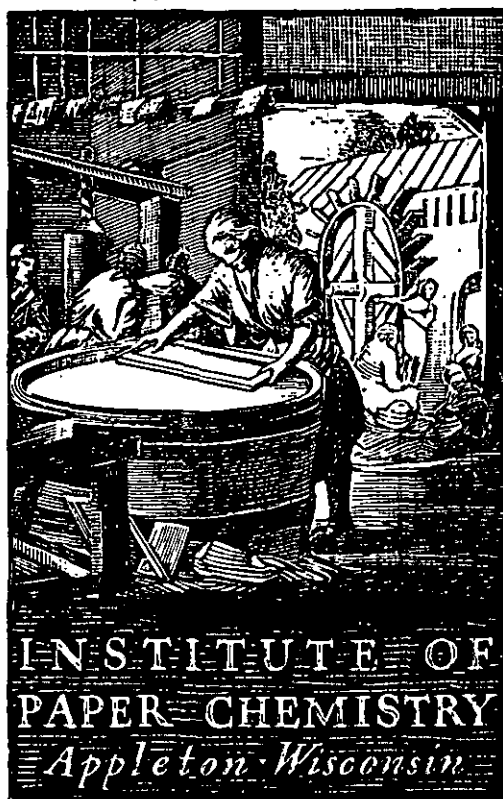




Institute of Paper Science and Technology
Central Files

**SELECTIVE DELIGNIFICATION OF WOOD AND
OTHER FIBROUS MATERIALS**

**REDUCED CHLORINE DIOXIDE ADDITION AND
IMPROVED BLEACHABILITY OF ASPEN CHLORINE
DIOXIDE-ALKALI PULPS**

Research Grant

Project 2500

Report Nine

A Progress Report

to

THE GRANTORS

October 29, 1969

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS
REDUCED CHLORINE DIOXIDE ADDITION AND IMPROVED BLEACHABILITY
OF ASPEN CHLORINE DIOXIDE-ALKALI PULPS

Research Grant

Project 2500

Report Nine

A Progress Report

to

THE GRANTORS

October 29, 1969

TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	2
REDUCED CHLORINE DIOXIDE ADDITION AND IMPROVED BLEACHABILITY OF ASPEN CHLORINE DIOXIDE-ALKALI PULPS	3
Discussion	3
Improvements in Chlorine Dioxide-Alkali Delignification	3
Background to Table I	7
Note on the Influence of Storage on Lignin Analyses	17
EXPERIMENTAL	20
Raw Materials	20
Fiberization	20
Alkali Conditioning	20
Lignin Modification	20
Alkali Extraction	21
Hypochlorite Reaction	21
Yield Data	22
Analytical and Other Methods	22
ACKNOWLEDGMENTS	22
LITERATURE CITED	23

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

REDUCED CHLORINE DIOXIDE ADDITION AND IMPROVED BLEACHABILITY
OF ASPEN CHLORINE DIOXIDE-ALKALI PULPS

SUMMARY

An unbleached aspen pulp was obtained in 67% yield from fiberized chips by delignification with 7.5% chlorine dioxide and alkali. The chlorine dioxide was accompanied by 1.33% chlorine which was shown to effectively replace 0.5% chlorine dioxide in delignification. Essentially similar results were obtained when lignin modification was preceded by alkali conditioning. Sodium hypochlorite solutions were used in single-stage bleaching to provide stable 90 GE pulps made at up to 65% yield.

It is noted that the proportion of acid-soluble lignin in pulps can increase during storage, although total lignin remained constant.

INTRODUCTION

The work described below relates to improving the status of the chlorine dioxide-alkali pulping process.

In attacking this objective, emphasis here has been placed firstly on reducing the amount of chlorine dioxide required in two ways. By splitting the addition of chlorine dioxide the total amount needed has been directly reduced and through substituting chlorine for part of that chlorine dioxide the amount has been further reduced. Secondly, attention has been given to bleaching pulps to high brightnesses without considerable yield loss.

Along with these efforts an endeavor has been made to take into account what has been learned previously about the role of alkali.

REDUCED CHLORINE DIOXIDE ADDITION AND IMPROVED BLEACHABILITY
OF ASPEN CHLORINE DIOXIDE-ALKALI PULPS

DISCUSSION

Improvements in Chlorine Dioxide-Alkali Delignification

Some exploratory work described in Report Three led to a 70%-yield pulp with encouraging freeness and opacity properties using a chlorine dioxide-alkali-chlorine dioxide-alkali delignification process requiring 9.0% chlorine dioxide and 44 hours' processing time. At that point in this project, attempts to do better were disappointing. Also pulp brightnesses up to only 65 GE were achieved.

For the above chlorine dioxide-alkali sequence, unbleached pulps now have been made as in Table I at about 65-70% yield with near 2.5 instead of 4% Klason lignin using only 7.5% chlorine dioxide and 9 hours' processing time. Furthermore, such pulps have been bleached to a relatively stable 90 GE brightness in one stage with hypochlorite without excessive shrinkage in yield. As well as clearly demonstrating the possibility of improving the process as in Table I, it is necessary to consider pulp properties and this will be covered in a later report.

The data in Table I have been compiled from the results of numerous experiments such as included in the tables belonging to the scheme set out in Fig. 1. In approaching this scheme, an effort has been made, as covered in Reports Six and Eight, to clarify a number of questions about the role of alkali since this was believed to be most significant in causing changes in fiber properties.

