for a further 2 minutes at 15 p.s.i.g., then covered with sodium hydroxide solution at room temperature with a nitrogen overpressure of 100 p.s.i.g. for 30 minutes. The chips were allowed to drain for 30 minutes. The concentration and volume of the sodium hydroxide solution were measured before and after each treatment and the sodium hydroxide uptake by the chips calculated from these values.

The aim levels of alkali impregnation for both species were 3.0, 4.0, and 7.0% NaOH based on the o.d. wood. The impregnated chips marked "*" in Table XI were used for subsequent treatments.

TABLE XI

UPTAKE OF SODIUM HYDROXIDE

NaOH Concn., g./l. Before	NaOH Concn., g./l. After	NaOH Uptake, % o.d.w.
	Loblolly Pine Chips	
15.4	13.0	2.9*
21.4	18.2	3.9
22.0	19.0	4.0*
39.0	33.2	7.1*
	Black Spruce Chips	
12.3	9.9	3.1*
13.3	10.8	3.2
17.6	13.2	4.0*
25.4	18.3	5.7
33.3	28.6	7.0*

FIBERIZATION OF ALKALI-IMPREGNATED CHIPS

The impregnated chips were steamed at 75 p.s.i.g. for times indicated in the tables and then fiberized in two passes through a 12-in. Sprout-Waldron laboratory refiner fitted with 17804 plates. The fiberization conditions for the two chip species are given in Table XII.

TABLE XII

FIBERIZATION CONDITIONS

	First Pass		Second Pass	
	Plate Gap, 0.001 in.	Consistency, %	Plate Gap, 0.001 in.	Consistency, %
Loblolly pine	65	ca. 5	15	ca. 4
Black spruce	80	ca. 5	15	ca. 4

The consistency during fiberization was effected by running cold water into the throat of the refiner.

The pH of the condensate collected during the steaming of the alkali-impregnated chips and the yields of the fiberized chips are given in Tables XIII-XVI.

TABLE XIII

pH OF CONDENSATE DURING STEAMING AT 75 P.S.I.G.
OF ALKALI-IMPREGNATED LOBLOLLY PINE CHIPS

Steaming Time, min.	NaOH, % o.d. wood 2.9	4.0	7.1
1.25		12.0	--
2.5	10.4	11.8	12.0
5.0	9.6	11.8	12.3
7.5	8.8		

TABLE XIV

YIELD OF LOBLOLLY PINE FIBERIZED CHIPS,
% O.D. WOOD

Steaming Time, min.	NaOH, % o.d. wood 2.9	4.0	7.1
1.25		93.3	88.2
2.5	92.9	92.8	87.0
5.0	91.3	93.0	86.7
7.5	91.1		

TABLE XV

pH OF CONDENSATE DURING STEAMING AT 75 P.S.I.G.
OF ALKALI-IMPREGNATED BLACK SPRUCE CHIPS

Steaming Time, min.	NaOH, % o.d. chips 3.1	4.0	7.0
1.25		12.0	12.3
2.5	10.2	10.4	12.3
5.0	8.8	9.5	10.3
7.5	8.1		

TABLE XVI

YIELD OF BLACK SPRUCE FIBERIZED CHIPS,
% O.D. WOOD

Steaming Time, min.	NaOH, % o.d. wood 3.1	4.0	7.0
1.25		91.2	87.4
2.5	93.8	90.2	85.2
5.0	91.8	90.0	84.1
7.5	92.6		

CHLORINE DIOXIDE OXIDATIONS

The fiberized chips were reacted in the aqueous phase with chlorine dioxide solution at 8% consistency with a starting temperature of 25°C. being increased to 35°C. in 60 minutes and being held at that temperature until all the chlorine dioxide had been consumed as indicated with potassium iodide/starch paper.

ALKALI EXTRACTIONS

The chlorine dioxide-treated fiberized chips were extracted with sodium hydroxide at 90°C. and a consistency of 12%.

WASHING

The products were well washed after the fiberizing step, the chlorine dioxide oxidation, and the alkali-extraction stages.

APPENDIX II

LIGNIN REMOVAL FROM ALKALI PRETREATED LOBLOLLY CHIPS

TABLE XVII

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	15 4			22 1				30 0			
	final	13 0			19 0				33 2			
NaOH uptake, %[a]		2 9			4 0				7 0			
Steaming at 75 p s i g												
Min		2 5	5 0	7 5	1 25	2 5	5 0		1 25	2 5	5 0	
pH condensate		10 4	9 6	8 8	12 0	11 8	11 8		--	12 0	12 3	
Fiberization 12-in laboratory Sprout-Waldron refiner, first pass at 0 065 in , second pass at 0 015 in												
Yield, %		92 9	91 3	91 1	93 3	92 8	93 0		88 2	87 0	86 7	
Lignin modification 25°C to 35°C in 60 min , 8% consistency												
ClO_2, %		4 5	4 5	6 0	7 5	9 0			4 5	6 0	7 5	9 0
Time, min		45	60	75	90	105			50	60	75	80
Final pH		1 6	1 9	1 7	1 6	1 5			1 8	1 5	1 2	1 8
Yield, %		91 9	89 3	89 0	88 4	88 0			84 1	83 8	83 2	82 7
Kappa no		90 1	106 3	101 1	94 5	84 7			100 4	94 5	84 3	81 4
Alkali extraction 30 min , 90°C , 12% consistency												
NaOH, %	4 0	6 0	8 0									4 0 6 0 8 0
Final pH	11 8	11 9	12 5									8 6 10 7 12 0
Yield, %	87 2	85 2	85 5									72 1 68 9 66 9
Kappa no	86 5	91 9	88 8									61 3 57 8 52 8
Klason lignin, %[b]	11 3	11 6	11 4									6 6 6 0 5 3
K lignin removed, %[c]	17 3	17 0	17 2									22 0 22 6 23 3
Carbohydrate loss, %[d]	-4 5	-2 2	-2 7									5 9 8 5 9 8
Alkali extraction 60 min , 90°C , 12% consistency												
NaOH, %	4 0	6 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	4 0 6 0 8 0
Final pH	11 5	11 9	12 2	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 10 6 11 7
Yield, %	87 4	85 0	83 7	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 68 0 65 9
Kappa no	88 6	86 8	83 8	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 53 8 50 5
Klason lignin, %[b]	11 6	11 1	10 5	11 5 11 1	10 4 9 4	8 7 7 2	6 7 5 9		10 8 9 8	9 3 8 3	7 7 6 4	6 3 5 5 5 0
K lignin removed, %[c]	17 0	17 5	18 1	17 1 17 5	18 2 19 2	19 9 21 4	21 9 22 7		17 8 18 8	19 3 20 3	20 9 22 2	22 3 23 1 23 6
Carbohydrate loss, %[d]	-4 4	-2 5	-1 8	1 4 2 4	1 9 3 4	2 6 6 8	5 4 6 7		3 8 6 4	4 6 7 5	7 2 9 7	6 1 8 9 10 5
Alkali extraction 120 min , 90°C , 12% consistency												
NaOH, %	4 0	6 0	8 0									4 0 6 0 8 0
Final pH	10 2	11 7	12 0									8 3 10 5 11 5
Yield, %	85 8	82 2	82 1									69 1 67 2 65 9
Kappa no	85 5	86 3	85 7									57 8 53 2 47 5
Klason lignin, %[b]	11 0	10 6	10 6									6 0 5 4 4 6
K lignin removed, %[c]	17 6	18 0	18 0									22 6 23 2 24 0
Carbohydrate loss, %[d]	-3 4	-0 2	-0 1									8 3 9 6 12 1

