The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Study of the Lignin Residues in Unbleached and Partially Bleached Sulfite Pulp

by Leslie Lundgren Larson

June, 1940

A STUDY OF THE LIGNIN RESIDUES IN UNBLEACHED AND PARTIALLY BLEACHED SULFITE PULP

A thesis submitted by

Leslie Lundgren Larsen

B. S. 1934 University of Idaho
M. S. 1936 University of Idaho

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy,
from Lawrence College,
Appleton, Wisconsin,

June 1940

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

A STUDY OF THE LIGNIN RESIDUES IN UNBLEACHED AND PARTIALLY BLEACHED SULFITE PULP

I. INTRODUCTION

Numerous papers have been published recently which attempt to clarify the mechanism of the chlorination which occurs when elementary chlorine is added to an unbleached pulp. Despite the large volume of research, investigators have not agreed entirely as to what chemical reactions take place in this process.

The bleaching action of chlorine on pulp is due chiefly to the formation of chlorinated lignin compounds that are partly soluble in water and somewhat more soluble in sodium hydroxide. In fact, it may be considered as a continuation of the purification already begun in the cooking process (1). Although there have been a great many publications on lignin, there is still very little known about its structure and behavior; this lack of knowledge probably accounts for the slight progress that has been made regarding the actual mechanism of the chlorination reaction in the bleaching of wood pulp.

It was the purpose of this investigation to study the process of sulfite pulp chlorination in order to determine what happens chemically to the lignin. In order to carry out this study two different pulps were prepared from a common source of wood and chlorinated with different percentages of the chlorine requirement. Material, chlorine, and sulfur balances were made in order to ascertain the distribution of chlorine and sulfur in the resulting products. The lignins were isolated from the pulps and the liquors at various stages by different methods, and their chemical nature was studied. Sodium hydroxide extractions were also made at different temperatures to determine their effect on the chlorinated lignins.

It was felt that an investigation of this type might possibly furnish a little clearer insight regarding the actual reactions taking place in the chlorination of lignin in sulfite pulp.

II. HISTORICAL

Payen (2) was probably the first to note the delignifying action of chlorine on woody material. Fremy and Terreil (3) later developed the method for determining cellulose by the use of chlorine, followed by extraction with sodium hydroxide. This method was improved by Cross and Bevan (4) in 1880 by their use of sodium sulfite in place of sodium hydroxide.

The use of chlorine water by de Vains (5) and gaseous chlorine by Cataldi (6) for cooking straw, together with the advent of equipment for handling chlorinated liquors, might be considered as forerunners of the bleaching process with gaseous chlorine.

A. RESULTS OF THE CHLORINATION OF PLANT SUBSTANCES

Although it is not directly related to the mechanism of sulfite pulp chlorination, it seems advisable to mention some work on the chlorination of uncooked plant substances.

When chlorine is added to water there is hydrolysis and an equilibrium is set up depending upon the temperature and concentration of the hydrogen and chloride ions. The equation for the reaction is:

$$Cl_2 + H_2O = H^+ + Cl^- + HClO$$

Schmidt-Nielsen (7) measured the oxidation potential of sodium hypochlorite solutions with platinum electrodes and concluded that, below a pH of 2.0, the reaction is similar to the addition of gaseous chlorine and that the reaction is chiefly chlorination. Only chlorination will be considered here.

There are three possible reactions of chlorine with organic compounds: (1) Addition to a double bond with no liberation of hydrochloric acid; (2) substitution of chlorine for labile hydrogen which would liberate one mole of hydrochloric acid per mole of chlorine consumed; and (3) oxidation with the liberation of two moles of hydrochloric acid per mole of chlorine consumed (8).

It is thus evident that a study of the ratio of hydrochloric acid liberated to the chlorine consumption in the chlorination process would throw some light on the reactions taking place.

Cross and Bevan (4) chlorinated jute and noted what they considered to be a definite chlorolignin compound ($C_{19}H_{18}Cl_4O_9$) with a chlorine content of 27 per cent. Prior to chlorination, the jute was boiled for ten to fifteen minutes in a 1 per cent sodium hydroxide solution. The chlorine consumption of the jute was sixteen to seventeen per cent on the weight of the fiber, half of which appeared as hydrochloric acid. However, work on pine, beech, sycamore, and birch previously treated with 1 per cent hot sodium hydroxide for ten to fifteen minutes showed a much greater percentage of hydrochloric acid formed (68 to 75 per cent of the chlorine added). The hot caustic treatment removed 11 to 18 per cent of the original material.

In studies on the chlorination of jute fiber, Strong (9) reported results somewhat different from those obtained by Cross and Bevan. Prior to chlorination, the jute was heated on a boiling water bath with 1 per cent sodium hydroxide for one hour. Strong reported an average combined chlorine content of 5.0 per cent, with 9.9 per cent of the chlorine in the form of hydrochloric acid, based on the ovendry weight of the sample. In further studies on Victorian mountain ash given the same pretreatment as the jute, Strong (10) reported similar findings; about two thirds of the chlorine consumed was converted into hydrochloric acid and one third combined with the lignin.

Heuser and Sieber (11) reported results similar to those of Cross and Bevan and Strong. They chlorinated steamed sprucewood at 0° C. to the point where all the lignin was removed and found that of the equivalent of 40.6 grams of chlorine added to 100 grams of wood, 31.1 grams formed hydrochloric acid and 9.5 grams combined with the lignin. This is about 75 per cent of the chlorine as hydrochloric acid. Heuser and Haug (12) later chlorinated straw and found similar results as regards hydrochloric acid formation.

Waentig (13) made a rather extensive study of spruce lignin in the chlorine pulping process. He found that the proportion of chlorine added which formed hydrochloric acid was about 70 per cent and was independent of the time and temperature of chlorination (six to twenty-four hours and 15 to 25° C.). The percentage of hydrochloric acid formed decreased with the addition of hydrochloric acid, indicating that the formation of hydrochloric acid depends upon the pH. In other words, the course of the chlorination reaction is influenced by the pH.

About half of the chlorinated lignin became water soluble during the chlorinations and showed a relatively low chlorine content (18.5 to 19 per cent).

The chlorolignins were also soluble in ethyl and methyl alcohols, acetone, and acetic acid. A larger amount of the lignin dissolved when the chlorinations were carried out in hydrochloric acid. The main portions of the chlorolignins were extracted with alcohol and showed chlorine contents varying from 25 to 39 per cent. The chlorine content of the lignin compounds increased slightly by increasing the temperature and the time of chlorination and markedly by raising the hydrochloric acid concentration. Pretreatment of the wood with water at 5 atmospheres pressure for four hours, 10 per cent ammonia for four hours at 138° C., 10 per cent calcium oxide for four hours at 5 atmospheres pressure, or 18 per cent sodium hydroxide for four hours at 5 atmospheres produced little change in the chlorine content of the final lignin. The chlorine content of lignins from other woods and straw were about the same as that from sprucewood.

A rather recent investigation has been made by Müller (18) in which he extracted the lignin from chlorinated sprucewood with alcohol. The crude products (22.5 to 27 per cent yields) separated on concentration and varied in chlorine content from 22.5 to 27 per cent. Extraction of the filtrate of chlorolignin with ether and isolation of the product gave 2 to 8.4 per cent of a material similar to the chlorolignins. The insoluble portion was precipitated with lime or barytes, and was claimed to be 50 to 80 per cent tannin.

Müller separated the crude chlorinated lignin into ether-soluble and ether-insoluble parts containing 26.8 per cent chlorine and 4.8 per cent methoxyl and 21.3 per cent chlorine and 4.5 per cent methoxyl, respectively.

In a more recent publication, Müller and Stalder (15) reported experiments with many types of plant constituents; the results showed that all could be chlorinated. The chlorine content varied from 34 per cent for lignin to 45 per cent for pyrocatechol. Lignins showed chlorine consumptions of 149 to 217 per cent with 115 to 173 per cent as hydrochloric acid and 34 to 44 per cent organically combined.

Jensen and Bain (16) prepared what they considered to be a homogenous lignin chloride by chlorinating spruce sawdust in a suspension of methyl alcohol. The lignin chloride was precipitated as a cream-white product by pouring the alcohol into water; analyses showed it to be a partially chlorinated alcohol lignin to which the formula $C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$ was ascribed. The homogenous fraction obtained by rechlorination compared fairly well to Brauns and Hibbert's methanol lignin (17).

B. CHLORINATION OF PULPS

Fotiev (18) has used Freudenberg's lignin formula (19) to explain the bleaching reactions. There are no double bonds in this lignin formula and he believes that chlorine is substituted for hydrogen in the para position to the methoxyl group on the benzene nucleus as a permutative reaction (reactions occurring with rapidity throughout the entire mass). According to Fotiev an oxidation reaction is assumed to take place at a much slower rate and less completely in the aliphatic part of the lignin molecule at the secondary alcohol group and at an oxygen bridge assumed in the lignin molecule to form smaller lignin fragments that are soluble in water and dilute alkali.

Fotiev further used the equation of Opfermann (20) to postulate the degrees of substitution and oxidation that occur on chlorination. Since, on substitution, one mole of chlorine forms one mole of hydrochloric acid and, on oxidation, two moles of hydrochloric acid, it is possible to determine the degree of each reaction when the hydrochloric acid concentration and amount of chlorine consumed are known.

Assuming that 100 grams of chlorine is used, then

$$y = 0.5x + (100 - x), \text{ or}$$

$$y = 100 - 0.5x$$

where y = grams of chlorine forming hydrochloric acid, x = grams of chlorine utilized by substitution, and $100 - x$ = grams of chlorine utilized by oxidation. If $x = 0$, $y = 100$; if $x = 50$, $y = 75$; and if $x = 100$, $y = 50$.

Rys (21) reported the amount of hydrochloric acid formed as 54 to 70 per cent of the chlorine added and Rauchberg (22) reported 70 per cent for ordinary bleaching; using 70 per cent as a typical figure, x would be 60 and the oxidation reaction would be 40 per cent.

Rauchberg (22) also showed that the percentage of hydrochloric acid formed increased as the amount of chlorine added was increased. When smaller amounts of chlorine (based on the pulp) were added, the reaction was chiefly one of substitution. This is also borne out by Rys (21), who gave values from 54 to 74 per cent, and by Fotiev (18), who showed that the course of the reaction depends upon the concentration of the chlorine added. For low concentrations of chlorine, about 95 per cent was used in the substitution reaction; the amount decreased to about 50 per cent when higher chlorine concentrations were used, indicating that, in the latter case, the substitution reaction is replaced by one of oxidation.

Voigtman (21) reported somewhat lower results for hydrochloric acid formation. In experiments using 50 per cent of the chlorine demand on Mitscherlich sulfite pulps of 7.1 and 5.4 per cent bleachability, he found 54.5 and 55.4 per cent of the chlorine as hydrochloric acid. He determined the latter by using a potentiometric titration method and called a pH of 4 the end point. As a check, the values for hydrochloric acid at a pH of 7 have been recalculated; the hydrochloric acid concentrations amounted to 65 and 70 per cent of the chlorine used, which agrees very well with other reported values. Voigtman believed that the increased caustic consumption (necessary to produce 70 per cent hydrochloric acid) as reported by other investigators was due to hydrolysis of unstable chlorolignin compounds.

There seems to be a point of chlorine saturation for pulp and other plant substances, as indicated by the Cross and Bevan method for preparing cellulose and as reported by Fotiev (18) and Hauchberg (22). These chlorolignins, as Hauchberg states, are partially soluble in water and in dilute alkali; the removal of the latter by solution in alkali during the bleaching process saves chlorine which would otherwise be consumed in the oxidation of these alkali-soluble products.

C. CHANGES IN LIGNIN ON CHLORINATION

From the various results reported in the literature, there are a few chemical changes that are commonly reported as taking place on the chlorination of lignin or materials containing lignin.

Chlorolignins prepared in aqueous solutions from lignin or isolated from chlorinated wood are not definite or uniform in chlorine composition (13, 16, 24). Jansen and Bain (16), however, claimed to have prepared a definite and uniform methyl chlorolignin by treating spruce sawdust with chlorine in methanol and rechlorinating the isolated product.

Chlorination of lignin or wood in aqueous solution results in loss of methoxyl and hydroxyl groups (14, 16, 24, 25). If, however, the halogenation of lignin is carried out in methyl alcohol as reported by Friedrich and Pelikan (26) and by Jansen and Bain (16) there is apparently no decrease of methoxyl. It is possible, in this case, that methoxyl groups have been split off from a part of the lignin molecule and others have been added at other parts by the action of the hydrochloric acid in the presence of methanol, as in the methanol lignin. This is confirmed by the work of Müller (27), who treated spruce sawdust with chlorine gas for two or more days, washed out most of the hydrochloric acid with water, and refluxed the material with 70 to 90 per cent ethyl alcohol containing 0.1 to 1.0 per cent hydrochloric acid. The alcohol lignin was precipitated into water and analysed. The lignin thus prepared was separated into ether-soluble and ether-insoluble fractions; these are reported to have the compositions $C_{30}H_{25}O_{11}Cl_8(OC_2H_5)$ and $C_{30}H_{31}O_{15}Cl_6(OC_2H_5)$, respectively;

they contain no methoxyl groups but have one ethoxyl group per lignin unit.

Another rather definite conclusion reported in the literature is the fact that treatment of chlorinated lignins with caustic soda splits off chlorine. Sarkar (28) carefully chlorinated powdered Willstätter lignin from jute for four hours and obtained a chlorine content of 25.8 per cent, which decreased to 17.7 per cent when treated with dilute sodium hydroxide. Harris and co-workers (24) reported similar findings in which Klason lignin from spruce and sugar maple, chlorinated in carbon tetrachloride, showed a decrease in chlorine content from 27.5 to 15.8 and 19.8 to 11.9 per cent, respectively, when treated with 5 per cent sodium hydroxide. Powell and Whittaker (29, 30) chlorinated alkali lignin from various woods and proposed a lignin molecule with twelve chlorine atoms ($C_{40}H_{27}O_8Cl_{12}(OH)_6OCH_3CHO$) which, after solution in alkali and reprecipitation, showed a loss of six chlorine atoms. Jansen and Bain (16) reported similar findings. When they tried to methylate their alcohol lignin chloride with caustic soda and dimethyl sulfate, there was a loss of seven of the thirteen chlorine atoms with no change in methoxyl content (after correction for chlorine loss), but an opening up of one hydroxyl group.

A point mentioned by several authors (11, 14, 31) working with chlorinated lignins is the fact that a hydrolytic action of acid is necessary to remove the lignin from the pulp or wood. This, they have concluded, is evidence that a bond exists between the cellulose and lignin.

In spite of the large amount of investigation on the presence of double bonds in lignin, this question is not settled. The double bond, however, is often mentioned as a possible place for chlorine addition. Hibbert and Taylor (32) indicated that part of the addition of hypochlorous acid to glycol lignin is due to an ethylene linkage. Hibbert and Sankey (31) concluded that lignin contains one or more double bonds. Fuchs and Horn (33), on bromination of sprucewood, Willstätter lignin, and acetylated sprucewood, concluded that primary lignin contains a hydrogen atom replaceable by bromine and a double bond capable of addition of two bromine atoms. Pomilio (34) postulated equations for the chlorination of wood which caused him to believe there is some addition taking place. Jansen and Bain (16) very recently ascribed the entrance of two of the thirteen atoms of chlorine to a double bond in their methyl lignin chloride.