Table I reveals noteworthy features regarding four-step chlorine dioxide-alkali delignification as follows:

TABLE I
SUMMARY OF DATA LEADING TO 90-GE ASPEN PULPS

Process step	Alk Cond.	First Lignin Modification				First Alkali Extraction			
Pulp code	ADD=ACC	ADD	ACC	DD ^a	CC ^a	ADD	ACC	DD	CC
Sodium hydroxide, % ^b	1.7	—2.0—		—2.3—		—5 0—		6.0	6.8
Chlorine dioxide	--	5.3	4.97	5.3	4.97	--	--	--	--
Available Cl ₂ , %	--	--	0.88	--	0.88	--	--	--	--
Total equivalent ClO ₂ , %	--	—5.3—				--	--	--	--
Consistency, %	6.0	—5.0—				—8 0—			
Temperature, °C.	50	—25 - 35—				—60—			
Time, min.	60	—210—		—180-210—		—40—			
Final pH	10.2	3.4	2.8	3.1	2.5	10.3	10 0	9.9	10.4
Yield, %	93.0	91.5	91.5	99.5	99.0	75.5	77.0	82 0	82 0
Total lignin, %	23.0	20.5	20.5	23.0	24.0	11.5	11.5	14.0	14 0
Klason, %	19.1	14.0	14.5	16.5	17 0	8 5	9 0	10.5	11 0

Process step	Second Lignin Modification				Second Alkali Extraction				Hypochlorite			
Pulp code	ADD	ACC	DD	CC	ADD	ACC	DD	CC	ADD	ACC	DD	CC
Sodium hydroxide	—0.75—				—1.5—		—3.0—		—0.6—		0.38	0.5
Chlorine dioxide, %	2.7	2.53	2 7	2.53	--	--	--	--	--	--	--	--
Available Cl ₂ , %	--	0.45	--	0 45	--	--	--	--	—3.0—			
Total equivalent ClO ₂ , %	—2.7—				--	--	--	--	--	--	--	--
Consistency, %	—5.0—				—8.0—				—12 0—			
Temperature, °C.	—25 - 35—				—60—				—40—			
Time, min.	205	~330	285	300	—40—				—180—			
Final pH	2.8	2.3	2 4	2.4	10 4	10.5	11.2	11.2	8 6	8 5	7.1	7 3
Yield, %	73.0	74.5	79.0	80.0	65.0	64 5	67.5	67.5	61.0	60 5	63 0	65.0
Total lignin, %	8.0	8.5	11.5	11 5	3.6	3.3	3 6	4 0	--	--	--	--
Klason, %	5.0	5 5	7 0	7 5	2.5	2.0	2 3	2 7	--	--	--	--
GE (ethanol)	--	--	--	--	--	--	--	--	90	90	90	90
Aged GE	--	--	--	--	--	--	--	--	88	88	87	87