[a] All percentages are based on the original o d chips

[b] Calculated from Klason lignin = 0 15 x Kappa no Not applicable to the higher Kappa no pulps

[c] Assuming chips contained 28 6% Klason lignin

[d] *Calculated from lignin removed and yield data*

APPENDIX III

NOTES ON FIBERIZATION OF RED MAPLE FOR BLEACHED PULP

Red maple chips were fiberized using the Bauer machine described in Progress Report Thirteen and related data are shown in Table XVIII.

TABLE XVIII

DATA FOR FIBERIZED RED MAPLE CHIPS

Refiner	No. 418 Pressurized Bauer
Code	A41
Chip treatment	I[a]
Moisture content, % wet basis	60.2
Weight used for run, lb. o.d.	83.2
Fiberization data	
Steam pressure, p.s.i.g./°C.	80/163
Steaming time, min.	3.0
Plate clearance, 0.001 in.	30
Run time, min.	8.80
Feed rate, o.d. tons/day	6.81
Load, brake h.p. days/o.d. ton[b]	10.2

[a] The chips were steamed to remove air and then impregnated with cold water (see Experimental for details).

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

When chips were fiberized as in Table XVIII, the refiner was fitted with two sets of no. 36326 plates. This differs from the situation applicable to red maple in Progress Report Fourteen for which the refiner was fitted with one set of no. 36326 plates and one set of no. 36325 plates. Advance communication of this change was not received. Although no photograph of the plates is available, the

sketches in Fig. 15 provide an indication of what the plate pattern is like. The difference between no. 36326 and 36325 plates is that the former has a peripheral dam not present in the latter.