On the other hand Sarkar (28) has stated that the estimation of chlorine as hydrochloric acid showed that Willstätter lignin contained no double bonds. Rassow and Zickmann (35) also concluded that there are no double bonds in Willstätter lignin. Freudenberg and co-workers (36) treated lignin (isolated from sprucewood by the Freudenberg method) with a solution of bromine in hydrobromic acid and found that under these conditions substitution but no addition took place.

From the above review the following conclusions concerning the chlorination experiments on lignin materials may be made:

(1) There is difference in the behavior of the methoxyl, hydroxyl, and chlorine groups in lignin since under various treatments they are partially replaced.

(2) The presence or absence of a double bond in lignin has not been proved.

(3) The addition of chlorine and the extent of the substitution in lignin are dependent on acid concentration, temperature, concentration of chlorine, and type of solvent.

(4) Chlorolignins are partially soluble in water but more soluble in dilute alkali.

(5) Hydrochloric acid is formed when lignin is chlorinated, the percentage formed depending upon the percentage of chlorine added. The greater the percentage added, the greater the percentage of hydrochloric acid formed.

III. ANALYTICAL METHODS AND PROCEDURES

The analytical methods and procedures employed in this investigation are given below and will be referred to by name in the future. In nearly every case at least duplicate determinations were made, and the analytical results given are average values.

A. METHODS OF PULP ANALYSES

1. Moisture. The method for testing pulp for moisture consisted in taking composite samples, usually not less than an equivalent of 2.0 grams ovendry, drying them in weighing bottles in an oven at 105° C. overnight, and weighing.

2. Ash. Institute Method 422, using platinum crucibles and a Meker burner, was used.

3. Lignin. Institute Method 428 was used in all cases where the percentage of lignin is given. Gooch crucibles were used and in some cases a diatomaceous silica filter-aid prepared by Johns-Manville, "Celite Analytical Filter-Aid", was used to increase the rate of filtration.

4. Methoxyl. Institute Method 18 was used in which pulp samples of about 0.2 gram were taken.

5. Chlorine Consumption of Pulp. TAPPI Standard Method T 202 m was used.

6. Permanganate Number of Pulp. TAPPI Tentative Standard T 214 m-37 was used.

7. Roe Chlorine Number of Pulps. The method is essentially the Johansson modification of the original Roe chlorination method (37).

8. Chlorine and Sulfur. Inasmuch as the chlorine and sulfur contents of the pulps were rather low, it was necessary, in order to obtain accurate values, to use fairly large samples (2 to 3 grams) for a determination. The Carius combustion method was attempted, but the high pressures caused some of the tubes to explode. It was desired to use one sample to make both the chlorine and sulfur determinations; thus, a new method was necessary.

The method devised for the determination was essentially a combination of the Kingstedt method for sulfur in pulp (38) and the Pregl method for chlorine analysis (39).

The organic matter was decomposed by oxidation with fuming nitric acid, using magnesium oxide as a catalyst. The chlorine was driven off as elementary chlorine or hydrochloric acid and caught in standard silver nitrate solutions, and the sulfur was left behind in the reaction flask as sulfate.

Figure 1 is a diagram of the apparatus used for the determination. The pulp sample (2.5 to 4.0 grams) was placed in the short-necked Kjeldahl flask A fitted with the Claisen distilling head B together with 0.7 gram of magnesium carbonate-magnesium hydroxide mixture ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) and a few boiling chips. A known amount of 0.05 N silver nitrate solution was placed in flask H and the absorbing column I and the water in the

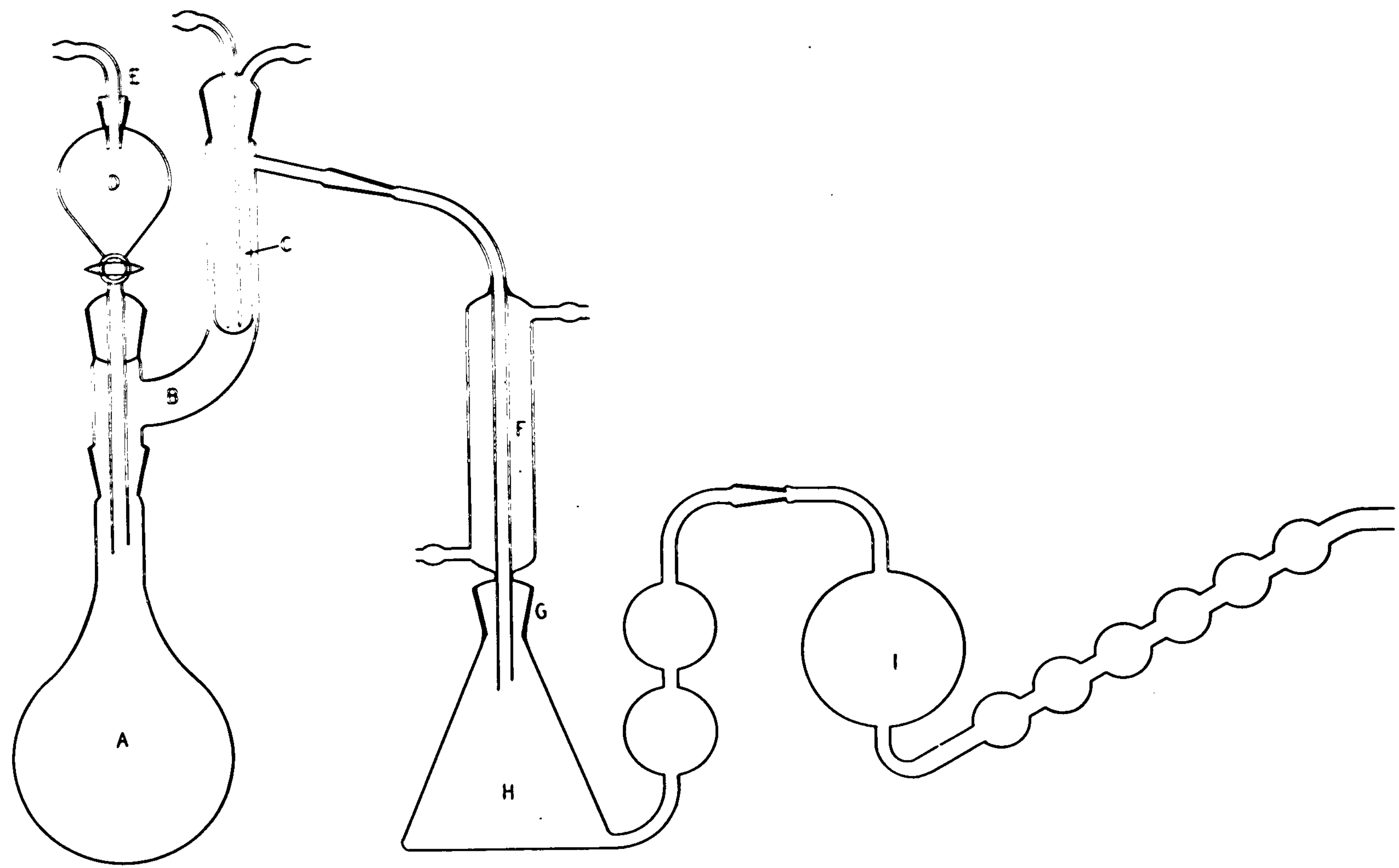


FIGURE 1

APPARATUS FOR SULFUR AND CHLORINE DETERMINATION refluxing condenser C and the condenser F started. The pulp was first moistened with 5 ml. of concentrated nitric acid added through the dropping funnel D and then treated with 20 ml. of fuming nitric acid. The sample was refluxed with a low flame for about one hour; after which the reflux condenser was turned off and the liquid distilled off to a low volume while carbon dioxide gas was passed through inlet E. In order to insure complete removal of the hydrochloric acid, about 10 ml. of water were added to the reaction flask and distilled over. Toward the end of the distillation, the distillate was tested with silver nitrate.

After the reaction was complete, the silver chloride and the excess silver nitrate solution was washed into a volumetric flask (200 ml.) and made up to volume with water. This solution was filtered to remove the silver chloride, and 50 ml. aliquot parts were titrated with 0.05 N potassium thiocyanate solution with ferric nitrate indicator (10 ml. of 10 per cent solution). The material in the reaction flask was washed into a 150 ml. beaker, evaporated to dryness on a steam or hot water bath, treated with 5 ml. of concentrated hydrochloric acid, and again evaporated to dryness to remove the last traces of nitric acid. The residue was dissolved in 10 ml. of 10 per cent hydrochloric acid and about 20 ml. of water, filtered to remove the silica, etc., made up to a volume of about 80 ml., heated on a hot water bath, and precipitated with hot barium chloride solution (7 to 10 ml. of 10 per cent solution). The solution was allowed to digest for at least two hours, set over night, filtered on a Berlin No. 1 porous crucible, and weighed as barium sulfate.

The method was checked against a sample of known sulfur and chlorine content that had been checked by the Carius method and also against some pulps that were run by the Carius method. The following are typical results:

TABLE I

COMPARISON OF METHODS FOR SULFUR AND CHLORINE ANALYSES

Sample	Carius Method S,%	Carius Method Cl,%	New Method S,%	New Method Cl,%
Known	11.45	12.40	11.52	12.32
				12.37
			11.40	12.40
				12.46
T2-75-20 (Pulp)	----	----	0.071	0.106
			0.073	0.104
T2-75 (Pulp)	0.12	0.17	0.09	0.16

B. METHODS OF LIGNIN AND LIQUOR RESIDUE ANALYSES

In all cases the sample was heated in an Abderhalden drier for at least two hours before analyses.

1. Ash. The ash determinations for samples of at least 200 mg. were carried out in platinum crucibles and the ash usually weighed on the semimicro balance. Smaller samples were weighed on the semimicro balance, ashed in micro porcelain crucibles in a muffle furnace, and weighed on the micro balance. Where a furnace was not handy a Meker burner was used.

2. Methoxyl. The methoxyl content was determined essentially by Institute Method 18 except that a semimicro balance and apparatus were used; the sample used was about 20 mg. The quantity of reagents were reduced to about half of the regular amount.

3. Nitrogen. The nitrogen content of benzidine lignins were determined in order to correct for the benzidine content of the lignins. The determinations were carried out according to Institute Method 705 a, "Determination of Nitrogen by the Kjeldahl Method (Semimicro)." Analyses of benzidine and acetanilide showed only 95 to 96 per cent of the theoretical nitrogen. However, the results were considered to be sufficiently accurate for the purpose of this work.

4. Chlorine and Sulfur. The analysis of chlorine and sulfur were carried out on the same sample by combustion in Carius tubes. The previously dried lignin samples were weighed into glass vials and placed in the combustion tubes with 3 to 5 ml. of fuming nitric acid and 100 to 200 mg. of silver nitrate. The sealed tubes were heated for four to six hours at 230 to 250° C.; the contents of the tubes were washed into 150-ml. beakers and evaporated to about 40 ml. When the silver chloride was difficult to wash from the tubes, a little ammonia was added and later neutralized. The silver chloride was filtered on small (5 cm.) tared ashless filter papers, washed, and dried overnight at 105° C.; then it was weighed.

The excess silver nitrate was removed by adding 10 per cent hydrochloric acid, evaporating the solution to about 40 ml., filtering, washing, and discarding the precipitate. A pinch of pure sodium chloride was added to the filtrate, which was evaporated to dryness to remove nitric acid, made up to 40 ml., and again filtered if any precipitate was present.

The sulfate was precipitated by adding 5 to 10 ml. of hot barium chloride-hydrochloric acid solution to the above filtrate. The samples were allowed to digest on a water bath for at least two hours, let stand overnight, filtered on a Berlin No. 1 porous crucible, and washed free of chloride. The crucibles were heated in a porcelain crucible fitted with an asbestos ring to keep the porous crucibles from touching the hot porcelain. The sulfate was weighed as barium sulfate.

In case the chlorine was not determined, the silver nitrate was not added to the combustion tubes and the solution was filtered before adding the barium chloride.

5. Acetyl Groups. Acetyl determinations on the acetylated samples were carried out by Institute Tentative Method 19 (1939), which is essentially the Freudenberg Method (40). As the method is designed for pulps, a few changes were made. For 50-mg. samples 0.01 *N* acid and base were used and for 150-mg. samples, 0.05 *N* acid and base. The quantities of alcohol and *p*-toluenesulfonic acid were decreased to three fifths of the values given. Where the 0.01 *N* reagents were used, most of the base was neutralized and the solution was concentrated to a smaller volume in order to make the end point change more pronounced.

C. METHODS OF LIQUOR ANALYSES

1. Conductometric Titration with Sodium Hydroxide for Acidity. The acid-base titrations were carried out with a conductivity apparatus, because the color of the liquors masked out any indicator color change. The apparatus used was very similar to that described by McElhinney and co-workers (41)

for the titration of soda black liquors. In each case a sample of 25 ml. of the liquor was diluted with freshly boiled distilled water and the cubic centimeters of 0.02 N base was plotted against the milliampere readings. Figure 2 is a typical curve. The first end point was taken as the neutralization point of the free hydrochloric acid.

2. Conductometric Titration of the Ionizable Chlorine with Silver Nitrate. Free chlorides were determined by titration with 0.05 N silver nitrate solution, using the apparatus described under C-1. The curves were rather clear cut as shown in Figure 3.

3. Total Chlorine and Sulfur. The analyses for total chlorine and sulfur in the liquors were made with the apparatus described above for the determination of chlorine and sulfur in pulps (see Figure 1). The method was essentially the same, except that the 25 ml. of liquor was evaporated nearly to dryness without the reflux condenser being in operation before the fuming nitric acid was added.

4. Total Solids. As a check on the hydrochloric acid in chlorination liquors, a determination of the total solids was carried out in the following way: A measured amount of the liquor was neutralized with a known quantity of standard sodium hydroxide (color change in liquor), evaporated to dryness in a platinum dish on a steam bath, and weighed. The proper correction was made for the amount of sodium chloride formed on neutralization.