^a No alkali conditioning

^b In all tables, all percentages are on an o.d fiberized chip basis

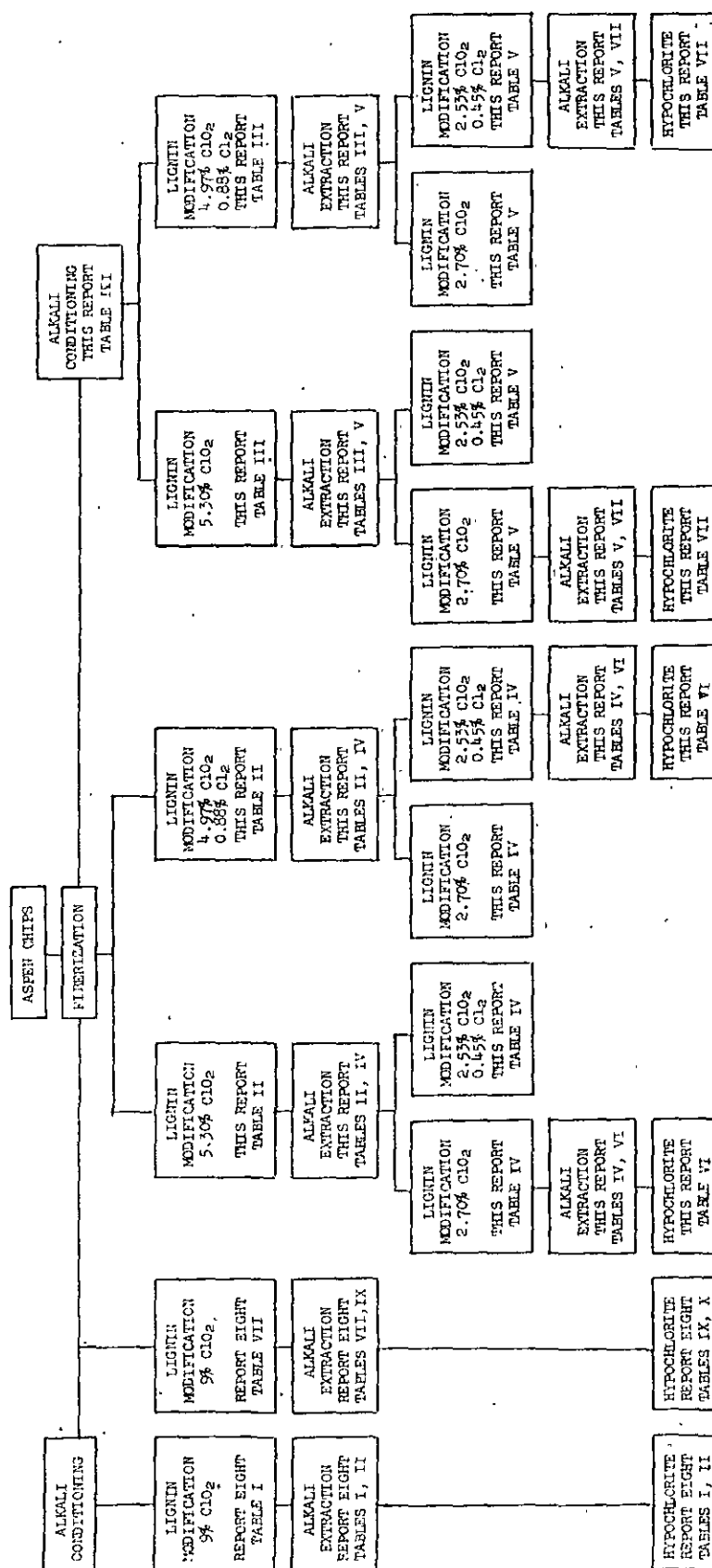


Figure 1. Experimental Scheme

- (1) essentially the same lignin contents after the second alkali extraction with or without alkali conditioning,
- (2) essentially the same lignin contents and yields when chlorine dioxide was replaced by a mixture of chlorine dioxide and chlorine having a mass ratio of 85:15,
- (3) approximately 1-2% yield loss during lignin modifications when there was no alkali conditioning, and
- (4) essentially in five steps, reminiscent of multistage bleaching, the whole process of delignification as in pulping and bleaching to 90 GE brightness has been achieved.

Obviously it would be advantageous to omit the step of alkali conditioning if pulp lignin content was the sole consideration. However, previous work had indicated both uniformity of delignification and fiber properties can be influenced by alkali conditioning, so that there are pros and cons for this step.

The evidence that at least some of the chlorine dioxide can be replaced by chlorine is of economic importance. Firstly, in practice it is simpler and cheaper to produce chlorine dioxide without having to purify it by removal of chlorine to less than about 85:15 on a weight:weight basis. Secondly, if the chlorine present can be substituted for chlorine dioxide on a chemical equivalent basis, as in Table I, this lowers the cost still further.

The quite small loss in yield during the lignin modifications means the aqueous effluents from these steps are very dilute and most of the dissolved solids are present in the alkali extraction liquors. At the present the full import of this is uncertain. It is the first occasion on which so little material has been dissolved in the lignin modification. This could be significant in consideration

of aqueous effluents. In addition, it bears out the concept of lignin modification in situ before solubilization in alkali as a desirable approach to minimizing the amount of more costly chemical needed for selective delignification.

The knowledge that pulping and bleaching to 90 GE brightness can be achieved in five steps reminiscent of multistage bleaching currently rests on a narrow base and it would be prudent to regard it with a feeling of considerable qualification. Nevertheless, if one envisages the prospect of a closed pulping and bleaching system, the idea of a process such as pointed to in Table I holds greater attraction.

Background to Table I

Although the experimental conditions set out in Table I partly evolved as the scheme in Fig. 1 was implemented, at an early date some parameters were established in order to limit the number of combinations possible. After setting the amount of chlorine dioxide at 9.0% for a process with one lignin modification, the total amount of chlorine dioxide was arbitrarily put at 8.0% for a process with a split lignin modification. To determine whether at least some chlorine could be tolerated it was decided to alternate for 8% chlorine dioxide a chemical equivalent mixture of chlorine dioxide and chlorine in which 15% was chlorine. This means the lowest total amount of chlorine dioxide added would be 7.5% or one sixth less than 9.0%, which is a significant reduction. A decision was made to divide on a 2:1 basis the chlorine dioxide used in a split lignin modification. Hence the amounts of chlorine dioxide and chlorine become settled as in Fig. 1.

Details of how each process step was carried out are included in the experimental part that follows.

Since it is known from the work in Reports Six and Eight that for a given degree of lignin modification the characteristics of the product obtained after alkali extraction can be influenced by the inclusion or exclusion of alkali conditioning as well as alkali extraction time, extraction temperature, alkali concentration and amount, these all need to be taken into account in chlorine dioxide-alkali delignification.

Looking with hindsight at Tables II and III, if the main purpose of alkali conditioning is regarded as being to facilitate uniform lignin modification without causing undesirable changes of either a chemical or physical nature, less alkali, a higher temperature, and shorter time may provide a better combination of conditions.

In considering the alkali extraction temperature after lignin modification, 60°C. was chosen following the work described in Report Six.

Data like those in Fig. 2 indicated the relationships between pH and time for extraction with various amounts of alkali were such that pH at a particular extraction time of more than about 20 min. is changing less rapidly than at first and can serve in choosing the amount of alkali for extraction.

The pH values, lignin analyses, and yields for various amounts of alkali used to extract small lots of pulp for particular times as in Tables II, III, IV, and V provide a view from which the amount of alkali needed to reach a certain alkaline final pH can be estimated. This is desirable in order to create a situation where alkali extractions are comparable by virtue of pH equivalence when the materials to be extracted have different histories. For example, in Tables IV and V each product after the first lignin modification was extracted with pH 10.9-11.4 after 5 minutes and 9.9-10.4 after 40 minutes. It is reasonable to conclude

TABLE II
FIRST LIGNIN MODIFICATION AND TRIAL EXTRACTIONS

I. Lignin Modification

Consistency, 5.0%; temperature, 25 → 35°C.; sodium hydroxide, 2.25%.