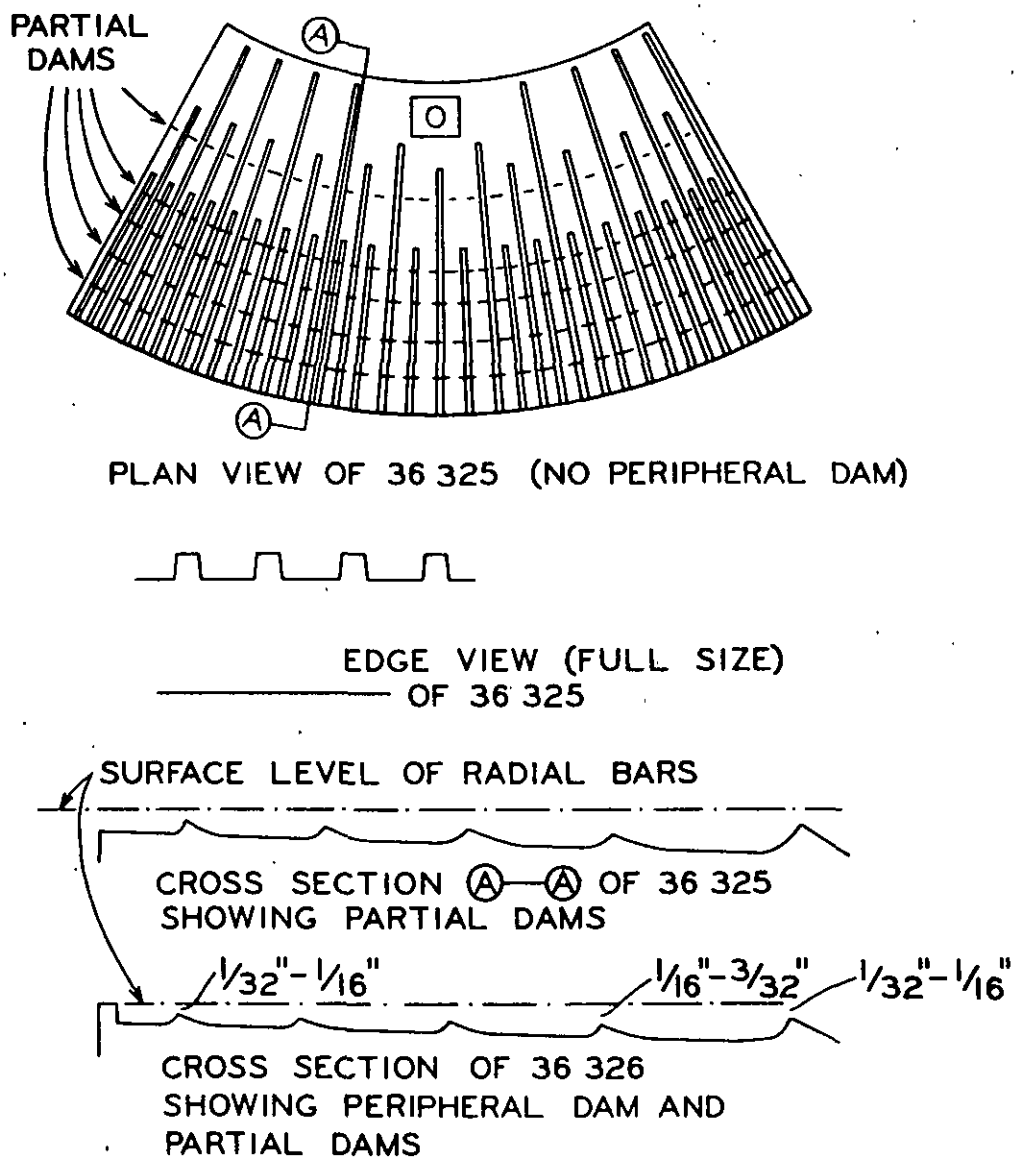

Figure 15. Sketches Indicating the Pattern and Dam Structure of No. 36326 36325 Plates on Bauer Pressurized Refiner. In Reality, the Radial Bars Are Evenly Spaced

With a peripheral dam on both sets of plates in the refiner, the amount of the coarser fraction of material is reduced. The net outcome of this, plus the use of 0.005-in. less plate clearance and higher fiberization steam pressure in Table XVIII compared with the conditions given in Progress Report Fourteen, was a higher power consumption and a finer fiberized product, as shown for the latter in Table XIX.

TABLE XIX

BAUER-McNETT CLASSIFICATION DATA

	Table XVIII A	W/PB/1[a] B
On 6 mesh, %	0.3[b]	21.9[c]
On 12 mesh, %	0.5	21.6
On 35 mesh, %	17.3	27.2
On 65 mesh, %	39.7	10.7
Through 65 mesh (by difference), %	42.2	18.6

[a] Progress Report Fourteen.

[b] Water temperature 7-9°C.

[c] Water temperature 17°C.

In view of the appreciable difference in the classification data for the fiberized material produced as in Table XVIII and identified in Table XIX by the letter "A", compared with the material produced previously as identified in Table XIX by the letter "B", it was deemed appropriate to run a check on the pulp properties. Hence a pulp was produced from A using conditions as applied earlier to B and summarized in Table XX.

TABLE XX

PREPARATION OF PULP FOR CHECK TEST

Material	A	B
Lignin modification:		
Consistency, %	6.5	6.0
Temp., °C.	25-35	25-35
Chlorine dioxide, %	9.0	9.0
Time, min.	125	140
Alkali extraction:		
Consistency, %	8.0	8.0
Temp., °C.	80	80
Sodium hydroxide, %	9.0	9.0
Time, min.	120	120
Final pH	10.8	11.1
Hypochlorite:		
Consistency, %	12.0	12.0
Temp., °C.	40	40
Available chlorine, %	2.8	3.0
Time, min.	120	120
Final pH	8.4	9.5
Yield, %	61.4	63.3
Screen rejects, % o.d.p.	0.3	0.3
Screening return, % o.d.p.	98.3	98.9
TAPPI brightness	81.5	80.7

The properties of pulps from A and B are illustrated by means of evaluation data given in Table XXI. From these it will be seen that the numerical level of Canadian freeness values is much lower for the present case (A) without there being a comparable change in handsheet drainage time. For the same case, sheet density is apparently greater but the sheets are significantly smoother and were much cleaner

on visual inspection. Specific scattering coefficient is about the same for both cases, whereas breaking length, stretch, tear, and M.I.T. fold are all higher initially for the present case.

TABLE XXI

COMPARISON OF PROPERTIES FOR PULPS FROM A AND B (SEE TEXT)

	A					B				
Beating time, min.	0	2	4	6	10	0	2	4	7	12
Canadian freeness, ml.	235	225	195	175	155	480	410	330	290	190
Handsheet drainage, sec.	5.4	6.0	6.3	7 3	11.0	4.6	4.8	5.3	6 8	12.1
Density, g./cc.	0.69	0.69	0.71	0 73	0.75	0.67	0.69	0.70	0.73	0.77
Bendtsen smoothness (back), ml./min.	595	485	540	590	615	850	620	470	460	460
Specific scattering coefficient, 650 nm.	265	260	250	240	225	275	270	255	235	200
Breaking length, km.	8.1	8.4	8.7	9.1	9.6	6 8	7 3	7.9	8.5	9.1
Stretch, %	2.8	2.9	3 0	2.9	3.1	2.4	2.6	2.7	3.0	3.0
Tear factor (Elmendorf)	65	69	68	66	64	61	60	63	57	57
Zero-span breaking length, km.	n.d.	n.d.	n.d	n.d.	n.d.	16	17	17	17	17
M.I.T. fold	165	180	240	210	300	50	80	120	260	580

Compared with handsheet data obtained previously for red maple chlorine dioxide-alkali pulp prepared from Asplund-fiberized chips, the results in Table XXI represent a compromise in terms of a narrowing of the handsheet density range, for example. For convenience, this is illustrated by the comparison made in Table XXII. This difference is believed to arise because it has not been possible to translate from the relevant fiberization conditions for the Asplund machine to the Bauer machine.

TABLE XXII

COMPARISON OF PROPERTIES FOR PULPS FROM BAUER AND ASPLUND MACHINES

	A (Bauer)					Asplund[a]				
Beating time, min.	0	2	4	6	10	1	3	6	10	22
Canadian freeness, ml.	235	225	195	175	155	520	480	440	360	150
Handsheet drainage, sec.	5.4	6.0	6.3	7.3	11.0	4.7	4.9	4.8	5.3	11.5
Density, g./cc.	0.69	0.69	0.71	0.73	0.75	0.59	0.61	0.64	0.66	0.74
Bendtsen smoothness (back), ml./min.	595	485	540	590	615	1630	1510	1080	900	898
Specific scattering coefficient, 650 nm.	265	260	250	240	225	n.d.	277	n.d.	265	210
Breaking length, km.	8.1	8.4	8.7	9.1	9.6	5.5	5.9	6.6	7.1	9.0
Stretch, %	2.8	2.9	3.0	2.9	3.1	1.9	2.0	2.4	2.6	2.9
M.I.T. fold	165	180	240	210	300	15	19	30	39	269

[a] Progress Report Twelve, Table XXIV, Pulp Vb.