5. Ash. Fifty ml. of the solution were evaporated to dryness on a

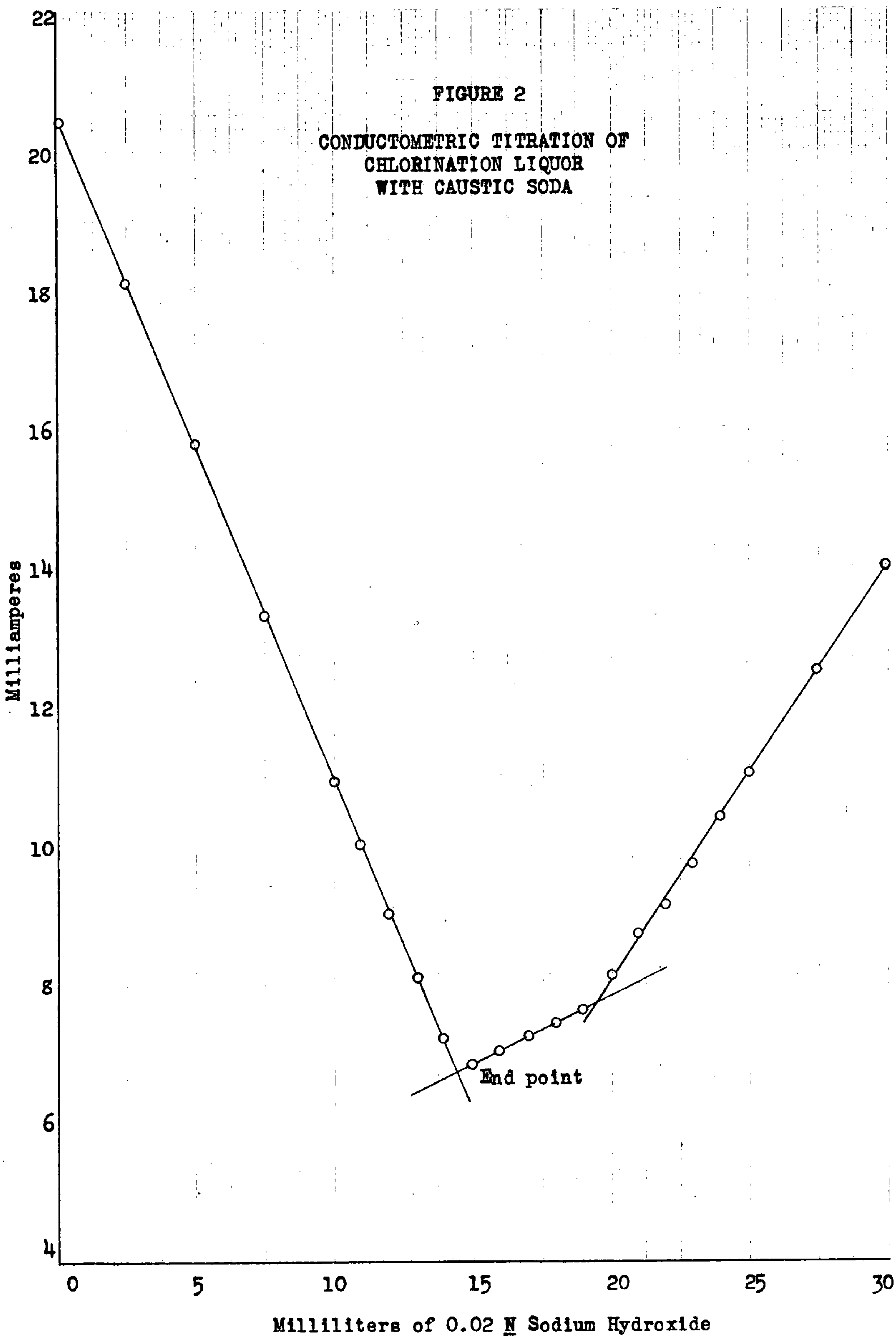


FIGURE 2
CONDUCTOMETRIC TITRATION OF
CHLORINATION LIQUOR
WITH CAUSTIC SODA
Milliamperes
22
20
18
16
14
12
10
8
6
4
End point
0
5
10
15
20
25
30
Milliliters of 0.02 N Sodium Hydroxide

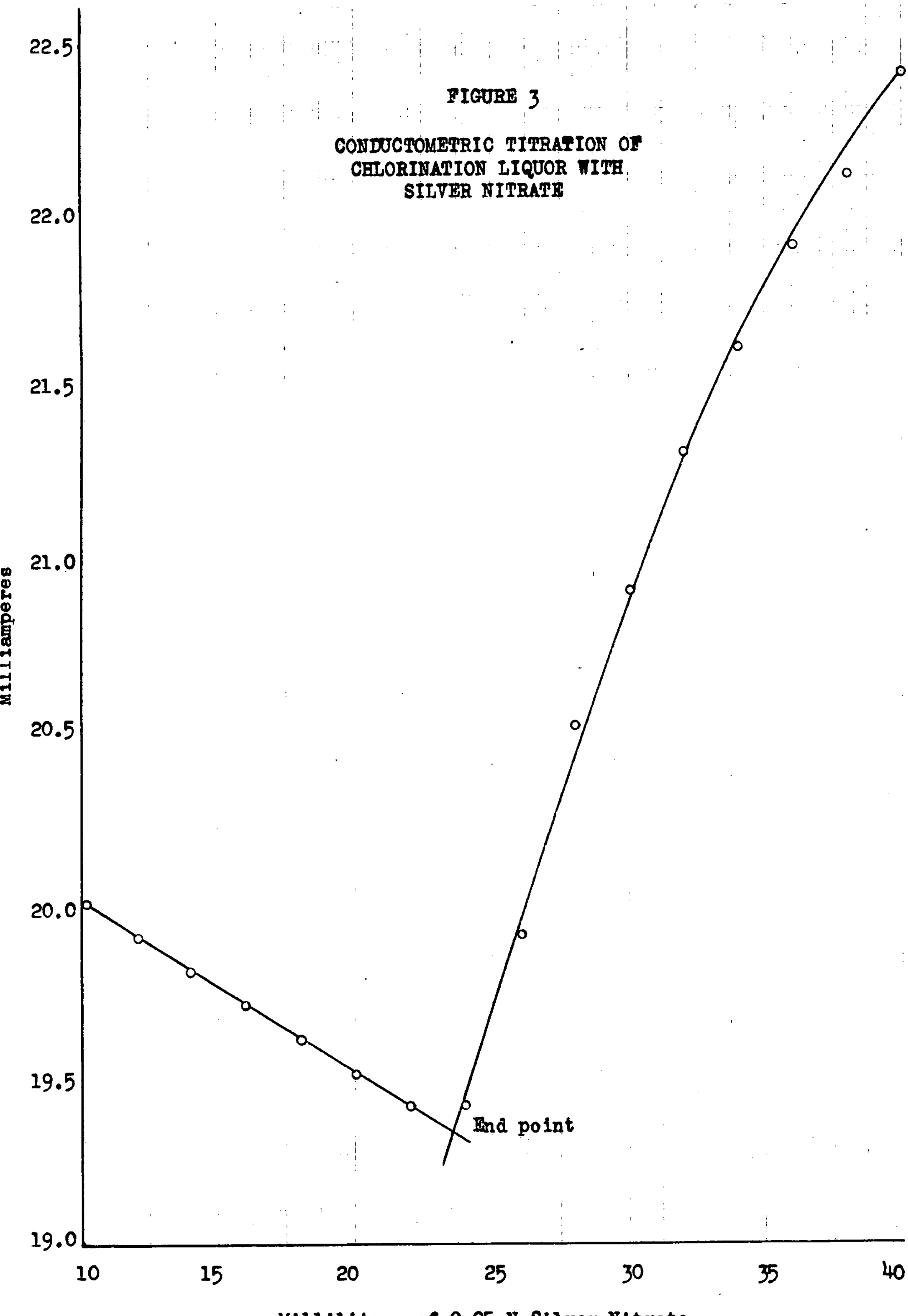


FIGURE 3
CONDUCTOMETRIC TITRATION OF
CHLORINATION LIQUOR WITH
SILVER NITRATE
Milliamperes
22.5
22.0
21.5
21.0
20.5
20.0
19.5
19.0
10
15
20
25
30
35
40
End point
Milliliters of 0.05 N Silver Nitrate

steam bath in a platinum dish and ignited over a Meker burner. In the case of the caustic liquors, the alkali was neutralized with sulfuric acid and ashed, because the sodium hydroxide tended to volatize. The ash was assumed to be sodium sulfate, in order that a correction could be made for the added weight.

6. Nonvolatile Solids. This determination was carried out on chlorination liquors only. The same sample was used as described above for ash. The material, after drying on the steam bath in a platinum dish, was weighed and reported as nonvolatile solids.

7. Benzidine Precipitation of Lignins. The lignin was precipitated from solution with benzidine hydrochloride, which was prepared by the method of Rassow and Kraft (42). In carrying out the precipitation, 10 ml. of the benzidine solution (40 grams per liter) were added to 100 ml. of the liquor. The solution was shaken, allowed to stand and coagulate, centrifuged, filtered through a Hirsch or small Büchner funnel (equipped with two fast filter papers topped with a hardened one), and finally washed free of chlorides (silver nitrate). The material was allowed to dry in a vacuum desiccator, after which it was pulverized.

8. Reducing Sugars. The filtrate from the benzidine precipitate was used for this determination. An attempt was made to use the raw liquor but the organic matter acted as a protective colloid which made it difficult to filter the cuprous oxide. The method chosen was essentially the one outlined in TAPPI Suggested Method O 403 sm-37 for the analysis of sugars in waste sulfite liquor. The excess benzidine was

precipitated by treating with 4 N sulfuric acid. Fifty ml. of the solution were treated with 25 ml. of Fehling solutions A and B. The remainder of the procedure was the same as outlined in the method.

9. Sulfates. One hundred ml. of the liquor were heated to boiling and 25 ml. of 10 per cent barium chloride added. The mixture was allowed to digest for about fifteen minutes; then it was cooled and filtered on a Berlin No. 2 porous crucible. The precipitate was heated in a porcelain crucible with an asbestos ring and weighed as barium sulfate. Duplicate samples were tested in each case. In one, hydrochloric acid was added before precipitation of the sulfate; after ignition each sample was treated with hydrochloric acid. The addition before precipitation seemed to have no effect, but the treatment after ignition in the case of sample T3-35 caused a loss of about 40 per cent of the original weight. This was due to colloidal organic matter precipitated with the barium sulfate; therefore, in each case the ignited residue was given a hydrochloric-acid treatment.

10. Color Transmission of Solutions. Transmission curves were taken on the liquors using the General Electric recording spectrophotometer. The absorption cell used was Eimer and Amend No. 31180, 30 by 20 by 5 mm. inside dimensions, U-shaped, with a liquid thickness of 5 mm. Two matched cells were used with two matched magnesium carbonate blocks, the entire system giving very close to 100 per cent transmission for distilled water over the 400 to 700 millimicron wavelength range. In practice the instrument operated at a reproducibility of ±0.2 per cent transmission. Preliminary tests showed that a pH above 1.4 had an important bearing on the transmission. In each case the pH was adjusted between 1.4 and 1.2 by

adding hydrochloric acid and distilled water before the transmission curves were taken.

LIST OF SAMPLE NUMBERS USED IN TABLES, METHODS AND DISCUSSION

(The symbols apply not only to the pulps but liquors, liquor residues, and lignins from the pulps).

(1) T2 - Sulfite Pulp prepared under conditions given in Table II

(2) T2-35 - Sulfite Pulp T2 chlorinated with 35 per cent of the Roe chlorine number

(3) T2-75 - Same as 2 but with 75 per cent

(4) T2-35-20 - Pulp T2-35 extracted with 2 per cent caustic at 20° C. as given in Table VIII

(5) T2-35-80 - Pulp T2-35 extracted same as 4 except at 80° C.

(6) T2-75-20 - Pulp T2-75 extracted same as 4

(7) T2-75-80 - Pulp T2-75 extracted same as 5

(8) T3 - Sulfite Pulp prepared under conditions given in Table II

(9) T3-35 - Sulfite Pulp T3 chlorinated with 35 per cent of the Roe chlorine number

(10) T3-75 - Same as 9 except with 75 per cent

(11) T3-35-20 - Pulp T3-35 extracted same as 4

(12) T3-35-80 - Pulp T3-35 extracted same as 5

(13) T3-75-20 - Pulp T3-75 extracted same as 4

(14) T3-75-80 - Pulp T3-75 extracted same as 5

(15) T3-Na - Alkali lignin from Pulp T3 prepared as described under B-1 of Part IV (Experimental Methods)

(16) T3-75-Na - Alkali lignin from chlorinated Pulp T3, soluble in acetone, prepared as described under B-2 of Part IV

(17) T3-75-Na-D - Same as Sample T3-75-Na but soluble in dioxane

(18) T3-MeOH-A - Methanol lignin from Pulp T3 purified by precipitation from water into methanol prepared as described under F-1 Part IV

(19) T3-MeOH-B - Same as Sample T3-MeOH-A but methanol soluble and precipitated from methanol into ether

(20) T3-75-MeOH - Methanol lignin from chlorinated Pulp T3 prepared as described under F-2 Part IV

(21) T3-75-A - Methanol lignin from same pulp as Sample T3-75-MeOH but soluble in a water-methanol mixture before addition of HCl. Described under F-2 Part IV

D. PREPARATION OF WILLSTÄTTER LIGNIN FOR ANALYSES

The only Willstätter lignins prepared were from the original sulfite cooks, using Pulps T2 and T3.

Hydrogen chloride gas was prepared by dripping concentrated sulfuric acid into a mixture of sodium chloride and concentrated hydrochloric acid. The gas was passed into concentrated hydrochloric acid cooled in an ice bath until the acid had a specific gravity of 1.224 at 0° C.

The crumpled pulp (25 per cent consistency) was allowed to air dry and then run through a Gösta Hall shredder. Fifty grams of the pulp were treated with 1000 ml. of the supersaturated hydrochloric acid and stirred for two hours at room temperature, diluted with 325 grams of ice and kept at room temperature for eighteen hours.

At the end of this period 325 ml. of water were added and the mixture filtered on a Büchner funnel (7 cm.) on a layer of two fast filter papers covered with an acid-hardened one. The precipitate was washed with 500 ml. of dilute hydrochloric acid (1:1) and 500 ml. of water. The residue was transferred to a beaker, boiled with water, filtered, and finally washed free of chlorides (silver nitrate test).

B. PREPARATION OF KLASON LIGNIN FOR ANALYSES

Klason lignin was prepared from the two sulfite, the four chlorinated, and eight caustic-extracted pulps. The same general procedure was used in each case and is essentially the same as Institute Method 428, except that larger quantities of pulp were used which made certain modifications necessary.

An equivalent of about fifty grams of ovendry pulp was allowed to dry overnight at 105° C. and then treated with 1000 ml. of 72 per cent sulfuric acid previously cooled to 10° C. The mixture was stirred by hand for about ten minutes in order to moisten the pulp. It was then stirred with a motor for three and one-half hours, after which 2750 grams of distilled water and ice were added. The material was centrifuged and finally filtered through a Büchner funnel equipped with two fast filter papers topped with a hardened one. The lignins were then boiled with fresh 3 per cent sulfuric acid for four hours, and again centrifuged, and filtered.

The filtrate in every case was slightly cloudy; therefore, it was boiled with 2 per cent sodium sulfate for two hours, centrifuged, filtered, the precipitate added to the original lignin, and the entire mass washed free of acid (litmus). In the preparations of lignin from the chlorinated pulps of T3, the material could not be washed completely free of acid; washing was continued until a pH of 4 to 5 (red-violet color with Congo red paper) was reached.

F. METHYLATION OF LIGNIN WITH DIAZOMETHANE

Diazomethane methylations were carried out on five different samples-- T3-Na, T3-75-Na, T3-75-MeOH, T3-MeOH-A, and T3-MeOH-B.

One gram of the material was suspended or dissolved in 15 ml. of the solvent used for the last purification as described under E and F of Part IV (Experimental Methods and Results). The diazomethane formed by the action of 10 ml. of sodium glycolate (6 grams of sodium in 100 ml. of glycol) on 5 ml. of nitrosomethylurethan was bubbled through the lignin solution or suspension for a period of one hour, using a stream of purified nitrogen gas.