Total equivalent chlorine dioxide, %	5.3	5.3
ClO ₂ , %	5.3	4.97
Cl ₂ , %	-	0.88
Time, min.. (to exhaustion)	180-210	180-210
pH after 5 min. → final pH	6.2 → 3.1	4.4 → 2.5
Yield, %	99.4	99.1
Total lignin, %	23.1	23.9
Klason, %	16.3	17.0
Acid sol., %	6.8	6.9
Code	D	C

II. Alkali Extraction of Small Lots

Consistency, 8.0%; temperature, 60°C.

Material	D					C				
Sodium hydroxide, %	3.0	4.0	6.0			4.0	6.0			
Time, min.	120	20	60	20	60	20	40	120	20	60
pH after 5 min.	9.9	10.4	10.9	11.2	11.2	10.4	10.3	10.2	--	--
Final pH	7.9	9.6	9.2	10.6	9.9	9.4	9.1	8.4	10.5	9.8
Yield, %	90.1	85.5	85.5	82.6	82.0	88.3	87.5	87.6	82.8	82.4
Total lignin, %	--	--	--	15.9	15.3	--	--	--	15.6	15.4
Klason, %	--	--	--	11.4	11.2	--	--	--	11.4	11.3
Acid sol., %	--	--	--	4.5	4.1	--	--	--	4.2	4.1

TABLE III

ALKALI CONDITIONING, FIRST LIGNIN MODIFICATION AND TRIAL EXTRACTIONS

I. Alkali Conditioning

Sodium hydroxide, %	1.7	pH after 5 min.	11.2	Total lignin, %	23.0
Consistency, %	6.0	Final pH	10.2	Klason, %	19.1
Temperature, °C.	50	Yield, %	93.0	Acid sol., %	3.9
Time, min.	60				

II. Lignin Modification

Consistency, 5.0%, temperature, 25-35°C., sodium hydroxide, 2.0%.

Total equiv. chlorine dioxide, %	5.3	5.3
ClO ₂ , %	5.3	4.97
Cl ₂ , %	-	0.88
Time, min. (to exhaustion)	210	210
pH after 5 min. - final pH	6.2 - 3.4	5.8 - 2.8
Yield, %	91.3	91.7
Total lignin, %	20.4	20.4
Klason, %	14.1	14.6
Acid sol, %	6.3	5.8
Code	AD	AC

III. Alkali Extraction of Small Lots

Consistency, 8.0%, temperature, 60°C.

Material	AD						AC			
Sodium hydroxide, %	3.0		4.0		5.0		4.0		5.0	
Time, min.	40	120	40	120	40	120	40	120	40	120
pH after 5 min.	10.1	10.2	10.6	10.6	10.9	11.1	10.4	10.3	10.6	10.7
Final pH	8.8	8.0	9.3	8.6	10.0	9.3	9.0	8.3	9.6	8.8
Yield, % (Y)	84.1	84.2	82.1	79.8	77.5	76.2	81.6	81.0	78.3	77.8
Total lignin, % (L)	15.9	16.2	15.2	13.8	12.6	11.9	14.4	13.9	12.3	11.9
Klason, %	11.5	11.7	11.1	10.2	9.5	9.0	10.5	10.1	9.2	8.8
Acid sol, %	4.4	4.5	4.1	3.6	3.1	2.9	3.9	3.8	3.1	3.1
Y - L	68.2	68.0	66.9	66.0	64.9	64.3	67.2	67.1	66.0	65.9