APPENDIX IV

NOTES ON PROCESS CONDITIONS FOR RED MAPLE DELIGNIFICATION

For the alkali conditioning step of the process in Table IV, it will be noted that 3.0% sodium hydroxide was added. Reaction time and corresponding yields or pH for three levels of alkali addition are shown in Fig. 16. This illustrates that most of the material loss occurs in 15 min. and that high pH's as would favor excessive swelling of the secondary wall or end peeling reactions are not encountered with the lower levels of alkali addition. After the oxidative lignin modification, carbohydrate losses from end peeling reactions in the alkali extraction step should occur less readily, assuming end groups have been oxidized.

The alkali extraction was carried out at 80°C. on the basis of previous work. This indication that at 80°C. compared with 70°C., although the yield of screen accepts was about the same, the pulp was bleached to a significantly higher brightness with the same amount of hypochlorite (Progress Report Fourteen, page 10). Figure 17 illustrates this situation.

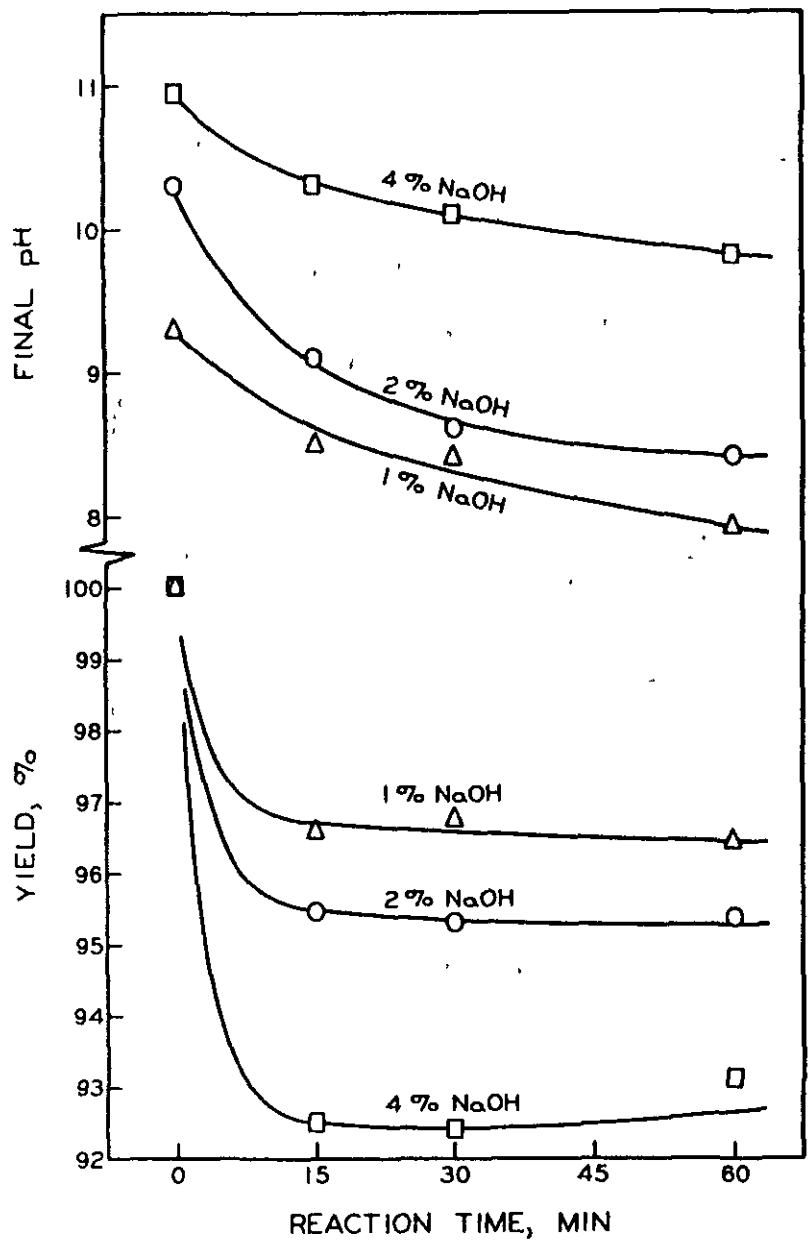

Figure 16. Reaction Time with Corresponding Yields and pH Values After Heating Red Maple Fiberized Chips (as in Table IV) with 1, 2, and 4% Sodium Hydroxide at 10% Consistency and 70°C.

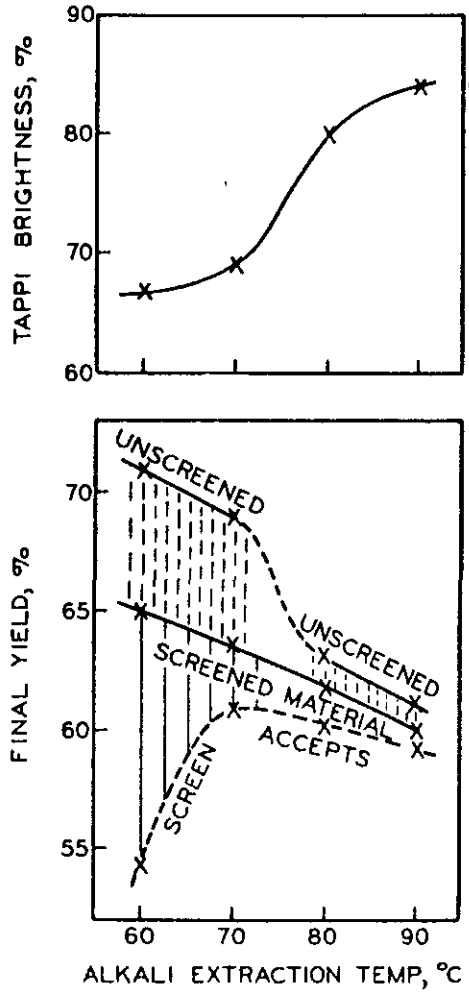

Figure 17. Alkali Extraction Temperature with Corresponding TAPPI Brightness and Final Yield Data After Lignin Modification, Alkali Extraction, and Hypochlorite Reaction of Red Maple Fiberized Chips (Progress Report Fourteen, page 10)