In all cases the lignin became lighter in color, flocculated, precipitated if in solution, and a considerable evolution of nitrogen was noticed. The supernatant liquid was yellow in color in the case of every lignin but Sample T3-75-MeOH, indicating that some material was soluble in the solvent.

A part of the methylated product was removed and purified for a methoxyl determination. The sample was added to absolute ether with vigorous stirring, washed twice with absolute ether, twice with petroleum ether, and dried in a vacuum desiccator over sulfuric acid.

A second methylation was carried out on each sample, using 2 ml. of nitrosomethylurethan and 4 ml. of sodium glycolate. In no case did the methoxyl content increase more than 0.35 per cent; thus, the methylations were considered complete.

G. ACETYLATION OF LIGNIN

Acetylation experiments were carried out on the five samples listed under F above. Half-gram samples of the products were added to 10 ml. of pyridine and water added until the material dissolved. In each case not more than eight drops of water were added, except for Sample T3-75-Na, in which it was necessary to use 1 ml. of water and 1 ml. of acetone for solution. The dissolved material was added slowly with vigorous stirring to a mixture of 15 ml. of pyridine and acetic anhydride (20 ml. of acetic anhydride were used for Sample T3-75-Na to allow for the excess water). The solutions were allowed to stand overnight.

The acetylated products of the alkali lignins were centrifuged, concentrated under reduced pressure (40 to 50° C.) to about 10 ml., precipitated with absolute ether with vigorous stirring, washed twice with absolute ether, once with petroleum ether, allowed to stand overnight with fresh petroleum ether, washed twice more with petroleum ether, dried under vacuum over sulfuric acid, and finally in an Abderhalden drier for forty-eight hours with postassium bisulfite and phosphorous pentoxide.

Sample T3-MeOH-A gelled and could not be centrifuged or concentrated. It was added to ether and treated the same as the alkali lignins described above.

The two methanol samples had a very small quantity of gelled material. They were concentrated under reduced pressure to about 15 ml., precipitated, washed, and dried, in the same way as the alkali lignins.

IV. EXPERIMENTAL METHODS AND RESULTS

A. PREPARATION AND CHARACTERISTICS OF THE SULFITE PULPS

Canadian black spruce logs cut three months prior to barking and chipping were used for the preparation of the sulfite pulps in this investigation. The physical properties are tabulated in Table II.

TABLE II

WOOD DATA

	Average	Maximum	Minimum
Age in Years	86	110	70
Diameter in Inches	6.0	6.3	5.7
Density lb./ft.^{3}	28.6	30.7	26.6
Percentage of Moisture	39.9		

Six 8-foot logs were peeled, chipped to 5/8 to 3/4-inch lengths in a semicommercial chipper, and screened on a 1/4-inch mesh wire. The slivers and large knots were picked out, the remaining chips mixed thoroughly, and stored in bags in a moistureproof box to minimize moisture loss.

The two pulps were prepared in upright, externally heated, circulating, stainless steel digesters. The digesters were not identical but differed chiefly in the design of the heat exchangers. A weighed quantity of chips of known moisture content were packed into the digesters and a perforated lead plate placed on the chips. Calcium base cooking acid, previously prepared and adjusted to a 6.20 per cent total and 1.20 per cent combined sulfur dioxide, was added until the liquor level was 1 inch below the top flange. The Palmrose iodate method (41) was used for testing the acid concentration.

After charging the digester with chips and acid, the cover was fitted with two pulp gaskets and bolted on, the circulating pump was started, and the steam valve was opened. The cooks were carried out as indicated in Table III.

TABLE III

COOKING CONDITIONS OF SULFITE PULPS

Cook	72	73
Digester	4	2
Total SO_2 (%)	6.22	6.22
Free SO_2 (%)	5.00	5.00
Combined SO_2 (%)	1.22	1.22
Liters of Acid	25	24
Weight of Wood (O. D.) (kg.)	6.30	5.80
Time to 110° C. (hr.)*	2	2
Time from 110 to 135° C. (hr.)*	3	3
Time at 135° C. (hr.)	3	1
Total Time of Cook (hr.)	8	6
Maximum Pressure (lb./in.^{2})	75	75

*The temperature rise was linear

During the last half-hour of the cook, the pressure was relieved to 50 pounds. At the end the pump was stopped, and the cook was blown into a blowpit, consisting of cylindrical 4 by 4-foot vertical tanks made of 2-inch southern pine and equipped with a stainless steel screen plate false bottom, and a 2-inch drain valve. The blowpit cover was equipped with an 8-inch vent stack to allow fumes to escape. After blowing, the remaining stock was washed into the blowpit with hot water and the liquor drained off. The pit was filled with hot water, and the stock was stirred for fifteen minutes at 125 revolutions per minute with a pulp disintegrator. The water was drained off, the blowpit filled again, and the contents stirred for five minutes. The stirring was repeated once more and the pit was finally filled with water and allowed to drain overnight by cracking the valve slightly. A muslin sack was placed over the blowpit valve and a cloth-covered screen was placed under the valve to catch any fines.

The pulp was screened through a semicommercial Appleton Iron Works screen with a 10 cut plate. The side hill screen was 80 mesh, and the wire below this screen was 100 mesh copper wire. In both cases the pulps were shivy; therefore the screenings were placed in a 5-pound Dilts beater and slushed for fifteen minutes with the roll five rounds above the grinding point. The slushed pulp was screened and the slushing repeated twice more for fifteen-minute intervals. The screened pulp was thoroughly mixed, pressed in a cider press to a consistency of about 25 per cent, broken into small pieces, thoroughly mixed, and stored in 5-gallon glass jars. The total weight and composite moisture tests were taken for yield determination. The final screenings, the fines passing through the side hill screen, and the dregs from the blowpit were dried, weighed, and discarded.

The data on the yields, the characteristics of the pulps, and the analyses of the lignins are given in Table IV.

B. CHLORINATION OF PULPS AND ANALYSES OF THE PRODUCTS

Four different chlorination experiments were carried out for the first part of the investigation. Pulps T2 and T3 were chlorinated with 35 and 75 per cent of the chlorine requirement as indicated by the Roe chlorine number.

In carrying out a chlorination, the pulp (25 per cent consistency) was diluted to a 3 per cent consistency and mixed with a Lightnin' mixer for twenty minutes. Enough water was filtered off so that, after the addition of the chlorine water, the consistency was three per cent.

The chlorinations were made with fresh chlorine water (5.5 to 6.5 grams per liter as given by the thiosulfate-potassium iodide titration) which was prepared the day of chlorination. The reactions were carried out in a 22-liter round bottom flask fitted with a mercury seal for the stirrer and held solidly in a tub containing water at $20\pm1^\circ$ C. A variable speed 1/12-h.p. motor was mounted over the flask and equipped with a stainless steel stirrer. An inlet tube that reached below the pulp surface was used for adding chlorine water. An outlet tube passing through a sodium thiosulfate absorption flask was used to collect any chlorine gas passing through.

TABLE IV

SULFITE PULPS

Data on Yields

	T2	T3
Wood Cooked (O. D.) (g.)	6300.0	5800.0
Screened Pulp (O. D.) (g.)	2921.0	3305.0
Fines and Screenings (O. D.) (g.)	196.0	382.0
Total Yield of Pulp (%)	49.5	63.6

Characteristics

	T2	T3
Permanganate Number	20.90	47.80
Roe Chlorine Number	5.90	19.61
TAPPI Chlorine Consumption	2.86	7.81
Lignin (%)	3.85	15.16
Sulfur (%)	0.32	0.86
Methoxyl (%)	0.74	2.78
Ash (%)	0.42	1.06

Analyses of Lignins

(The sulfur and methoxyl are corrected to ash-free basis)

	T2	T3
S in Klason Lignin (%)	4.51	4.79
MeO in Klason Lignin (%)	11.71	13.27
Ash in Klason Lignin (%)	0.95	0.21
S in Willstätter Lignin (%)	4.83	4.85
MeO in Willstätter Lignin (%)	11.97	13.07
Ash in Willstätter Lignin (%)	0.33	0.19

For the experiments with 75 per cent chlorine requirement the flask was also equipped with another inlet and outlet tube which afforded four-minute interval sampling for pH recording on a Cameron recording meter.* This sampling was accomplished by using a three-way stopcock, a reservoir (100 ml. capacity), and air pressure. This method was used so that small liquor samples could be taken out at intervals and returned in order that the consistency remained the same.

The conditions of chlorination are given in Table V.

TABLE V

CONDITIONS OF CHLORINATION

Pulp	T2-35	T2-75	T3-35	T3-75
Pulp Used (O. D.) (g.)	600	600	600	600
Total Liters of Water Used	17.4	17.4	17.4	17.4
Required Chlorine Added (%)	35	75	35	75
Total Grams of Chlorine Added	12.4	26.6	41.2	88.2
Time for Adding Chlorine (min.)	7	16	18	30
Time for Chlorine Exhaustion (min.)	50	80	75	240

The chlorine water was siphoned into the mixture and the mass stirred except during the time of sampling for pH. The mixing action was thorough, the pulp passing down along the shaft and up along the sides of the flask. The chlorinations were taken to exhaustion of the free chlorine (starch iodide paper test).

*Kindly furnished by the Wilkens-Anderson Company

In order to save some of the liquor for analyses, a portion of the mixture was filtered on a large Büchner funnel. All of the pulp was washed thoroughly with water at 20° C. on a cloth-covered box until free from acid (phenolphthalein indicator), pressed in a cider press to approximately 25 per cent consistency, and stored in a wax-paper lined carton.

The data on yields, characteristics of the chlorinated pulps, and analyses of the lignins are given in Table VI. The analyses of the liquors and the benzidine lignins from the liquors are given in Table VII. Figure 4 shows the change of pH on chlorination of Pulps T2 and T3 with 75 per cent of the chlorine demand.

For the isolation of the dissolved material, a part of the chlorination liquor was concentrated under reduced pressure (temperature not over 40° C.) to a small volume and finally dried in a vacuum desiccator over calcium chloride and caustic soda. The solid was pulverized in a mortar and analyzed in the same way as the lignins.

As shown by analyses the lignins in the pulps were sulfonated. It was, therefore, not surprising that a considerable part of the lignin became soluble in water on chlorination. As it was desired to study the dissolved lignin, it was isolated by precipitation with benzidine.

In order to determine the effect of alkali on the removal of chlorine from the lignins found in solution, a portion of the solid fraction was given a sodium hydroxide treatment under the same conditions as those used later for the extraction of the chlorinated pulps. The mixture was allowed to stand for sixty minutes, made up to 250 ml. with water, neutralized with

TABLE VI

CHLORINATED PULPS

Data on Yields

	T2-35	T2-75	T3-35	T3-75
Pulp Chlorinated (O. D.) (g)	600	600	600	600
Pulp Yield (O. D.) (g.)	588.6	586.1	548.5	518.1
Yield (%)	98.1	97.7	91.4	86.3
Chlorine Reacting (grams added--grams in trap*) (g.)	12.4	26.4	41.2	67.9

Characteristics

	T2-35	T2-75	T3-35	T3-75
Permanganate Number	12.1	6.7	29.0	21.0
Roe Chlorine Number	3.08	2.32	10.72	6.08
Lignin (%)	2.05	1.34	8.88	5.44
Sulfur (%)	0.17	0.10	0.53	0.42
Chlorine (%)	0.14	0.17	0.64	0.67
Methoxyl (%)	0.57	0.29	1.66	0.99
Ash (%)	0.33	0.22	0.92	0.64

Analyses of Klason Lignins

(The values for sulfur, chlorine, and methoxyl are corrected to ash-free basis)

	T2-35	T2-75	T3-35	T3-75
Sulfur (%)	3.72	2.49	3.43	2.10
Chlorine (%)	2.46	6.02	4.62	4.97
Methoxyl (%)	9.31	6.46	10.63	6.48
Ash (%)	2.29	0.32	0.99	0.38

*For the 35 per cent bleaches the chlorine in the trap was negligible, for Pulp T2-75, 0.2 grams, and for Pulp T3-75, 0.3 grams.

TABLE VII

CHLORINATION LIQUORS

Analyses of Liquors

(All the values given refer to grams in total volume of liquor)

	T2-35	T2-75	T3-35	T3-75
pH of Liquor	2.01	1.72	1.50	1.32
Solids, after Neutralization (Corrected for Alkali Added) (g.)	29.60	54.50	86.60	156.00
Solids, Without Neutralization (g.)	20.7	37.1	62.3	93.1
Ash (g.)	3.1	5.3	5.7	7.8
Sulfur as Sulfate (g.)	0.23	0.60	0.37	0.73
Total Sulfur (g.)	0.75	1.58	2.10	3.30
Reducing Sugars as Glucose (g.)	1.0	1.9	1.8	5.9
Total Chlorine (g.)	11.2	24.2	35.7	77.1
Ionizable Chlorine ($AgNO_3$ Tit.)(g.)	9.6	20.4	30.1	66.1
Free HCl (NaOH Cond. Tit.) (g.)	7.2	17.6	24.9	59.7
Chlorine as HCl (Same as above but calculated to Cl) (g.)	7.0	17.1	24.2	58.0
Lignin as Determined by Benzidine precipitation (g.)	9.5	15.0	34.4	40.0

Analyses on Benzidine Lignins

(The values for sulfur, chlorine, and methoxyl are corrected to ash-and benzidine-free basis)

	T2-35	T2-75	T3-35	T3-75
Sulfur (%)	3.88	3.42	3.49	2.65
Chlorine (%)	14.27	17.49	13.79	19.83
Methoxyl (%)	4.10	2.81	4.90	2.54
Nitrogen (%)	1.7	1.7	1.4	1.4
Ash (%)	0.49	0.42	0.34	0.29