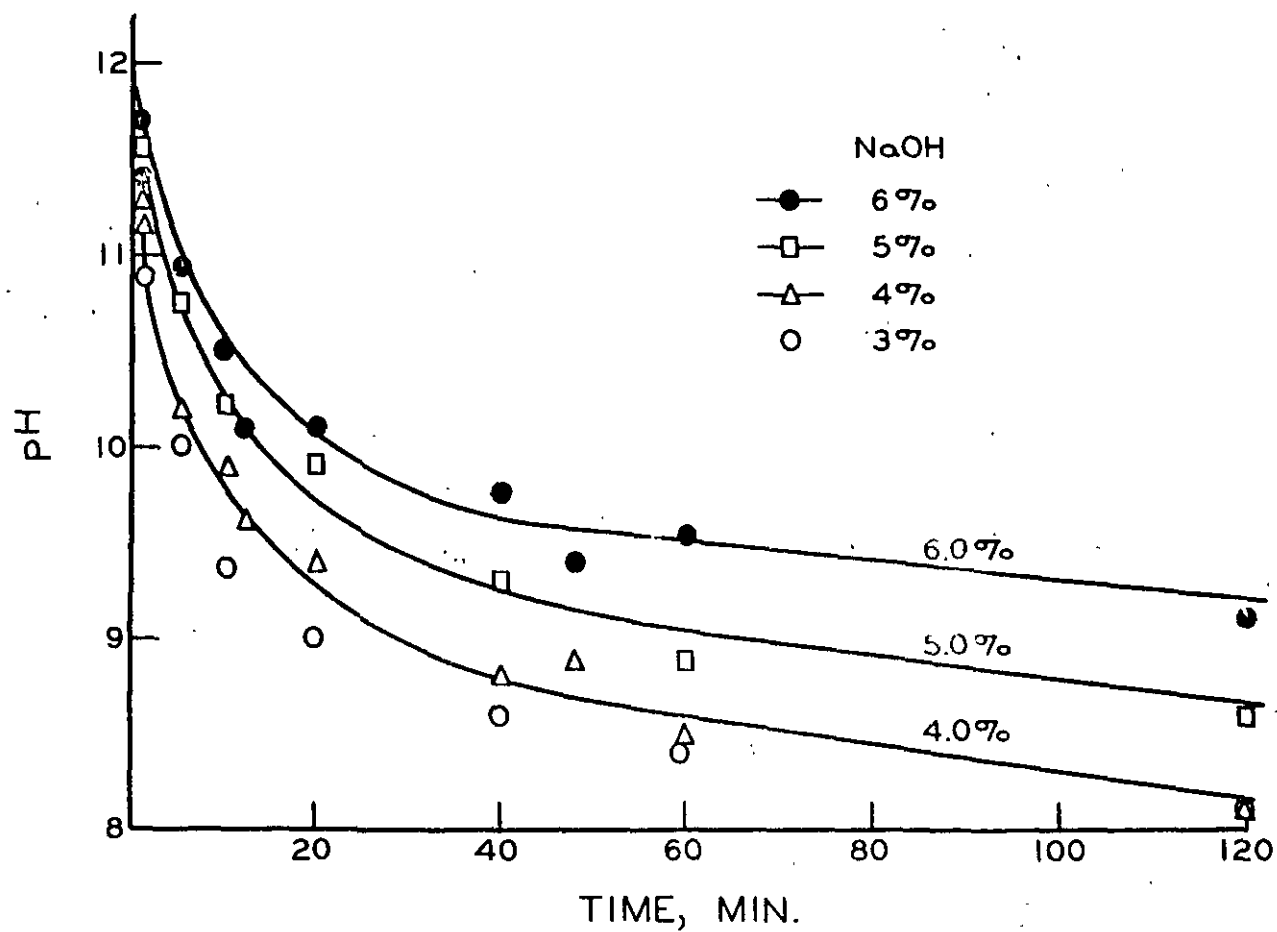


Figure 2. Change of pH During Extraction with Different Amounts of Alkali After Lignin Modification

TABLE IV

FIRST ALKALI EXTRACTION, SECOND LIGNIN MODIFICATION, AND TRIAL EXTRACTIONS

I. Lignin Modification

As in Table II

II. Alkali Extraction

Consistency, 8.0%; temperature, 60°C.; time, 40 min.

Material	D	C
Sodium hydroxide, %	6.0	6.8
pH after 5 min. -- final pH	11.2 -- 9.9	11.4 -- 10.4
Yield, %	81.8	82.1
Total lignin, %	14.2	14.1
Klason, %	10.6	10.8
Acid sol., %	3.6	3.3
Code	DE	CE

III. Lignin Modification

Consistency, 5.0%; temperature, 25 -- 35°C.; sodium hydroxide, 0.75%.

Material (washed dil. HAc)	DE		CE	
Total equiv. chlorine dioxide, %	2.7		2.7	
ClO ₂ , %	2.7	2.53	2.7	2.53
Cl ₂ , %	--	0.45	--	0.45
Time, hr. (to exhaustion)	4.75	3.5	4.25	5.0
pH after 5 min. -- final pH	2.5 -- 2.4	2.4 -- 2.4	2.5 -- 2.4	2.5 -- 2.4
Yield, % (Y)	78.8	79.1	80.7	79.9
Total lignin, % (L)	11.4	11.1	11.0	11.4
Klason, %	7.2	7.7	7.7	7.6
Acid sol., %	4.2	3.4	3.3	3.8
Y - L	67.4	68.0	69.7	68.5
Code	DED	--	--	CEC

IV. Alkali Extraction of Small Lots

Consistency, 8.0%; temperature, 60°C.

Material	DED								CEC			
Sodium hydroxide, %	2.0		3.0		4.0		6.0		2.0		3.0	
Time, min.	40	120	40	120	40	120	120		40	120	40	120
pH after 5 min.	10.6	10.2	10.9	11.5	11.3	11.8	12.1		10.2	10.5	11.0	11.0
Final pH	8.8	8.7	10.6	11.0	11.2	11.6	12.0		9.5	8.8	10.7	10.4
Yield, %	70.0	69.6	67.1	66.1	65.5	64.3	64.1		70.2	68.7	66.6	65.7
Total lignin, %	7.1	7.4	5.2	3.2	3.8	--	2.3		6.3	5.9	4.0	3.7
Klason, %	5.0	5.4	3.8	1.9	2.7	--	1.4		4.3	4.1	2.6	2.5
Acid sol., %	2.1	2.0	1.4	1.3	1.1	--	0.9		2.0	1.8	1.4	1.2

TABLE V

FIRST ALKALI EXTRACTION, SECOND LIGNIN MODIFICATION, AND TRIAL EXTRACTIONS
WITH ALKALI CONDITIONINGI. Alkali Conditioning (as in Table III)II. Lignin Modification (as in Table III)III. Alkali Extraction

Consistency, 8.0%; temperature, 60°C.; time, 40 min.; sodium hydroxide, 5.0%.