APPENDIX V

TABLE XXIII

CONDITIONS OF BLEACHING RED MAPLE KRAFT PULP[a]

Batch no.	1[b]	2[c]
Chlorination: Cl_2 2.5%[d], consistency 3%, 25°C.		
Time to near exhaustion, min.	45	45
Final pH	2.3	2.3
Alkali extraction: NaOH 1.7%, consistency 10%, 65°C., 90 min.		
Final pH	11.5	11.3
Hypochlorite: Consistency 10%, 35°C., 105 min.		
Available chlorine, %	0.75	0.5
Final pH	9.8	8.5
Residual av. Cl_2, %	0.37	0.13
Chlorine dioxide: ClO_2 0.6%, consistency 10%, 70°C., 240 min.		
Final pH	4.0	3.7
Residual ClO_2, %	0.13	0.11
Shrinkage on bleaching, %	5.7	2.8
Overall yield, % o.d. wood	45.9	47.2
TAPPI brightness	89.8	88.3
Steam-aged brightness	82.4	80.7

[a] Screened unbleached pulp as in Progress Report Twelve, page 107.

[b] For Valley beater at 50 and 10 p.s.i.g. dewatering pressure.

[c] For filler retention studies.

[d] All percentages based on original o.d. pulp unless stated otherwise.

APPENDIX VI

BLEACHED PULP EVALUATION DATA

TABLE XXIV

DUPLICATE VALLEY BEATER EVALUATION OF BLEACHED RED MAPLE KRAFT PULP

Beating time, min.	0	4	12	24	0	4	12	24
pH	4.9				5.2			
Canadian freeness, ml.	565	505	380	195	545	480	370	210
Handsheet drainage time, sec.	4.9	5.1	6.1	13.6	4.9	5.2	5.9	11.9
Gage pressure, p.s.i.	———	50	———		———	50	———	
Handsheet M.C., % wet basis	49.4	50.5	53.2	57.4	49.4	48.6	51.1	55.3
Handsheet density, g./cc.	0.613	0.643	0.716	0.811	0.617	0.647	0.716	0.801
Bendtsen smoothness, ml./min.	367	337	307	277	347	396	302	290
Breaking length, km.	3.83	5.00	7.07	9.36	3.95	4.91	7.14	8.90
Stretch, %	1.6	2.2	3.0	3.7	1.6	2.0	3.0	3.2
Tensile energy absorption, g.cm./cm.^{2}	24.6	45.9	91.8	134	25.4	41.6	89.6	120
Tensile stiffness, kg./cm.	312	341	377	412	328	346	393	423
Tear factor	44.1	52.0	76.9	75.2	40.7	59.0	77.6	81.2
M.I.T. fold	4	8	41	943	3	7	54	639
Spec. scattering coefficient	419	398	342	259	427	391	331	264
Spec. absorption coefficient	0.760	0.772	1.07	1.26	0.945	0.893	0.959	1.02
Shive count, no./cm.^{2}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gage pressure, p.s.i.	———	10	———		———	10	———	
Handsheet M.C., % wet basis	57.7	59.6	63.0	68.4	57.7	59.0	61.4	67.6
Handsheet density, g./cc.	0.386	0.436	0.522	0.678	0.380	0.427	0.519	0.658
Bendtsen smoothness, ml./min.	856	667	642	330	890	796	643	352
Breaking length, km.	2.31	3.27	5.17	8.00	2.08	3.09	5.07	7.95
Stretch, %	1.0	1.5	2.5	3.3	0.9	1.4	2.3	3.3
Tensile energy absorption, g.cm./cm.^{2}	9.61	20.2	55.8	110	7.59	16.9	50.0	110
Tensile stiffness, kg./cm.	253	277	330	392	223	269	326	397
Tear factor	24.6	38.9	62.7	78.4	22.0	36.2	63.4	79.3
M.I.T. fold	1	2	11	163	1	2	9	123
Spec. scattering coefficient	518	497	443	337	521	504	439	341
Spec. absorption coefficient	0.972	0.870	1.04	1.43	0.913	0.947	0.941	1.13
Shive count, no./cm.^{2}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE XXV