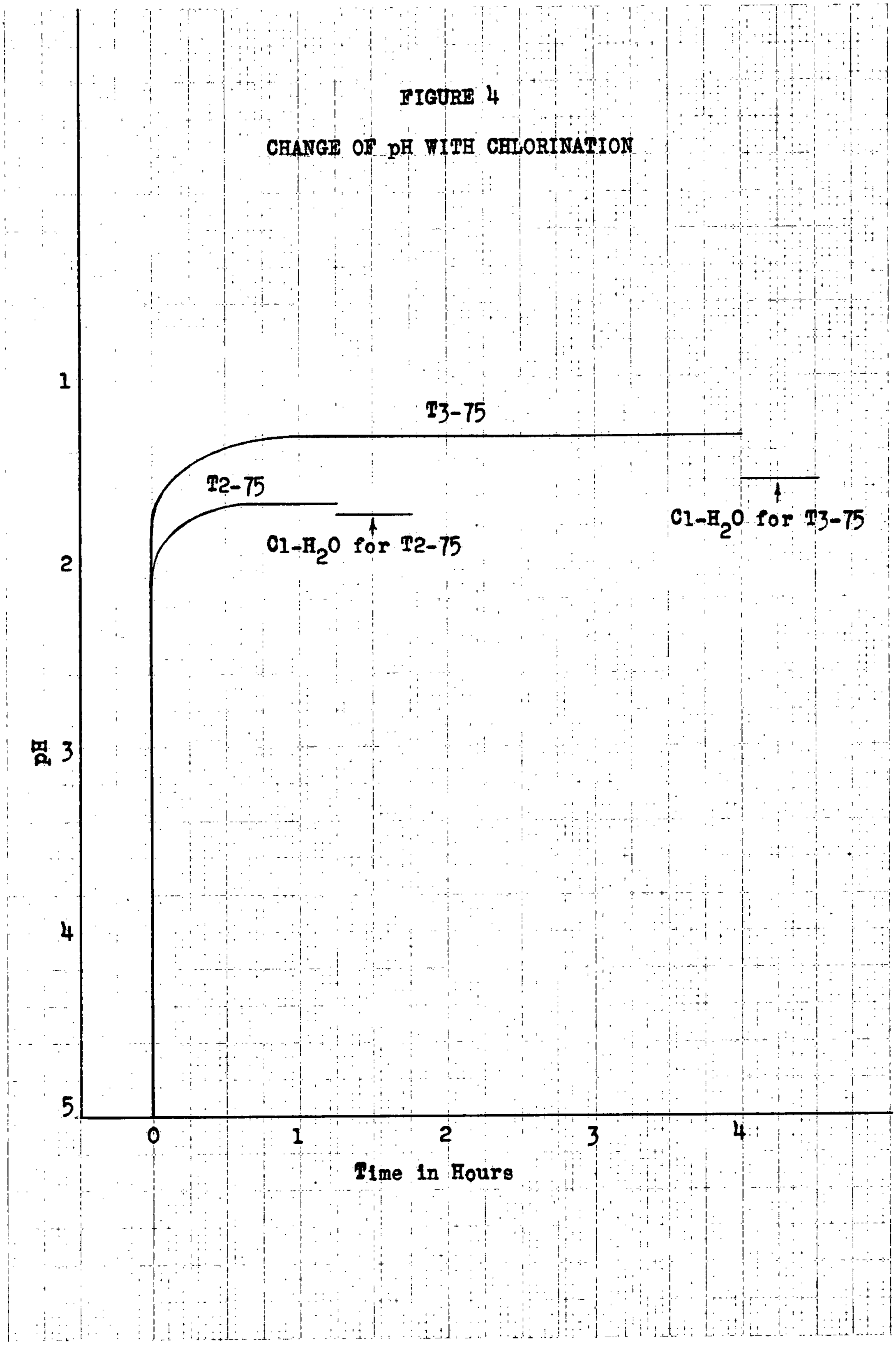


FIGURE 4
CHANGE OF pH WITH CHLORINATION
T3-75
T2-75
Cl-H2O for T2-75
Cl-H2O for T3-75
pH
1
2
3
4
5
0
1
2
3
4
Time in Hours

hydrochloric acid, treated with benzidine, and the lignin isolated as described in C-7.

The analytical results on the residues and the benzidine lignins from the caustic-treated residues are given in Table VIII.

TABLE VIII

RESIDUES FROM CHLORINATION LIQUORS

Analyses of Residues

	T2-35	T2-75	T3-35	T3-75
Sulfur (%)	4.52	4.98	3.66	3.90
Chlorine (%)	20.15	19.53	17.66	21.12
Methoxyl (%)	2.40	1.53	3.72	1.54
Ash (%)	11.61	11.05	8.19	7.96
Yield of Benzidine Lignin (%)	38.0	32.7	39.4	37.9

Analyses of Benzidine Lignins from Caustic-Treated Residues

(Values for sulfur, chlorine and methoxyl are corrected to ash-and benzidine-free basis)

	T2-35	T2-75	T3-35	T3-75
Sulfur (%)	3.87	2.91	3.51	2.50
Chlorine (%)	13.08	14.69	13.51	17.24
Methoxyl (%)	4.22	2.63	5.11	2.32
Nitrogen (%)	1.7	1.3	1.6	1.3
Ash (%)	0.37	0.98	0.26	0.52

C. CAUSTIC EXTRACTION OF CHLORINATED PULPS AND ANALYSES OF THE PRODUCTS

Caustic extractions were made on each of the chlorinated pulps, described under B above, at 20° C. and 80° C. The conditions chosen for extraction are given in Table IX. The differences in consistencies and concentrations were due to changes of moisture content in the pulps.

The extractions were made in 1-gallon bottles, which were kept in the bath at the desired temperature for forty-five minutes. The contents were stirred by hand intermittently with a large glass rod. At the end of the reaction period the pulps were filtered on a large Büchner funnel and pressed, using a muslin cloth previously washed with 2 per cent caustic soda. The liquors were collected for analysis.

The pulps were washed thoroughly on a cloth-covered box with water at the same temperature as that used for extraction, pressed, crumpled, and stored in Mason fruit jars.

In the 80° C. extractions, the pulps (25 per cent consistency) were heated in a closed bottle in a water bath at 80° C. and then treated with the desired amount of hot caustic solution. The actual temperature of the stock was 75 to 77° C.

The data on the yields, the characteristics of the extracted pulps, and the analyses of the lignins from the extracted pulps are given in Table X. The results on the liquors and of the benzidine lignins from these liquors appear in Table XI.

TABLE IX

CONDITIONS OF CAUSTIC EXTRACTION

	T2-35-20	T2-35-80	T2-75-20	T2-75-80	T3-35-20	T3-35-80	T3-75-20	T3-75-80
Temp. of Extraction (° C.)	20	80	20	80	20	80	20	80
Weight Pulp Used (O. D.) (kg.)	0.190	0.185	0.202	0.202	0.189	0.195	0.200	0.200
Total Vol. Water (l.)	2.075	2.065	1.950	2.050	1.810	1.820	1.800	1.800
NaOH Added (g.)	4.5	4.5	4.5	4.5	4.0	4.0	4.0	4.0
Consistency (%)	8.4	8.2	9.4	9.0	9.5	9.8	10.0	10.0
NaOH (%) (O. D. Fiber Basis)	2.37	2.43	2.23	2.23	2.11	2.05	2.00	2.00

TABLE X

CAUSTIC EXTRACTED PULPS

Data on Yields

	T2-35-20	T2-35-80	T2-75-20	T2-75-80	T3-35-20	T3-35-80	T3-75-20	T3-75-80
Pulp Extracted (O. D.) (g.)	190	185	202	202	189	195	200	200
Pulp Yield (O. D.) (g.)	187	180	201	202	185	187	194	194
Yield (%)	98.4	97.3	99.5	100.0	97.9	95.6	97.0	97.0
Characteristics								
Permanganate Number	10.4	10.2	6.3	5.5	26.3	25.7	18.5	16.1
Roe Chlorine Number	2.62	2.25	1.40	1.22	9.75	9.18	5.23	5.02
Lignin (%)	1.95	1.75	0.75	0.64	6.66	5.95	4.62	4.05
Sulfur (%)	0.14	0.12	0.07	0.06	0.44	0.39	0.25	0.23
Chlorine (%)	0.12	0.08	0.11	0.09	0.29	0.24	0.19	0.19
Methoxyl (%)	0.49	0.46	0.29	0.30	1.54	1.46	1.02	0.94
Ash (%)	0.56	0.76	0.34	0.46	1.13	1.00	0.84	0.79
Analyses of Klason Lignins (The values for sulfur, chlorine, and methoxyl are corrected to ash-free basis)								
Sulfur (%)	3.76	4.00	2.94	2.78	3.14	3.29	3.04	3.10
Chlorine (%)	2.97	2.64	3.35	2.82	1.56	1.33	4.76	4.33
Methoxyl (%)	10.91	10.86	8.12	7.86	12.78	12.59	11.61	11.60
Ash (%)	1.49	3.47	4.14	2.47	0.31	0.36	0.43	0.46

TABLE XI

LIQUORS FROM CAUSTIC EXTRACTION

Analyses of Liquors
(All values given refer to grams in total volume of liquor)

	T2-35-20	T2-35-80	T2-75-20	T2-75-80	T3-35-20	T3-35-80	T3-75-20	T3-75-80
Solids (g.)	6.3	7.8	6.3	9.8	7.8	13.0	10.0	13.2
Ash (g.)	3.7	3.9	3.9	4.8	2.4	3.5	3.3	4.0
Chlorine (g.)	0.22	0.28	0.24	0.30	0.83	1.02	1.36	1.51
Sulfur (g.)	0.06	0.09	0.07	0.09	0.22	0.33	0.16	0.25
Sugars as Glucose (g.)	0.13	0.16	0.11	0.16	0.14	0.21	0.25	0.30
Yield of Benzidine Lignin (g.)	0.48	1.48	0.44	1.13	3.03	7.55	4.13	6.14

Analyses of Benzidine Lignins
(The values for sulfur, chlorine, and methoxyl are corrected to ash- and benzidine-free basis)

Sulfur (%)	——	4.11	——	——	3.46	3.77	2.81	2.70
Chlorine (%)	——	7.61	——	——	8.54	8.41	12.29	11.01
Methoxyl (%)	9.38	8.76	5.90	6.50	7.34	7.36	3.73	4.32
Nitrogen (%)	2.2	2.0	2.5	2.6	1.8	1.7	2.0	2.0
Ash (%)	——	0.37	——	——	0.49	0.20	0.60	0.54

D. DETERMINATION OF CARBON DIOXIDE EVOLUTION DURING CHLORINATION

The apparatus used for the detection of carbon dioxide evolution on chlorination of the sulfite pulps is shown in Figure 5.

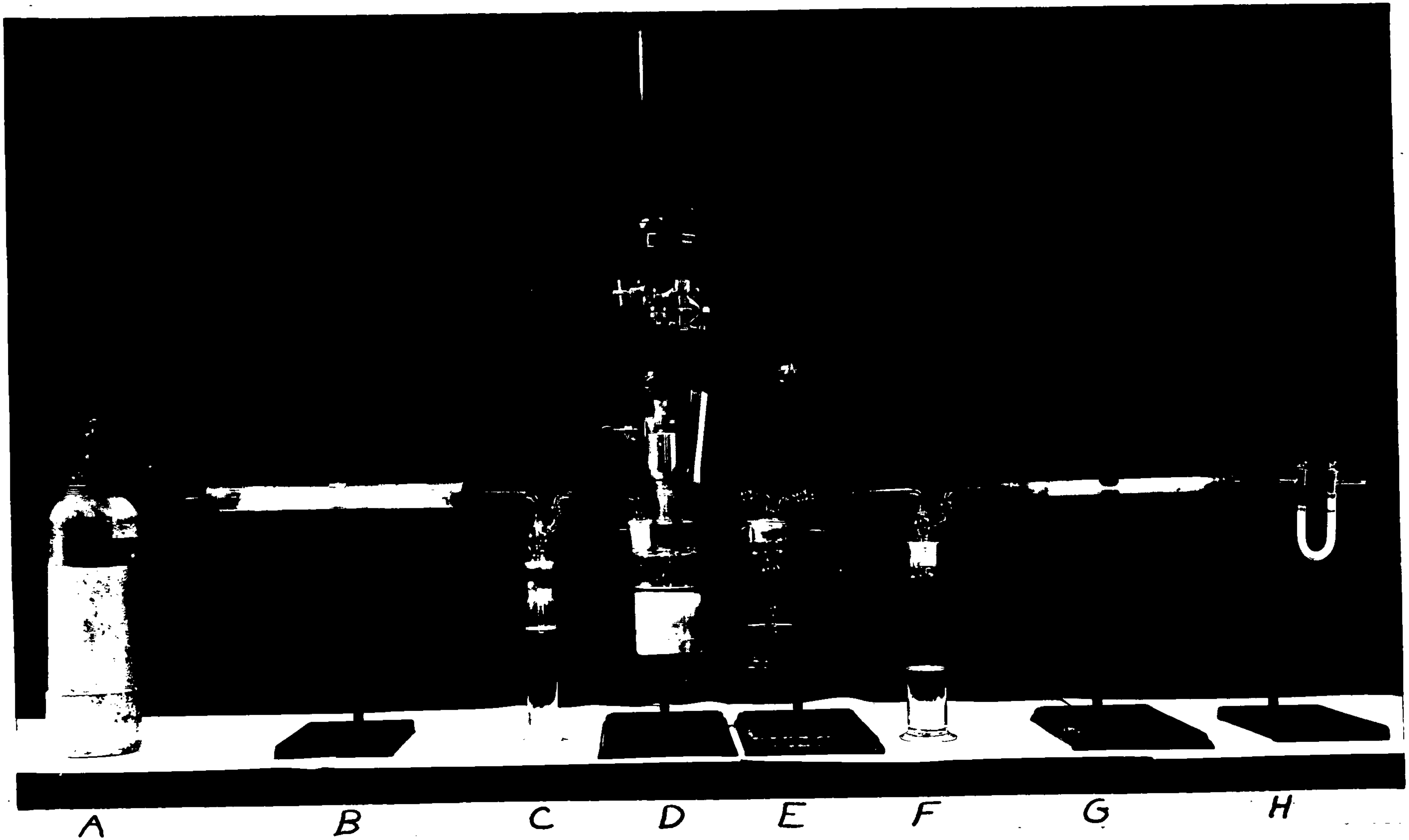
Nitrogen gas was washed free of carbon dioxide by passing through pellet caustic soda and finally through a 50 per cent solution of caustic. The nitrogen passed into the reaction flask and the carbon dioxide evolved were swept through the apparatus to the Ascarite tube where it was absorbed. Any chlorine that came off was caught in the potassium iodide-red phosphorus trap. The gases were dried by passing through a wash bottle of concentrated sulfuric acid and finally through powdered phosphorus pentoxide. The carbon dioxide was collected in an Ascarite tube equipped with ground glass stoppers and weighed.

In order to check the accuracy of the method, carbon dioxide determinations were carried out in duplicate runs using pure sodium carbonate (99.92 per cent pure); the yields in each case were 100.8 per cent, indicating that the method was suitable for the purpose at hand.

In carrying out a determination, an equivalent of 5 grams of pulp (25 per cent consistency) was added to 200 ml. of water, thoroughly disintegrated with a stirrer, heated to boiling to drive off any carbon dioxide present, and then placed in the reaction flask. The final charge after adding the chlorine water was 450 grams (1.11 per cent consistency). A water bath at 50° C. was placed around the reaction flask and the mixture stirred for ten minutes with nitrogen gas passing through the system (about one hundred bubbles per minute). The Ascarite tube was then attached and the calculated amount of chlorine water added.

FIGURE 5

APPARATUS FOR DETECTION OF CARBON DIOXIDE EVOLUTION ON CHLORINATION



A = Nitrogen Cylinder
B = Pellet Caustic
C = 50 Per Cent Solution of Caustic
D = Reaction Flask with Seal
E = KI and Red Phosphorus
F = Concentrated Sulfuric Acid
G = Phosphorus Pentoxide
H = Ascarite Tube

The run was continued for one hour, after which the nitrogen gas and stirrer were turned off and the Ascarite tube detached. The tube was allowed to set for twenty minutes before weighing. Two runs were made on Pulp T3, using 65 per cent of the Roe chlorine number with nitrogen in one case and air in the other. The weights indicated that air was as good as nitrogen; therefore, air was used in subsequent runs.

The amount of carbon dioxide evolved on chlorination of the pulps seemed negligible (1 to 2 mg. for 5 grams of pulp); hence tests were then carried out on the isolated lignin. One run was made using 1.0 gram of purified dioxane lignin with 1.0 gram of chlorine, the yield of carbon dioxide being 3.81 per cent. Two other runs were made using purified calcium lignisulfonate and an equal amount of chlorine. In one case 4.25 grams of purified cotton linters were mixed with the lignin to see if the fibers retained carbon dioxide. The yield without the linters was 1.97 per cent and the one with the linters 1.81 per cent.