Material	AD	AC
pH after 5 min. -- final pH	11.0 - 10.3	10.9 - 10.0
Yield, %	75.6	77.2
Total lignin, %	11.3	11.5
Klason, %	8.6	8.9
Acid sol., %	2.7	2.6
Code	ADE	ACE

IV. Lignin Modification

Consistency, 5.0%; temperature, 25 - 35°C.; sodium hydroxide, 0.75%.

Material	ADE		ACE	
Total equiv. chlorine dioxide, %	2.7			
ClO ₂ , %	2.7	2.53	2.7	2.53
Cl ₂ , %	--	0.45	--	0.45
Time, hr. (to exhaustion)	3.25	5-6	3.25	5-6
pH after 5 min. -- final pH	5.4 - 2.8	5.1 - 2.7	6.2 - 3.2	3.7 - 2.3
Yield, % (Y)	72.9	73.5	73.8	74.7
Total lignin, % (L)	8.1	8.7	8.5	8.6
Klason, %	5.1	5.8	5.5	5.5
Acid sol., %	3.0	2.9	3.0	3.1
Y - L	64.8	64.8	65.3	66.1
Code	ADED	--	--	ACEC

V. Alkali Extraction of Small Lots

Consistency, 8.0%; temperature, 60°C.

Material	ADED						ACEC					
Sodium hydroxide, %	1.0	1.5	2.0	3.0			1.0	1.5	2.0	3.0		
Time, min.	40	120	40	40	120	120	40	120	40	40	120	120
pH after 5 min.	10.4	9.6	11.2	11.7	10.8	11.2	9.3	9.0	10.8	11.3	11.3	11.9
Final pH	9.7	9.0	10.7	11.4	10.5	--	8.2	7.7	10.0	10.8	9.8	11.1
Yield, %	66.1	65.5	64.4	61.8	61.6	61.0	67.9	68.1	65.9	64.4	64.0	61.5
Total lignin, %	4.8	--	4.0	3.1	2.4	--	5.7	--	4.6	3.7	3.1	--
Klason, %	3.0	--	2.5	2.0	1.0	--	3.5	--	2.8	2.2	1.9	--
Acid sol., %	1.8	--	1.5	1.1	1.4	--	2.2	--	1.8	1.5	1.2	--

that the higher yields and total lignins after the first alkali extraction, as discernible when the data in Tables IV and V are compared, can be attributed to the omission of alkali conditioning. The alternative explanation that the higher yields and total lignins are attributable to the use of insufficient alkali for extraction is considered unlikely.

From the second lignin modification according to the scheme in Fig. 1 there are eight products. Of the eight, four included and four did not include alkali conditioning. Each set of four revealed no marked within-set differences in either yield or lignin content, as may be seen from Tables IV and V. Therefore, further work on the four uncoded products was dropped and attention directed to the products obtained using either chlorine dioxide or chlorine dioxide plus chlorine in both parts of the split lignin modification step.

Although the amounts of alkali in the second extractions as in Tables VI and VII were chosen on the basis of the extraction of small lots of material as laid out in Tables IV and V with the expectation of a final pH $\approx$ 10.5, this was not realized. Nevertheless, total lignin contents (Tables VI and VII) are comparable for all four products, while yields for the two obtained without alkali conditioning, viz. DD and CC, are apparently greater than for the other two, viz. ADD and ACC.

Each of these four products when bleached with hypochlorite reached a relatively stable 90 GE brightness with about 3% yield loss as detailed in Tables VI and VII. These are regarded as encouraging results. It may be noted the brightness sheets were formed in ethanol. This is a nonstandard practice followed here to avoid confusing the measurement of reflectance by the possibility of a significant amount of transmittance occurring through bonded areas of the brightness tabs.

TABLE VI
SECOND ALKALI EXTRACTION AND TRIAL HYPOCHLORITE REACTIONS

- I. Lignin Modification (as in Table II)
 II. Alkali Extraction (as in Table IV)
 III. Lignin Modification (as in Table IV)
 IV. Alkali Extraction

Sodium hydroxide, 3.0%; consistency, 8.0%; temperature, 60°C.; time, 40 min.

Material	DED	CEC
pH after 1 min. → final pH	11.5 → 11.2	11.6 → 11.2
Yield, %	67.6	67.8
Total lignin, %	3.6	4.0
Klason, %	2.3	2.7
Acid sol., %	1.3	1.3
Pulp	DD	CC

- V. Hypochlorite Reaction (unscreened pulps)

Consistency, 12.0%; temperature, 40°C.

Pulp	DD				CC			
Available chlorine, %	1.5	—3.0—	4.0		1.5	—3.0—	4.0	
Sodium hydroxide, %	0.38	0.38	0.4	0.5	0.5	0.5	0.5	0.6
pH after 1 min.	--	--	11.1	--	--	--	11.1	11.4
Final pH	8.2	7.1	7.0	7.8	9.0	7.3	7.3	7.6
Time, min. (starch/I ⁻)	80	>185	>180	>185	90	>180	180	>180
Yield, %	64.6	63.2	64.1	62.9	65.1	64.6	64.6	63.7
GE (ex. ethanol)	87	90	87 ^a	91	86	90	88 ^a	91
Aged GE	84	87	83	89	83	87	84	88
Canadian freeness (T 227 m-58)	387	207	--	259	392	312	--	327

^a No SO₂ wash.