TRIPLICATE VALLEY BEATER EVALUATION OF BLEACHED RED MAPLE HOLOPULP

Beating time, min.	0	3	7	13	0	3	7	13	0	3	7	13
pH	4.8				4.9				5.4			
Canadian freeness, ml.	215	205	175	160[a]	210	200	180	170[a]	215	205	190	170[a]
Handsheet drainage time, sec.	6.0	6.5	7.8	14.0	5.9	6.6	8.1	15.6	5.8	6.6	8.0	12.7
Gage pressure, p.s.i.	50				50				50			
Handsheet M. C., % wet basis	49.6	49.5	51.2	54.7	48.4	48.7	53.2	53.4	45.3	46.7	52.7	55.4
Handsheet density, g./cc.	0.741	0.747	0.764	0.793	0.717	0.732	0.754	0.792	0.745	0.747	0.751	0.783
Bendtsen smoothness, ml./min.	524	484	616	550	435	458	531	596	369	390	412	430
Breaking length, km.	8.27	8.51	8.80	9.40	8.15	8.73	8.84	9.51	7.82	7.94	8.40	8.87
Stretch, %	3.3	3.3	3.6	3.5	3.2	3.2	3.2	3.4	3.4	3.6	3.5	3.4
Tensile energy absorp., g.cm./cm.^{2}	119	123	139	145	117	123	127	145	118	127	128	133
Tensile stiffness, Et, kg./cm.	414	422	418	440	(559)	(557)	(578)	(595)	412	415	427	437
Tear factor	69.9	70.5	69.7	68.2	70.6	71.6	69.0	67.5	74.7	75.8	71.8	70.4
M.I.T. fold	88	177	165	347	125	142	235	720	176	233	220	579
Spec. scattering coefficient	245	241	226	193	243	235	232	204	251	250	247	226
Spec. absorption coefficient	0.952	0.982	0.968	1.34	1.09	1.08	1.13	1.19	1.07	1.14	1.37	1.20
Shive count, no./cm.^{2}	0.0	0.06	0.02	0.0	0.06	0.02	0.02	0.0	0.0	0.0	0.02	0.0
Gage pressure, p.s.i.	10				10				10			
Handsheet M.C., % wet basis	61.9	63.0	63.7	66.7	57.0	58.8	59.8	60.1	61.1	62.3	63.8	66.0
Handsheet density, g./cc.	0.591	0.607	0.643	0.696	0.622	0.640	0.650	0.700	0.579	0.603	0.619	0.663
Bendtsen smoothness, ml./min.	504	616	533	520	573	554	533	541	588	592	590	503
Breaking length, km.	6.81	7.33	7.80	8.75	7.16	7.43	7.92	8.89	6.51	6.49	7.17	8.09
Stretch, %	2.9	3.2	3.1	3.2	2.9	2.8	3.1	3.3	3.1	3.0	3.0	3.4
Tensile energy absorp., g.cm./cm.^{2}	86.8	100	104	122	95.1	94.2	110	132	86.9	84.4	91.9	119
Tensile stiffness, Et, kg./cm.	368	388	399	431	(502)	(528)	(533)	(562)	362	366	398	397
Tear factor	73.1	72.7	72.8	70.0	72.5	68.7	69.4	70.5	70.4	74.7	75.9	77.4
M.I.T. fold	30	45	55	184	51	60	86	338	35	52	79	124
Spec. scattering coefficient	335	321	310	257	337	331	320	258	349	334	322	285
Spec. absorption coefficient	1.02	0.99	0.95	1.29	1.04	0.96	5.06	1.13	1.16	1.08	1.24	1.36
Shive count, no./cm.^{2}	0.0	0.02	0.0	0.05	0.02	0.05	0.0	0.0	0.0	0.03	0.0	0.0

[a] Fines in freeness effluent.

APPENDIX VII

HYDRODYNAMIC PROPERTIES OF RED MAPLE BLEACHED PULPS

For the two pulps, samples of stock obtained at each of the four beating intervals were used to determine filtration resistance with a research-model constant-rate filtration apparatus (9). The technique used has been described previously (10-12). Apparent wet mat density as a function of compacting pressure was measured by the procedure described at an earlier date (13). Specific surface and effective specific volume were calculated from plots of time-pressure drop values from filtration measurements and correlated values of wet mat density which are applicable to a modified Kozeny-Carman equation as discussed previously (11).

Filtration resistance results are given in Table XXVI and the results for specific surface, specific volume, and compressibility are given in Table XXVII.

TABLE XXVI

FILTRATION RESISTANCE DATA - BLEACHED RED MAPLE HOLOPULP AND KRAFT PULP

Filtration resistance, $\underline{R} \times 10^{-8}$, cm./g.

A. Bleached Red Maple Holopulp

Pressure Drop, $\Delta\underline{P}$, cm. H_2O	Beating Time, min. 0	3	7	13
10	2.56	3.00	3.65	5.23
20	3.80	4.49	5.59	8.32
30	4.87	5.80	7.29	11.1
40	5.83	6.99	8.89	13.7
50	6.98	8.16	10.4	16.2
60	7.68	9.30	11.9	18.6
70	8.57	10.4	13.4	23.2
80	9.43	11.5	14.8	23.2
90	10.3	12.5	16.2	25.4

B. Bleached Red Maple Kraft Pulp

Pressure Drop, $\Delta\underline{P}$, cm. H_2O	Beating Time, min. 0	4	12	24
10	0.95	1.23	1.69	3.85
20	1.20	1.60	2.30	5.54
30	1.42	1.89	2.79	6.97
40	1.60	2.15	3.24	8.28
50	1.75	2.40	3.67	9.60
60	1.91	2.61	4.08	10.8
70	2.06	2.83	4.46	12.0
80	2.20	3.05	4.82	13.2
90	2.33	3.25	5.15	14.4

TABLE XXVII

SPECIFIC SURFACE, SPECIFIC VOLUME, AND COMPRESSIBILITY CONSTANTS – BLEACHED RED MAPLE HOLOPULP AND KRAFT PULP

A. Bleached Red Maple Holopulp

	Beating Time, min.			
	0	3	7	13
Specific surface, $\underline{S}_w$, cm.^{2}/g.	27,800	30,400	33,800	41,200
Specific volume, $\underline{v}$, cc./g.	3.26	3.50	3.64	3.77
Compressibility constants, c.g.s. units				
$\underline{M}$	0.00187	0.00182	0.00182	0.00182
$\underline{N}$	0.374	0.374	0.374	0.374

B. Bleached Red Maple Kraft Pulp

	Beating Time, min.			
	0	4	12	24
Specific surface, $\underline{S}_w$, cm.^{2}/g.	15,500	17,800	21,700	33,800
Specific volume, $\underline{v}$, cc./g.	2.73	2.95	3.17	3.58
Compressibility constants, c.g.s. units				
$\underline{M}$	0.0022	0.0022	0.0022	0.0022
$\underline{N}$	0.350	0.350	0.350	0.350

APPENDIX VIII

EXPERIMENTAL – HARDWOOD

RAW MATERIALS

The red maple (Acer rubrum L.) chips used in this report were from the same supply as described in Progress Report Twelve with the screened chips having a moisture content of 35.2% wet basis and a density of 31.5 lb. (o.d.)/cu. ft. green.

Water impregnation of the chips was carried out batchwise as follows: The equivalent of about 15 lb. o.d. chips was packed into a basket and placed in a 2-cu. ft. stainless steel digester and steamed at 15-20 p.s.i. for 2 min.; the pressure was relieved to atmospheric followed by steaming again at 15-20 p.s.i. for a further 2 min. The basket of chips was then transferred to a second 2-cu. ft. stainless steel digester, covered with distilled water, and an overpressure of 100 p.s.i. supplied from a nitrogen gas cylinder applied for 30 minutes. The water-impregnated chips were allowed to drain for 15 min. before being emptied into a plastic-lined barrel.