To see if more carbon dioxide was evolved when higher percentages of the chlorine requirement were used, a series of runs were made with varying percentages of the chlorine demand. Table XII gives the average milligrams of carbon dioxide obtained from 5 grams of pulp for at least two runs with each percentage of the Roe chlorine number used.

TABLE XII

CARBON DIOXIDE EVOLUTION ON CHLORINATION

Chlorine Demand Used (%)	40	60	80	100	120	140
CO_2 Evolved From T2 (mg.)	0.9	1.4	2.1	1.9	1.7	1.9
CO_2 Evolved From T3 (mg.)	1.3	1.1	1.5	1.8	1.8	2.0

B. PREPARATION AND PURIFICATION OF ALKALI LIGNIN

1. Alkali Lignin from Pulp T3. The alkali lignin from Pulp T3 (Sample T3-Na) and from its chlorinated pulp (Sample T3-T5-Na) were prepared under identical conditions (preparation described under B-2). This was achieved by using an autoclave in which four iron beakers could be placed. In this way the two cooks were carried out at the same time.

The cook was carried out using an equivalent of 100 grams of oven-dry pulp, 20 grams of sodium hydroxide, and 480 ml. of water. The pulp and liquor were placed in the iron containers, the autoclave was filled with caustic liquor of the same strength as used for cooking to a point just above the liquor level in the containers, sealed, and placed in a wax bath which was heated to 180° C. The temperature of the cook was taken by means of a thermometer inserted in a well in the autoclave. The temperature reached 160° C. in one hour, when the pressure was relieved until steam began to exhaust. After one hour of heating at 160° C. the autoclave was taken out of the bath, the pressure relieved in ten minutes, and the pulp removed.

The pulp was filtered on a Büchner funnel and the liquor collected. The pulp was then washed with a liter of water, immersed in water, and allowed to stand over the weekend. This wash water was filtered off, and the pulp extracted with fresh water in a Soxhlet extractor until the liquid was clear and showed no alkalinity. The pulp was pressed to a 25 per cent consistency and stored in a glass jar. The yield of pulp was 70.6 grams with a lignin content of 6.77 per cent.

The filtrate and washings from the cook were concentrated under reduced pressure (50° C.) to a final volume of about 400 ml. Carbon dioxide (made from hydrochloric acid and marble chips) was passed through a sodium bicarbonate wash bottle and bubbled into the solution during the vacuum distillation to prevent oxidation of the organic matter.

An excess of concentrated hydrochloric acid was added to the concentrated liquor whereby a part of the lignin was precipitated. The mixture was then placed in a cellophane bag and dialyzed. Distilled water was passed on the outside of the bag at the rate of about 2 liters per hour while the mixture was stirred with a motor. At night the material was allowed to stand without stirring or water change. This dialysis was carried out for four days at the end of which time the water on the outside of the bag showed no test for chloride or sulfate after standing overnight.

With the removal of the electrolytes, the lignin solution became colloidal. To isolate it, the solution was concentrated under reduced pressure and the water replaced by repeated additions of dioxane. The dioxane-insoluble portion (0.50 grams) was centrifuged off and the lignin precipitated by dropping the dioxane solution into absolute ether with vigorous stirring. The lignin separated out in yellow granular particles. This was washed twice with ether and twice with petroleum ether and dried in a vacuum desiccator over sulfuric acid. The yield of lignin was 9.27 grams.

In order to purify the lignin further, 4.27 grams were redissolved in dioxane containing a little water, precipitated again with ether, and washed as described above. The yield was 3.98 grams.

One gram of the lignin was methylated twice with diazomethane in a suspension of methyl alcohol as described under E of Part III. The methoxyl content increased from 12.91 to 17.68 per cent with one methylation and to 17.75 per cent after the second methylation.

A sample (0.66 gram) of the lignin was dissolved in 10 ml. of pyridine and four drops of water and acetylated as described under F of Part III. The yield of acetylated lignin was 0.70 gram.

The results of the analyses on the original, acetylated, and methylated lignins are given in Table XIII.

2. Alkali Lignin from Chlorinated Pulp T3. An equivalent of 300 grams of ovendry sulfite Pulp T3 (25 per cent consistency) was disintegrated at slightly less than three per cent consistency in a 5-gallon crock. Enough chlorine water (5.79 grams per liter) was added to carry out the chlorination with 75 per cent of the Roe chlorine requirement at 3 per cent consistency (44.12 grams of chlorine).

The operation was carried out in an open crock at room temperature (27° C.) for 210 minutes to chlorine exhaustion (starch iodide test paper).

The pulp was washed thoroughly with water on a cloth-covered box until free from acid, pressed in a cider press to approximately 25 per cent consistency, and stored in a 1-gallon jar. The yield of pulp was 257 grams or 85.8 per cent.

One hundred grams of the chlorinated pulp were cooked at the same time

TABLE XIII

ANALYSES OF ALKALI AND METHANOL LIGNINS

Lignin Sample	S %	Cl %	MeO %	AcO %	Ash %
T3-Na	2.37	——	12.91	——	3.16
Methylated	2.18	——	17.75	——	2.23
Acetylated	2.12	——	10.31	19.5	2.04
T3-75-Na	2.36	3.40	7.74	——	4.37
Methylated	2.47	3.11	14.57	——	4.32
Acetylated	2.63	3.95	6.18	17.0	3.82
T3-75-Na-D	1.61	3.71	7.95	——	4.88
T3-MeOH-A	4.05	——	14.47	——	5.27
Methylated	3.88	——	19.72	——	5.02
Acetylated	3.74	——	11.63	15.8	5.65
T3-MeOH-B	3.60	——	12.02	——	7.12
Methylated	3.49	——	14.89	——	7.19
Acetylated	3.47	——	9.95	18.2	7.03
T3-75-MeOH	2.51	13.86	8.81	——	7.43
Methylated	2.19	13.62	10.27	——	7.27
Acetylated	2.51	13.40	6.58	19.6	5.12
T3-75-A	2.00	22.78	3.24	——	12.12

and under identical conditions as Pulp T3 which was described under B-1. The yield of pulp was 79.1 grams with a lignin content of 2.11 per cent.

The method of purification of the lignin was the same as for Pulp T3 with the exception that all the material after concentration under reduced pressure was not soluble in dioxane. The insoluble part was centrifuged off and the lignin precipitated by dropping the dioxane solution into ether and washing as described under Pulp T3 (designated as T3-75-Na-D). The yield was 0.82 gram of a light-brown lignin. The analyses are given in Table XIII.

The dioxane-insoluble portion was dissolved in acetone containing a few drops of water. The acetone-water-insoluble residue of 0.21 gram was removed by centrifuging, and the filtered solution was poured into ether. The precipitate was washed with ether, petroleum ether, and dried as described above. The yield of a dark-brown lignin was 3.12 grams.

In order to purify the acetone-water-soluble lignin further, 2.62 grams were dissolved in acetone and water, centrifuged, filtered, precipitated with dry ether, and washed as previously described. The yield was 2.49 grams.

One gram of the material was methylated in a suspension of acetone (purified over potassium permanganate) as described under B of Part III. On the first methylation, the methoxyl content increased from 7.74 to 14.50 per cent, and on the second to 14.57.

A sample (0.46 gram) of the original lignin was dissolved in 10 ml. of pyridine, 1 ml. water, and 1 ml. of purified acetone and acetylated as described under F of Part III. The yield of acetylated lignin was 0.54 gram.

The results of the analyses on the original, methylated, and acetylated lignins are given in Table XIII.

F. PREPARATION AND PURIFICATION OF METHANOL LIGNIN

1. Methanol Lignin from Pulp T3. For the preparation of methanol lignin it is necessary to remove all water from the pulp if possible without drying it. This was achieved by the following procedure. An equivalent of 100 grams of ovendry pulp (25 per cent consistency) was triturated twice with anhydrous methanol which was then filtered off. The pulp was placed in a Soxhlet extractor and extracted twice with absolute methanol for twelve-hour intervals. Fresh methanol was then used and lime added to the flask to retain the last traces of water. This extraction was continued for another eight hours.

The pulp thus prepared was refluxed for twelve hours in a 2-liter ground glass flask on a water bath with 800 ml. of anhydrous methanol containing 2 per cent hydrogen chloride. The alcohol solution was filtered off, the pulp transferred to a Soxhlet extractor and extracted with absolute methanol for eight hours. The yield of pulp after extraction was 93.5 grams with a lignin content of 9.52 per cent. The lignin content before extraction was 15.16 per cent.

The methanol extract containing the methanol lignin was concentrated under reduced pressure and any water present was removed by distillation with three 25-ml. portions of dioxane. The residual product was dissolved in 40 ml. of a mixture of methanol and dioxane, the lignin isolated by precipitation with dry ether, and washings made as described under E-1. The yield was 6.0 grams of a cream-colored lignin.

The dried material could not be redissolved in methanol or dioxane but was soluble in water. A water solution was prepared and the lignin precipitated with absolute methanol (designated as T3-MeOH-A). The latter was washed twice with ether, twice with petroleum ether, and dried in a vacuum as previously described. The yield was 2.05 grams of a brown lignin having a purple cast.

A sample (1 gram) of the lignin was suspended in absolute methyl alcohol and methylated as described under E of Part III. On the first methylation the methoxyl content increased from 14.47 to 19.79 per cent and did not change after a second methylation.

A sample of the original unmethylated lignin (0.46 gram) was dissolved in 10 ml. of pyridine containing two drops of water and acetylated as described under F of Part III. The yield of acetylated lignin was 0.37 gram.

The results of the analyses of the original, methylated, and acetylated lignins are given in Table XIII.

The aqueous methanol mother liquor from the precipitation of Sample

T3-MeOH-A was concentrated under reduced pressure, dissolved in methanol-dioxane, and reprecipiated with ether as previously described (designated as T3-MeOH-B). The yield was 2.41 grams of a cream-colored product.

A 1-gram sample was methylated in absolute methyl alcohol. The methoxyl content increased from 12.02 to 14.74 per cent and then to 14.89 per cent after remethylation.

The acetylation was carried out by dissolving 0.47 gram of the original lignin in 10 ml. of pyridine and eight drops of water. The yield of the acetylated product was 0.44 gram.

The results of the analyses on the original, methylated, and acetylated lignins are given in Table XIII.

2. Methanol Lignin from Chlorinated Pulp T3. An equivalent of 72.6 grams of ovendry chlorinated Pulp T3 (25 per cent consistency), prepared as described under E-2, was given the same methanol treatments as described under F-1. The yield of pulp was 68.0 grams with a lignin content of 3.62 per cent. The yield of a light-yellow lignin was 3.50 grams.

The dried lignin was insoluble in dioxane, methanol, and water, or any mixture of the three. Finally 2.74 grams of the material was dissolved in acetone containing a few drops of water, precipitated by pouring into ether, and washed as previously described. The yield was 2.11 grams.

A 1-gram sample was methylated in a suspension of purified acetone. The methoxyl content increased from 8.81 to 9.89 and then to 10.27 per cent on remethylation.

The acetylation was carried out by dissolving 0.46 gram of the original lignin in 10 ml. of pyridine and four drops of water. The yield of the acetylated product was 0.38 gram.

The results of the analyses on the original, methylated, and acetylated samples are given in Table XIII.

The water-methanol solution obtained from the dehydration of the pulp was a yellow color; it was concentrated under reduced pressure, the water removed by repeated distillation with dioxane, and the lignin precipitated by dropping it into ether (designated as T3-75-A). The product thus obtained from 65.5 grams of chlorinated pulp weighed 1.17 grams and was cream colored. The analyses on this product are given in Table XIII.

V. DISCUSSION OF EXPERIMENTAL RESULTS

In working with commercial sulfite pulps the lignin content is so low that large quantities of material are needed for isolation of lignin products. For this reason the sulfite pulps were purposely made raw with considerable differences in lignin content so that any large changes owing to the degree of cooking could be determined. The degrees of chlorination and temperatures of caustic extraction were also made at wide intervals to check any marked differences due to these variables.

A. DISTRIBUTION OF MATERIALS ON CHLORINATION AND EXTRACTION OF PULPS

1. Chlorination. Since pulps are of a heterogeneous nature, the question is often asked regarding the distribution of their components in the chlorination process. An attempt was made to determine this distribution from the data of Tables V and VI; the results are summarized in Table XIV.

It cannot be said that the material balances are perfect, but, because of the nature of the operations carried out and the difficulty of obtaining a correct moisture content of roughly broken-up pulps, the balances are quite satisfactory.

The data of Table XIV show that on chlorination of a sulfite pulp a part of the lignin is rendered soluble and, from a comparison of the loss of pulp (Item 8) with the decrease of lignin (Item 9) in the chlorinated pulp, it can be seen that these losses are of the same order as when a

TABLE XIV

MATERIAL BALANCE ON CHLORINATION

	T2-35	T2-75	T3-35	T3-75
(1) Pulp Chlorinated (O.D.) (g.)	600	600	600	600
(2) Cl Consumed (g.)	12.4	26.4	41.2	87.9
(3) Total Nonaqueous Material Added (1+2) (g.)	612.4	626.4	641.2	687.9
(4) Pulp Yield (O.D.) (g.)	588.6	586.1	548.5	518.1
(5) Solids in Liquor (g.)	29.6	54.5	86.6	156.0
(6) Total Solids Recovered (g.)	618.2	640.6	635.1	674.1
(7) Material Yield (%)	101.0	102.2	99.2	98.0
(8) Loss of Pulp (g.)	11.4	13.9	51.9	81.9
(9) Loss of Lignin from Pulp (g.) (600 x % Lignin) - (Pulp Yield x % Lignin)	11.0	15.2	42.4	62.7

pulp with a normal lignin content (Pulp T2) is used. In other words, with normal pulps, lignin only is removed on chlorination regardless of the amount of chlorine used. With a pulp of high lignin content (Pulp T3) the loss in weight of pulp is from 18 to 23 per cent higher than the decrease in the lignin content. This means that on chlorination of a pulp with a high lignin content substances other than lignin present in the sulfite pulp are rendered soluble and the amount of these dissolved products seem to depend upon the amount of chlorine used—that is, the greater the percentage of chlorine used, the greater the percentage of nonlignin products dissolved.

Another interesting point is that the decrease in lignin content on chlorination of the two pulps is in both cases (35 and 75 per cent) of the same order. This means that on chlorination of a pulp with 35 per cent of the required chlorine, the decrease in lignin is about 44 per cent, and with 75 per cent of the required chlorine, about 65 per cent, no matter whether a pulp with a low lignin content, as in Pulp T2, or a pulp with a high lignin, as in Pulp T3, is used. This indicates that in both cases the chlorine seems to be entirely used up in a reaction with the lignin. The nature of the material dissolved in addition to the lignin has not been investigated, but there is little doubt that, on account of the locally high concentration of hydrochloric acid at the fiber surface and the heat formation, easily hydrolyzable carbohydrates are rendered soluble; this follows from the copper number of the filtrates.