TABLE VII

SECOND ALKALI EXTRACTION AND TRIAL HYPOCHLORITE WITH ALKALI CONDITIONING

- I. Alkali Conditioning (as in Table III)
- II. Lignin Modification (as in Table III)
- III. Alkali Extraction (as in Table V)
- IV. Lignin Modification (as in Table V)
- V. Alkali Extraction

Consistency, 8.0%; temperature, 60°C.; time, 40 min.; sodium hydroxide, 1.5%.

Material	ADED	ACEC
pH after 1 min. → final pH	11.2 → 10.4	11.3 → 10.5
Yield, %	64.8	64.3
Total lignin, %	3.6	3.3
Klason, %	2.3	2.0
Acid sol., %	1.3	1.3
Pulp	ADD	ACC

- VI. Hypochlorite Reaction (unscreened pulps)

Consistency, 12.0%; temperature, 40°C.

Pulp	ADD			ACC		
Available chlorine, %	1.5	3.0	6.0	1.5	3.0	4.0
Sodium hydroxide, %	0.5	0.6	0.7	0.5	0.6	0.7
pH after 5 min.	10.9	11.3	11.5	10.7	10.9	11.0
Final pH	9.5	8.6	8.3	8.9	8.5	8.4
Time, min. (starch/I ⁻)	120	>180	>180	150	180	180
Yield, %	61.5	60.9	60.2	61.9	60.6	60.1
GE (ex. ethanol)	85.3	90.0	91.3	87.1	90.3	91.4
Aged GE	82.9	87.9	89.5	85.0	88.2	89.7
Canadian freeness (T 227 m-58)	473	402	322	372	372	332

A logical sequel to the above experiments as summarized in Table I is to consider the papermaking properties of a fully bleached pulp made by a route based on the knowledge obtained to date. This will be covered in a forthcoming report.

Note on the Influence of Storage on Lignin Analyses

From Table XIII of Report Six the Klason and acid-soluble lignin values in the regular lignin analyses, for example, are not smoothly related to extraction time although the sums of the two forms of lignin successively decrease with longer extraction time, as might be expected.

It is noted that these analyses were carried out in duplicate after different periods of storage and by two analysts, as in the following table:

TABLE VIII
DATA RELATED TO SAMPLES AS LISTED

Sample Code	Storage, months	Analyst	Graphical Symbol
A-21	3	1	O
A-18	3	1	O
A-19	9	2	▲
A-33	3	1	O
A-32	3	1	O
A-34	5	2	Δ
A-34	9	2	▲
A-31	3	1	O
A-42	1	1	□
A-41	8	2	▼
A-39	1	1	□
A-39	3	2	▽
A-40	8	2	▼
A-38	1	1	□
A-37	8	2	▼
A-36	1	1	□

When the data are plotted as in Fig. 3, it appears that samples stored for 8-9 months had significantly lower Klason lignin:acid-soluble lignin values because some of the Klason lignin seems to appear as acid-soluble lignin after extended storage. This accounts for the relationships referred to in Table XIII of Report Six.