CHLORINE DIOXIDE, HYPOCHLORITE, AND ALKALI REACTIONS

All reactions were carried out in plastic bags with the products being mixed at regular intervals. After each reaction, the products were well washed with distilled water with dewatering being effected in a laundry-type spin drier with the products being contained in a nylon cloth bag.

PULPS USED FOR FIGURE 9

The pulps used to give results as in Fig. 9 were composites of most of the pulps described in Table III, page 15. Pulp Kappa number "70" was a composite of those pulps which had 40% ClO_2 in the lignin modification stage with the exception

that the two extremes in the alkali extraction stage, i.e. 5.0% NaOH for 20 min. and 9.0% NaOH for 120 min., were excluded. The average Kappa number for this composite pulp was close to 70. Similarly, pulps Kappa number "50" and "30" were composites of those pulps which had 5.5 and 7.0% ClO_2 respectively in the lignin modification stage with the exception that the extremes in the alkali extraction, i.e. 5.0% NaOH for 20 min. and 9.0% NaOH for 120 min., were excluded. The average Kappa numbers for these two composite pulps were close to 50 and 30 respectively.

WET PRESSING

The red maple bleached holopulp used in the wet pressing work was prepared as for the 57%-yield pulp in Table VII, and the bleached red maple kraft was prepared as in Appendix V. Pulp beatings were carried out in a 1-1/2 lb. Valley beater according to TAPPI Standard Method T 200 ts-66 but with the following exceptions:

1. All dilutions were made with distilled water.
2. The beater charge was 340 g. o.d. pulp.
3. The weight on the end of the bedplate lever was 2.0 kg. for the bleached holopulp and 5.5 kg. for the bleached kraft.
4. Stock (2640 ml.) was withdrawn at each interval. A portion of 640 ml. was set aside for the hydrodynamic test work and the remaining 2 liters were used to determine Canadian freeness according to TAPPI Standard Method T 227 m-58 and to prepare two sets of handsheets essentially according to TAPPI Standard Method T 205 m-58 with one set being pressed at 50 p.s.i.g. pressure and the other set being pressed at 10 p.s.i.g. pressure. At each pressure, nine 1.2-g. handsheets were formed; two were formed entirely with distilled water and were used to determine specific scattering coefficient and specific absorption coefficient; the remaining seven were formed in deionized water, two being used to determine moisture content immediately after the second pressing and the remaining five used for physical testing.

   The handsheet testing procedures used are fully described in Progress Report Eight and Progress Report Twelve. Handsheet drainage times were determined according to TAPPI Standard Method T 221 sm-72 and the shive count was calculated from the number of shives per 12 $cm.^2$ on each of the five handsheets.

FURNISHES WITH FILLERS

The two fillers used in this work were Huber SWW filler-grade clay and Titanox AWD (anatase water dispersible) titanium dioxide.

The pulps used were:

1. a bleached red maple holopulp prepared as for the 57%-yield pulp described in Table VII,
2. a bleached red maple kraft prepared as in Appendix V and beaten in a 1-1/2 lb. Valley beater at 2.0% consistency to 350 ml. Canadian freeness, and
3. a commercial bleached softwood kraft consisting of 30% redwood and 70% Douglas-fir beaten to 450 ml. Canadian freeness.

For each handsheet forming run, the required amount of a pulp furnish (see page 34 for details of the two pulp furnishes used) was taken, dispersed in a British disintegrator for 300 counts, and diluted to a concentration of dispersed pulp furnish at 1.5%. Distilled water was used throughout the experiments.

The clay pigment was dispersed using 3 meq. of sodium tetraphosphate (Quadrafos) and 2 meq. of sodium hydroxide per 100 grams of clay at 50-60% solids in a Waring Blendor for 3 minutes. The titanium dioxide was similarly dispersed using 1.5% sodium hexametaphosphate (Calgon-T). The dispersed slurries were then diluted to 10% solids and used in this form as required for the handsheet preparation.

The dispersed pulp furnish as prepared above was kept at the 1.5% consistency and slowly stirred with a "Lightnin'" mixer. The pulp was sized with 2% pale rosin size based on the weight of the pulp, and stirring was continued for 15 minutes. The dispersed pigments used in the study were then added to the pulp, after the rosin was well mixed in the furnish, and the slurry was stirred for an additional 25 min. The system was then flocculated with 4% alum based on weight of pulp. After

stirring for an additional 5 minutes, the slurry had a pH of 4 to 4.5. The furnish was then diluted with distilled water to 0.5% consistency in preparation for making the sheets.

The handsheets were formed on an 8-inch diameter Rapid-Köthen mold using a recirculating white water system. A 100 x 110-mesh fourdrinier wire screen was used. Five gallons of distilled water, adjusted to pH 4.5 with alum, were used to start the circulation system.

Handsheets were prepared using an aliquot of the pulp slurry sufficient to produce a sheet weight equal to 1.85 g. o.d. (60 g.s.m.). The recirculating system was used to provide the white water for dilution of the furnish in the deckle box to approximately 0.04% concentration. This system was used to build up solids in the white water.

Sheet 1 was used for ash determination; sheets 2 through 20 were discarded, while building up the white water concentration, with the exception that sheets 15 and 16 were used to recheck basis weight of the handsheets and to adjust the slurry aliquot. Sheets 21-35 were pressed at 50 p.s.i. for 5 minutes between blotters and then dried for 7 minutes on a stainless steel drum drier at 220-230°F. The sheets numbered 21, 24, 27, 30, and 33 were used for physical testing and sheets 22, 25, 28, 31, and 34 were used for brightness and scattering coefficient measurements. These latter sheets were also ashed to obtain the actual filler present in the final sheet. Sheets 23, 26, 29, 32, and 35 were saved for future reference.