Item 5 of Table XIV gives the content of solids in the filtrate from the chlorinated pulps. This filtrate contains not only the material dissolved from the pulp after chlorination, but also free hydrochloric acid formed during the chlorination. In order to recover the total solids including the hydrochloric acid, the waste liquor was neutralized with a known amount of sodium hydroxide; this quantity and the amount of water formed on neutralization are taken into consideration in the calculations. A balance of these dissolved products in the filtrate from the chlorinations is given in Table XV.

Items 3 and 4 of Table XV should be a check, assuming that the only

TABLE XV

BALANCE OF SOLID PRODUCTS IN CHLORINATION LIQUORS

	T2-35	T2-75	T3-35	T3-75
(1) Solids in Liquor (Item 5, Table XIV) (g.)	29.6	54.5	86.6	156.0
(2) Solids in Liquor Without Neutralisation (g.)	20.7	37.1	62.3	93.1
(3) HCl by Difference (1 - 2) (g.)	8.9	17.4	24.3	62.9
(4) HCl (Conductometric Titration) (g.)	7.2	17.6	24.9	59.7
(5) Ash of 2 (g.)	3.1	5.3	5.7	7.8
(6) Lignin Removed from Pulp in Chlorination (600 x % Lignin) - (Yield x % Lignin) (g.)	11.0	15.2	42.2	62.7
(7) Reducing Sugars as Glucose (g.)	1.0	1.9	1.8	5.9
(8) Chlorine Organically Combined (Total Chlorine - Chlorine as HCl) (g.)	4.2	7.1	11.5	19.1
(9) Sum of Items 4, 5, 6, 7 and 8	26.5	47.1	86.1	155.2

volatile material in the chlorination liquor besides water is hydrogen chloride. In consideration of the large amount of liquor (17.4 liters) used, the checks are quite satisfactory, particularly for Pulps T2-75 and T3-35.

Item 9 represents the sum of the individual solid components of the liquor as determined experimentally (Items 4, 5, 6, 7 and 8). This sum should equal the solid components of the liquor (Item 1) as determined by evaporation after neutralization and correction for added sodium hydroxide. This is approximately twice in the case of Pulps T3-35 and

T3-75. The increasing concentrations of hydrochloric acid with the increasing amount of chlorine used also tends to remove more ash from the pulps as shown in Item 5 (<u>see</u> Tables IV and VI).

2. <u>Caustic Extraction</u>. Several theories have been made concerning the advantages of caustic extraction of chlorinated pulps, and at this point it seems logical to discuss the amount and type of materials removed in this operation. In Table XVI a material balance and in Table XVII a balance of the liquor solids are given. The data are taken from Tables X and XI.

From an inspection of Table XVI, the material balances are seen to be fairly good for this operation, considering the type and quantity of materials encountered; however, the inaccuracies of the different analyses (particularly the pulp yields) make it impossible to draw any definite conclusions regarding the type of material removed from the pulps on caustic extraction. The data for Pulps T2-35 and T3-75 indicate that the lignin removal is only a small part of the loss in the pulp, but in Pulps T2-75 and T3-35 the lignin removal represents practically the complete loss in the pulp. When the reducing sugars are compared with the lignin removed from the pulp (Table XVII), the sugars can be seen to be from 3 to 50 per cent as great as the lignin removed. Thus, these results tend to indicate that the lignin removal is still considerably greater than that of the reducing sugars.

The increase in the ash content of the pulps on extraction with caustic soda is not very great (Item 10 of Table XVI). This increase

TABLE XVI

MATERIAL BALANCE ON CAUSTIC EXTRACTION

	T2-35		T2-75		T3-35		T3-75	
Temperature of Caustic Extraction (° C.)	20	80	20	80	20	80	20	80
(1) Weight of Pulp Used for Extraction (O.D.) (g.)	190	185	202	202	189	195	200	200
(2) Caustic Added (g.)	4.5	4.5	4.5	4.5	4.0	4.0	4.0	4.0
(3) Total Solid Material Added (g.)	194.5	189.5	206.5	206.5	193.0	199.0	204.0	204.0
(4) Pulp Yield (O.D.) After Extraction (g.)	187	180	201	202	185	187	194	194
(5) Solids in Liquor (g.)	6.3	7.8	6.3	9.8	7.8	13.0	10.0	13.2
(6) Total Recovery (g.)	193.3	187.8	207.3	211.8	192.8	200.0	204.0	207.2
(7) Material Yield (%)	99.4	99.1	100.3	102.4	99.8	100.4	100.0	101.4
(8) Loss of Pulp (g.)	3.0	5.0	1.0	0.0	4.0	7.0	6.0	6.0
(9) Loss of Lignin from Pulp (g.)	0.26	0.65	1.21	1.44	4.48	6.20	1.92	3.02
(10) Increase of Ash in Pulp (g.)	0.42	0.76	0.23	0.48	0.35	0.08	0.35	0.25

TABLE XVII

BALANCE OF SOLID PRODUCTS IN CAUSTIC LIQUORS

	T2-35		T2-75		T3-35		T3-75	
Temperature of Caustic Extraction (° C.)	20	80	20	80	20	80	20	80
(1) Solids (g.)	6.3	7.8	6.3	9.8	7.8	13.0	10.0	13.2
(2) Ash (g.)	3.7	3.9	3.9	4.8	2.4	3.5	3.3	4.0
(3) Chlorine in Liquor (g.)	0.22	0.28	0.24	0.30	0.83	1.02	1.36	1.51
(4) Reducing Sugars (g.)	0.13	0.16	0.11	0.16	0.14	0.21	0.25	0.30
(5) Lignin Removed from Pulp on Extraction (g.)	0.26	0.65	1.21	1.44	4.48	6.20	1.92	3.02

is due to adsorption of caustic soda on the pulp. Inasmuch as all the analytical data are based on the ash-free basis, it was considered unnecessary to wash the pulp with dilute acid.

Another interesting item is the relatively small amounts of materials removed from the pulps on extraction. It is often stated that most of the chlorinated lignin is removed only by the extraction process, but chlorination itself, as indicated here, removes considerably more. For Pulp T2-35 this difference is negligible. In the case of Pulp T2-75 the loss on chlorination is 2.6 per cent but the following caustic extraction removed only 0.5 per cent. With a harder pulp, such as T3, the differences, when 35 per cent chlorine is used, are 8.6 and 3.5 per cent, respectively; for Pulp T3-75, 13.5 per cent is removed on chlorination, but only 3 per cent on extraction. These results indicate also that a hydrolytic action takes place on carbohydrate material in the chlorination process. The greater difference in yields for the 75 per cent over the 35 per cent bleaches indicates that the greater the degree chlorination, the greater the percentage of material removed in the chlorination process alone, but, in the alkali extraction, the amounts removed are almost the same.

B. <u>CHLORINE BALANCE ON CHLORINATION AND EXTRACTION OF PULPS</u>

1. <u>Chlorination</u>. Another point often brought up in regard to chlorination concerns the quantity of hydrochloric acid formed when pulps are chlorinated. There apparently has been no published information regarding the distribution of the remaining part of the chlorine, except that it

is considered to be chlorine organically combined. In order to obtain some information in this regard, a chlorine balance for the chlorination experiments was made (see Table XVIII).

The results show that most of the chlorine consumed (87 to 92 per cent) is found to be present in the waste bleaching liquor and that from 56 to 66 per cent is found as hydrochloric acid. The latter values are in accord with those reported by Rys (21) and Rauchberg (22), who found that 54 to 70 per cent of the chlorine added is converted into hydrochloric acid. The data further show, as can be seen from Items 1 and 6 in Table XVIII, that the formation of hydrochloric acid increases more rapidly with higher percentages of chlorine than the amount of chlorine consumed.

Since the pulps have a considerably lower chlorine content than they should to account for the remainder of the chlorine added, it may be concluded that chlorine splits off when the pulp is washed and/or dried. (This will be discussed also under caustic extraction.)

An excellent check was obtained on the chlorine content of the liquors, as indicated in Items 8 and 9. If the chlorine content for the hydrochloric acid (Item 6) is subtracted from the total chlorine (Item 2), the values obtained (Item 8) agree very closely with the chlorine content of the nonvolatile solids as given in Item 9. This indicates that the chlorine held by the lignin and other solid material in the liquor is stable to heat and drying.

The chlorine content of the dried pulp as given in Item 11 is not

TABLE XVIII

CHLORINE BALANCE ON CHLORINATIONS

	T2-35	T2-75	T3-35	T3-75
(1) Chlorine Added (g.)	12.4	26.4	41.2	87.9
(2) Chlorine in Liquor (g.)	11.2	24.2	35.7	77.1
(3) Total Chlorine in Liquor (%)	90.4	91.8	86.6	87.8
(4) Ionizable Chlorine in Liquor ($AgNO_3$ Titration) (g.)	9.6	20.4	30.1	66.1
(5) Total Chlorine as Ionizable Chloride ($AgNO_3$ Titration) (%)	77.4	77.3	73.1	75.2
(6) Chlorine as Free HCl (Conductometric Titration) (g.)	7.0	17.1	24.2	58.0
(7) Total Chlorine as Free HCl (Conductometric Titration) (%)	56.4	64.7	58.7	66.0
(8) Chlorine in Liquor not as HCl (2 - 6) (g.)	4.2	7.1	11.5	19.8
(9) Chlorine in Nonvolatile Solids (g.)	4.16	7.25	11.00	19.65
(10) Chlorine not in Liquor (1 - 2) (g.)	1.2	2.2	5.5	10.8
(11) Chlorine in Chlorinated Pulp (g.)	0.8	1.0	3.5	3.5
(12) Chlorine Added That Was Left in the Pulp (%)	6.5	3.8	8.5	4.0
(13) Chlorine in Klason Lignin (Yield x % Lignin x % Cl in Lignin) (g.)	0.29	0.42	2.23	1.40
(14) Chlorine Accounted For (3 + 12) (%)	96.9	95.6	95.1	91.8

accounted for in the Klason lignin as given in Item 13. The chlorine found in the lignins is 36, 42, 64, and 40 per cent, respectively, of that found in the dry pulps, T2-35, T2-75, T3-35, and T3-75. This indicates a loss of chlorine during the lignin isolation process, which was also mentioned under E of Part III. If it is assumed that the chlorine in the dried pulp is all attached to the lignin, the chlorine content calculated from the chlorine and the lignin content of the pulps would be 6.6, 12.7, 7.2, and 12.4 per cent for these lignins.

2. Caustic Extraction. Table XIX shows the chlorine balance for caustic extractions. The outstanding point is the large amount of chlorine found in the caustic liquor plus the caustic extracted pulp. It was desirable to extract the chlorinated pulps while they were still in the moist condition. Thus, the low values of Item 2 in Table XIX are accounted for by the loss of chlorine on drying the pulps for analyses. A retabulation of the chlorine balance is given in Table XX, in which the difference in chlorine found in the extracted pulps was added to the amount of chlorine in the dried pulp. The sum of these two values is given in Item 4, and the final chlorine balance in Item 6 of Table XX.

The chlorine balances on chlorination are fairly good considering the fact that small samples were analyzed and the results multiplied by a large factor. There is also the possibility that some chlorinated material may have been washed out on washing of the pulp with water during the process of removing the waste liquor, which could account for the loss of chlorine. Voigtman (21) has also mentioned this as a possibility.

TABLE XIX

CHLORINE BALANCE ON CAUSTIC EXTRACTION

	T2-35		T2-75		T3-35		T3-75	
Temperature of Extraction (° C.)	20	80	20	80	20	80	20	80
(1) Chlorinated Pulp Extracted (O.D.) (g.)	190	185	202	202	189	195	200	200
(2) Total Chlorine in Original Pulp (g.)	0.27	0.27	0.32	0.32	1.04	1.07	1.18	1.18
(3) Chlorine in Extracted Pulp (Yield x % Cl) (g.)	0.22	0.15	0.22	0.18	0.54	0.45	0.37	0.37
(4) Chlorine in Total Liquor (g.)	0.22	0.28	0.24	0.30	0.83	1.02	1.36	1.51
(5) Chlorine Accounted For (3 + 4) (g.)	0.44	0.43	0.46	0.48	1.37	1.47	1.73	1.87
(6) Chlorine Accounted For (%) (5 ÷ 2) (g.)	164	159	145	150	132	137	147	158
(7) Chlorine in Klason Lignin from Pulp (Yield x % Lignin x % Chlorine) (g.)	0.11	0.08	0.05	0.04	0.19	0.15	0.43	0.34
(8) Chlorine Found in Klason Lignin (7 ÷ 3) (%)	50	53	22	22	35	33	126	92

TABLE XX

RECAPITULATION OF CHLORINE BALANCE ON CHLORINATION

	T2-35	T2-75	T3-35	T3-75
(1) Chlorine not in Liquor, Item 10 Table XVIII (g.)	1.2	2.2	5.5	10.8
(2) Chlorine in Dry Pulp, Item 11 Table XVIII (g.)	0.8	1.0	3.5	3.5
(3) Excess Chlorine Found in Caustic Extraction (g.)	0.5	0.5	1.0	1.6
(4) Sum of 3 and 4 (g.)	1.3	1.5	4.5	5.1
(5) Chlorine Accounted for in Pulp (% of Total Added)	10.5	5.7	11.0	5.8
(6) Total Chlorine Accounted for (Item 5, Table XX + Item 3 Table XVIII) (%)	100.9	97.5	97.6	93.6

The percentage of chlorine in the caustic-extracted pulp accounted for in the Klason lignin is given in Item 8 of Table XIX. The checks for percentage chlorine found in the lignin for each pulp, irrespective of the temperature of extraction, is rather interesting.

C. SULFUR BALANCE ON CHLORINATION AND EXTRACTION OF PULPS

1. Chlorination. The fate of sulfur in the pulp during the process of chlorination is interesting from the standpoint of the stability of the lignosulfonates. Table XXI shows the sulfur balance for the chlorinated pulps.

Considering the small quantities of sulfur present and the large amount of material involved, the sulfur balances are fairly good. Less sulfur is

TABLE XXII

SULFUR BALANCE ON CHLORINATION

	W2-35	W2-75	W3-35	W3-75
(1) Sulfur in Pulp Before Chlorination (g.)	1.92	1.92	5.16	5.16
(2) Sulfur in Chlorinated Pulp (g.)	1.00	0.58	2.91	2.18
(3) Sulfur in Chlorination Liquor (g.)	0.75	1.58	2.10	3.30
(4) Sulfur Accounted for (%)	92	112	96	111
(5) Sulfur in Klason Lignin from Pulp of Item 2 (g.)	0.45	0.20	1.67	0.59
(6) Sulfur in Klason Lignin (5 ÷ 2) (%)	45	35	57	27
(7) Sulfur in Liquor as Sulfate (g.)	0.25	0.60	0.37	0.73
(8) Sulfur in Pyridine Lignin from Liquor of Item 3 (g.)	0.37	0.51	1.20	1.59
(9) Sulfur in Pyridine Lignin (8 ÷ 3) (%)	49	32	57	46

accounted for in the Klason lignin in the 75 per cent chlorinations than in the 35 per cent chlorinations. The percentage of sulfur in the chlorinated pulps accounted for in the Klason lignin is about the same, except for Pulp W3-75, as the percentage of the sulfur in the liquor accounted for in the pyridine lignins. This is indicated by Items 6 and 9.