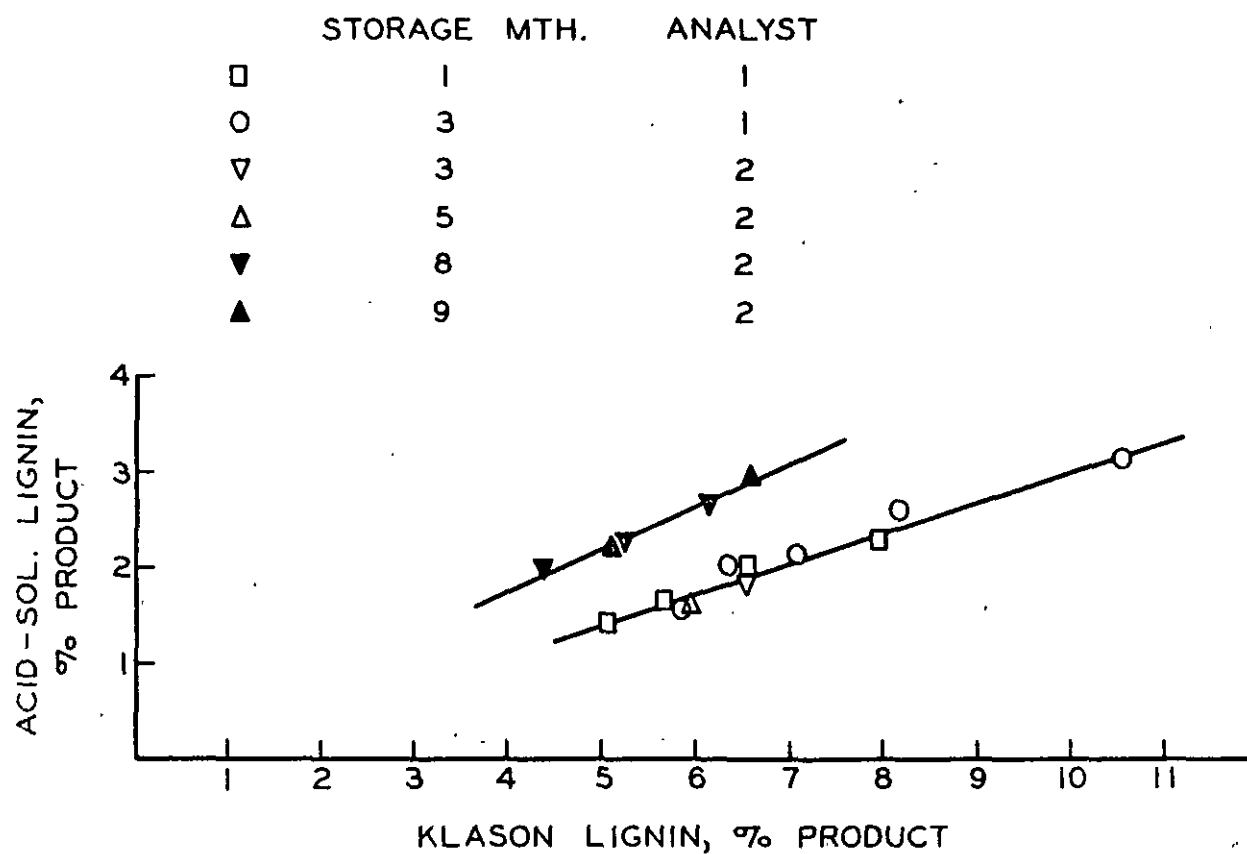


Figure 3. Evidence of Lower Klason Lignin:Acid-Soluble Lignin Ratios After Extended Storage

EXPERIMENTAL

RAW MATERIALS

Chip Lot A3/55 was used.

FIBERIZATION

Fiberized chips were prepared in a 36-in. double-disk Bauer machine fitted with no. 36109 pattern plates set at a 0.025-in. gap. Before using the machine, it was heated by purging with steam for about an hour. Other details of the procedure followed are as indicated in Report Eight, page 93.

The fiberized material was cooled by a water spray, then dewatered on a muslin-covered box, centrifuged, and passed through a pulp shredder before being sampled for moisture content. The next process step was initiated within six hours.

ALKALI CONDITIONING

The preliminary alkali conditioning was carried out using a technique similar to that described in Report Eight, page 93. Details of the experimental conditions are included in Table III.

LIGNIN MODIFICATION

For lignin modification, chlorine dioxide solutions were prepared in the usual way according to the laboratory method of Ernest (1). Solutions containing a mixture of chlorine dioxide and chlorine were prepared by combining calculated amounts of a solution containing one component, then analyzing the combined solution for chlorine dioxide and chlorine (see footnote on next page).

The lignin modifications were carried out in closed polyethylene containers of appropriate size essentially as described in Report Eight, page 93, except for some variation in that the product was first collected on a sintered-glass funnel, washed with deionized water, then dewatered in a centrifuge and passed through a pulp shredder. Other details are provided in Tables II, III, IV, and V.*

ALKALI EXTRACTION

The alkali extractions were carried out using the conditions as noted in Tables II, III, IV, V, VI, and VII. After extraction, the collected pulps were washed with distilled water on a fritted-glass funnel, then soaked at roughly 8% consistency for about one hour in dilute acetic acid using equivalent to approximately half the amount of alkali added for extraction. The pulps were again collected, washed on a fritted-glass funnel with deionized water, and the larger amounts centrifuged, then shredded.

HYPOCHLORITE REACTION

The hypochlorite reactions were carried out using the conditions noted in Tables VI and VII. After filtering, the pulps were washed with water, then soaked at about 5% consistency in excess dilute sulfurous acid for one hour, unless noted to the contrary.

* The formula for g.p.l. Cl_2 [The Bleaching of Pulp. TAPPI Monograph Series No. 27: 372 (1963)] is unclear and incorrect. It should be $[(N - (A/4) \times 0.71)]$, where N = titration as under C, A = the additional titration as under D, and ml. sample = 5.

YIELD DATA

As a general rule, yields were calculated on the larger amounts of material from a particular process step by sampling the shredded, centrifuged, and washed products.

ANALYTICAL AND OTHER METHODS

Analysis of chlorine water--TAPPI Standard T 611 m-47.

Analysis of hypochlorite liquor--TAPPI Standard T 611 m-47.

Klason lignin analysis--TAPPI Standard T 222 m-54, except that the extraction step was omitted and smaller samples were used.

Acid-soluble lignin analyses were carried out according to the method of Pearl and Busche (2).

Brightness sheets--TAPPI Standard T 611 m-47.

Brightness measurements--TAPPI Standard T 452 m-58.

Aged brightness was determined after heating the brightness tabs at 105°C. in a forced-air-ventilated oven for one hour.

Pulp freeness--TAPPI Standard T 227 m-58.

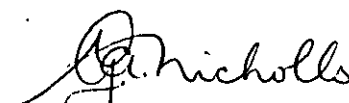
ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance and cooperation of various Institute members including: Mrs. E. Cary, Messrs. H. M. Corbett, R. G. Jamieson, J. R. Peckham, D. G. Sachs, J. R. Taggart, and V. J. Van Drunen. For financial support we are much indebted to the Grantors.

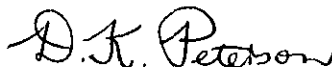
LITERATURE CITED

1. Ernest, F. M., Paper Trade J. 143:46-50(Aug. 24, 1959).
2. Pearl, I. A., and Busche, L. R., Tappi 43: 961-70(1960).

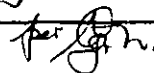
THE INSTITUTE OF PAPER CHEMISTRY



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



D. K. Peterson*



* Dr. David K. Peterson, formerly of the staff of The Institute of Paper Chemistry where this work was performed; present address: Indiana Institute of Technology, Fort Wayne, Indiana.