The ash content of the sheets and of the filler material was determined by heating the oven-dried weighed sheets and the pigments in a muffle furnace for two hours at 900°C. Allowance must be made for water of crystallization lost from the clay filler. The percentage actual filler in the sheet was obtained from Equation (1).

$$\frac{\%\ \text{Filler}}{\text{in sheet}} = \frac{\text{wt. of actual filler}}{\text{wt. of sheet}} = \frac{\%\ \text{ash in sheet} - \%\ \text{ash in pulp}}{\%\ \text{ash of pigment} - \%\ \text{ash in pulp}} \times 100 \qquad (1)\ .$$

The percentage retention was then obtained from Equation (2):

$$\%\ \text{Retention} = \frac{\%\ \text{filler in sheet} \times 100}{\%\ \text{filler added}\ (100 - \%\ \text{filler in sheet})} \times 100 \qquad (2)\ .$$

These formulas are used since the value for ash content of paper is based on pulp plus filler, but the value for the ash in the pulp is based on the pulp alone.

Specific scattering coefficient, specific absorption coefficient, and the handsheet strength properties were determined as described in Progress Reports Eight and Twelve.

APPENDIX IX

INITIAL RESULTS ON THREE-COMPONENT FURNISHES

TABLE XXVIII

RETENTION DATA FOR HUBER SSW FILLER CLAY

Furnish: 70% red maple holopulp, 215-ml. Canadian freeness;
30% bleached redwood/Douglas-fir kraft, 450-ml. Canadian freeness;
Canadian freeness of furnish, 225 ml.

Clay Added, % on o.d. fiber	pH	Canadian Freeness, ml.	No. 1 Handsheet			Handsheets 22-34		
			Ash, %	Filler Content, %	Retention, %	Ash, %	Filler Content, %	Retention, %
0	4.2	390	0.50	--	--	0.51	--	--
5	4.3	435	2.56	2.40	49	4.07	4.16	87
10	4.2	400	4.28	4.38	46	7.25	7.82	85
20	4.2	405	7.87	8.60	47	13.32	14.95	88

Furnish: 70% bleached red maple kraft, 350-ml. Canadian freeness;
30% bleached redwood/Douglas-fir kraft, 450-ml. Canadian freeness;
Canadian freeness of furnish, 320 ml.

Clay Added, % on o.d. fiber	pH	Canadian Freeness, ml.	No. 1 Handsheet			Handsheets 22-34		
			Ash, %	Filler Content, %	Retention, %	Ash, %	Filler Content, %	Retention, %
0	4.2	440	0.33	--	--	0.35	--	--
5	4.3	430	1.97	1.91	39	3.74	3.95	82
10	4.1	430	3.45	3.63	38	6.51	7.18	77
20	4.2	325	6.00	6.60	35	11.16	12.59	72

TABLE XXIX

RETENTION DATA FOR TITANOX AWD FILLER

Furnish: 70% red maple holopulp 215-ml. Canadian freeness;
30% bleached redwood/Douglas-fir kraft 450-ml. Canadian freeness;
Canadian freeness of furnish 320 ml.

TiO_2 Added, % on o.d. fiber	pH	Canadian Freeness, ml.	No. 1 Handsheet Ash, %	No. 1 Handsheet Filler Content, %	No. 1 Handsheet Retention, %	Handsheets 22-34 Ash, %	Handsheets 22-34 Filler Content, %	Handsheets 22-34 Retention, %
0	4.2	405	0.53			0.55		
2	4.2	420	1.61	1.09	55	2.14	1.60	81
5	4.4	405	3.39	2.88	59	4.63	3.90	81
10	4.3	400	5.94	5.44	58	8.39	7.89	86

Furnish: 70% bleached red maple kraft 350-ml. Canadian freeness;
30% bleached redwood/Douglas-fir kraft 450-ml. Canadian freeness;
Canadian freeness of furnish 340 ml.

TiO_2 Added, % on o.d. fiber	pH	Canadian Freeness, ml.	No. 1 Handsheet Ash, %	No. 1 Handsheet Filler Content, %	No. 1 Handsheet Retention, %	Handsheets 22-34 Ash, %	Handsheets 22-34 Filler Content, %	Handsheets 22-34 Retention, %
0	4.2	445	0.44			0.42		
2	4.4	430	1.61	1.18	60	1.99	1.57	80
5	4.3	430	3.08	2.65	54	3.58	3.17	66
10	4.2	430	6.88	6.47	69	8.42	8.04	87

TABLE XXX

HANDSHEET TEST DATA FOR HUBER SSW AND TITANOX AWD FILLERS

	70% Red Maple Holopulp 215-ml. C.F.				70% Bl. Red Maple Kraft 350-ml. C.F.			
Clay added, %	0	5	10	20	0	5	10	20
TAPPI brightness	82.2	81.1	81.9	80.4	83.4	82.4	82.2	82.2
Spec. scattering coefficient	326	364	371	435	412	426	458	481
Spec. absorption coefficient	1.81	2.02	1.73	2.73	1.40	2.03	3.40	2.45
Density, g./cc.	0.574	0.572	0.552	0.576	0.571	0.572	0.577	0.575
Breaking length, km.	5.83	4.49	5.33	4.03	4.63	4.45	3.55	3.78
Stretch, %	2.4	2.2	2.5	2.1	2.3	2.2	1.8	2.0
Tensile stiffness, Et, kg./cm.	437	357	371	336	378	372	322	331
Tear factor	103	92.7	94.6	94.0	99.5	110	90.9	86.2
M.I.T. fold	102	23	38	11	20	15	9	7
TiO_2 added, %	0	2	5	10	0	2	5	10
TAPPI brightness	82.2	83.8	86.6	87.8	83.2	85.9	86.7	89.5
Spec. scattering coefficient	323	413	501	618	422	516	601	850
Spec. absorption coefficient	1.57	1.64	1.45	1.41	2.01	1.29	1.37	1.19
Density, g./cc.	0.555	0.560	0.571	0.576	0.546	0.544	0.554	0.550
Breaking length, km.	5.65	6.60	5.40	5.12	4.69	4.47	4.34	3.60
Stretch, %	2.5	2.7	2.4	2.4	2.2	2.2	2.3	1.9
Tensile stiffness, Et, kg./cm.	376	401	386	371	354	361	351	334
Tear factor	101	105	99.7	94.9	109	106	109	103
M.I.T. fold	83	108	57	29	17	22	15	9