The sulfur content of the liquors will be discussed further under Section F-2.

2. Caustic Extraction. The sulfur balances on caustic extractions are given in Table XXIII. The balances are excellent except for Pulp

73-75 and, in consideration of the small values, even they are quite satisfactory. The percentage of sulfur in the extracted pulp accounted for in the Klason lignin is slightly higher than in the chlorinated pulps (average 49, as compared with 41). The same is also true for the benzidine lignins from the liquors (average 67, as compared with 46).

The sulfur contents of the lignins from the caustic extracted pulps will also be discussed later under Section F-2.

D. CHANGES IN BLEACHABILITIES ON CHLORINATION AND EXTRACTION OF PULPS

The term "bleachability" is rather indefinite and should be defined. In this investigation the Roe chlorine number was used exclusively when speaking of the chlorine demand. The permanganate number was also determined for all the pulps as a check on the bleachability. Since lignin is the principal product to be removed in chlorination, the lignin content is naturally a measure of the bleachability. Chart 1 shows the lignin content (L), Roe chlorine number (R), and permanganate number (K) for each of the pulps studied.

All these values are decreased from 39 to 48 per cent (average 44) on giving the two pulps a chlorination with 35 per cent of the chlorine demand. The figures for the 75 per cent treatments vary from 56 to 69 per cent (average 64). These values show that, in spite of the addition of more than twice the chlorine in the 75 per cent bleach, the decrease in the values R, K, and L are only roughly one and a half times, which indicates that some chlorination, in addition to the amount necessary

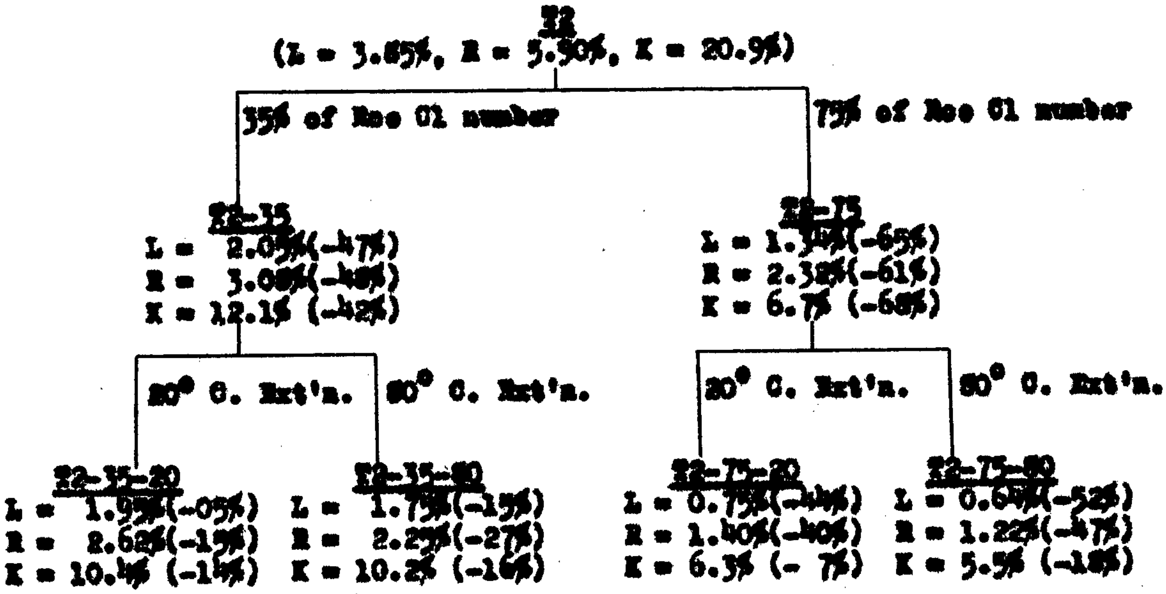
TABLE XXII

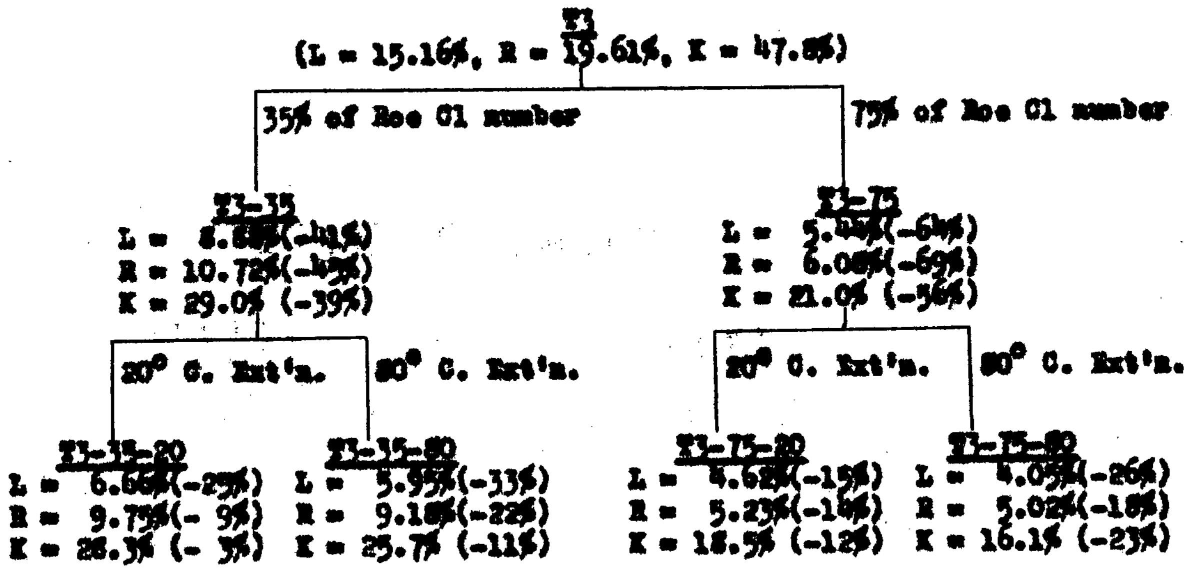
SULFUR BALANCE ON CAUSTIC EXTRACTION

	T2-35		T2-75		T3-35		T3-75	
Temperature of Extraction (° C.)	20	80	20	80	20	80	20	80
(1) Sulfur in Pulp Before Extraction (g.)	0.32	0.31	0.20	0.20	1.00	1.03	0.84	0.84
(2) Sulfur in Extracted Pulp (g.)	0.26	0.22	0.14	0.12	0.81	0.73	0.49	0.45
(3) Sulfur in Extraction Liquor (g.)	0.06	0.09	0.07	0.09	0.22	0.33	0.16	0.25
(4) Recovery of Sulfur (%)	100	100	105	105	103	103	78	84
(5) Sulfur in Klason Lignin From Extracted Pulp (g.)	0.14	0.13	0.05	0.04	0.39	0.37	0.27	0.24
(6) Sulfur in Klason Lignin (5 ÷ 2) (%)	54	59	36	33	48	51	55	53
(7) Sulfur in Benzidine Lignin From Extraction Liquor (g.)	——	0.06	——	——	0.11	0.29	0.12	0.17
(8) Sulfur in Benzidine Lignin (7 ÷ 3) (%)	——	67	——	——	50	76	75	68

CHART I

BLEACHABILITY RESULTS





Legend

L = Klason lignin from pulps
R = Roe chlorine number
K = Potassium permanganate number

to dissolve the lignin, is taking place in the 75 per cent bleaches.

For the caustic-treated pulps, the decreases are slightly more erratic than for the chlorinated pulps; but if the averages are taken in each case, the decreases for Pulps T2 and T3-35-20, T2 and T3-35-80, T2 and T3-75-20, and T2 and T3-75-80 are 10, 20, 22, and 30 per cent, respectively. These values indicate that the hot caustic treatment is about 10 per cent more effective for lowering the bleachability values than the cold treatment. It is also shown that, with the 75 per cent chlorine treatment, the caustic extraction is about 10 per cent more effective than the 35 per cent treatment. These values, however, indicate that, per unit of chlorine added, a 35 per cent chlorine treatment is more effective than the 75 per cent.

The average lowerings of total bleachability--i.e., from the original pulp to the alkali-extracted pulp--for Pulps T2 and T3-35-20, T2 and T3-35-80, T2 and T3-75-20, T2 and T3-75-80 are 49, 53, 68, and 71 per cent, respectively. This shows that the hot extraction as carried out in this work is only 3 to 4 per cent more effective than the cold for the given treatments. Thus, the practicability of a hot treatment would depend upon the expense of heating the material, assuming other properties, such as strength characteristics, to be the same.

B. DETERMINATION AND ISOLATION OF LIGNIN

1. From the Pulps. All methods for lignin determination and isolation can be criticized in several ways and particularly in the case of

altered lignins as studied in this investigation. The lignins in the original pulps are present as lignosulfonates which in themselves are very complicated. Furthermore, after a chlorination and a caustic extraction, the lignin in the pulp is still more altered and more difficult to handle and characterize.

The concentrated acid methods for isolation and determination of lignin from pulps have been criticized on the basis that sulfur and chlorine are split off and that some of the lignin, that is more severely attacked by chlorine, is rendered soluble in the acid. If, on the other hand, organic solvents are used to dissolve the lignin, it is very difficult to remove all the lignin from the pulp and to isolate it from solution quantitatively. Dissolving the lignin with caustic and precipitating it from solution has three disadvantages: (1) Complete removal is difficult; (2) isolation from the solution is not easy; and (3) the splitting off of groups, particularly chlorine, is more common than with the strong acids.

In spite of the large number of methods proposed for isolating lignin, the ideal method for separating it from sulfite pulp has not been found. The lignins isolated from the original pulps by the Klason and Willstätter methods (see Table IV) agreed very well as regards the methoxyl and sulfur content. This indicates that the Klason method of lignin separation did not increase the sulfur content. Since the Klason method for lignin separation is easier to carry out, it was decided to determine and isolate the lignins from all the pulps by this method.

2. From the Liquors. The same difficulty is encountered for liquors

as for pulp when it comes to isolating the lignins. A method that would give quantitative yields of lignin as it exists with no impurities would be ideal, but all known methods can be criticized. Methods using basic lead acetate and basic barium acetate are unsuitable, because they precipitate sugars with the lignins and the salts are difficult to remove. In precipitating with acids, a large excess is necessary and the precipitation is incomplete. It was finally decided to use benzidine to precipitate the lignins from solutions and to correct for the benzidine content by analyzing the lignins for nitrogen. The disadvantages of this method are that the precipitate is slightly soluble in water, and sulfate and sulfite impurities are also precipitated. In this work the presence of sulfates and sulfites were considered negligible.

F. CHEMICAL CHARACTERISTICS OF THE LIGNINS

1. Chlorine Content. Mention has been made by Weidner (44) that, during the isolation of lignin from chlorinated pulp with concentrated sulfuric acid, chlorine is split off. This fact is borne out in the results given in Chart II.

In all probability there was not as much chlorine split off by the sulfuric acid as was indicated by the difference in percentage of chlorine in the lignins from solution and the Klason lignins, for the more completely chlorinated portions of the lignin are probably more readily soluble. Furthermore, it was difficult to wash the isolated lignin free of hydrochloric acid.

CHART II

CHLORINE CONTENT OF LIGNINS

(All Values are Corrected to Sulfonate-, Benzidine-, and Ash-Free Basis)

T2

- 35% of Roe Cl number
  - **T2-35**
    Cl in L = 2.71%
    Cl in BL = 15.80%
    Cl in BR = 14.50%
    - 20° C. Ext'n.
      - **T2-35-20**
        Cl in L = 3.29%
        Cl in BL = -----
    - 80° C. Ext'n.
      - **T2-35-80**
        Cl in L = 2.94%
        Cl in BL = 8.50%
- 75% of Roe Cl number
  - **T2-75**
    Cl in L = 6.33%
    Cl in BL = 19.11%
    Cl in BR = 15.65%
    - 20° C. Ext'n.
      - **T2-75-20**
        Cl in L = 3.62%
        Cl in BL = ----
    - 80° C. Ext'n.
      - **T2-75-80**
        Cl in L = 3.04%
        Cl in BL = ----

T3

- 35% of Roe Cl number
  - **T3-35**
    Cl in L = 5.06%
    Cl in BL = 15.11%
    Cl in BR = 14.82%
    - 20° C. Ext'n.
      - **T3-35-20**
        Cl in L = 1.70%
        Cl in BL = 9.36%
    - 80° C. Ext'n.
      - **T3-35-80**
        Cl in L = 1.45%
        Cl in BL = 9.30%
- 75% of Roe Cl number
  - **T3-75**
    Cl in L = 5.25%
    Cl in BL = 21.29%
    Cl in BR = 18.45%
    - 20° C. Ext'n.
      - **T3-75-20**
        Cl in L = 5.15%
        Cl in BL = 13.21%
    - 80° C. Ext'n.
      - **T3-75-80**
        Cl in L = 4.69%
        Cl in BL = 11.82%

Legend

Cl = Chlorine
L = Klason lignin from pulps
BL = Benzidine lignin from liquors
BR = Benzidine lignin from caustic-treated residues of chlorination liquors

When the chlorination residues are treated with caustic soda solution, they go into solution, from which they are precipitated by benzidine. A chemical determination of the products recovered show in every case a loss of chlorine and this is considerably greater for 75 per cent than 35 per cent bleaches.

The chlorine content of the Klason lignins from the caustic-extracted pulps are lower in every case (but Pulp TB-35) than from the chlorinated pulps. This indicates that caustic soda tends to remove some chlorine from the lignin which is not removed by the strong acid during the lignin isolation.

The chlorine content of the benzidine lignins from the caustic-extraction liquors are all considerably lower than the benzidine lignins from the chlorination liquors or caustic-treated residues. The hot caustic also splits off more chlorine than the cold. All these observations have been mentioned in the literature as taking place on treatment of chloro-lignins prepared from wood with caustic.

2. Sulfur Content. The Klason and Willstätter lignins from the two sulfite pulps have essentially the same sulfur content (average 4.74 per cent), and the methoxyl content for the Willstätter and Klason lignins are nearly the same for each pulp.

In order to obtain a picture of the sulfur content of the various lignins during different stages, Chart III was prepared.

CHART III

SULFUR CONTENTS OF LIGNINS

(All Values are Corrected to Chlorine-, Benzidine-, and Ash-Free Basis)

T2
(S in L = 4.51%)

- 35% of Roe Cl number
  - **T2-35**
    S in L = 3.82%(-15.4%)
    S in BL = 4.52%
    S in BR = 4.45%
    - 20° C. Ext'n.
      - **T2-35-20**
        S in L = 3.87%
        S in BL = ——
    - 80° C. Ext'n.
      - **T2-35-80**
        S in L = 4.11%
        S in BL = 4.45%
- 75% of Roe Cl number
  - **T2-75**
    S in L = 2.65%(-41%)
    S in BL = 4.19%
    S in BR = 3.41%
    - 20° C. Ext'n.
      - **T2-75-20**
        S in L = 3.04%
        S in BL = ——
    - 80° C. Ext'n.
      - **T2-75-80**
        S in L = 2.86%
        S in BL = ——

T3
(S in L = 4.69%)

- 35% of Roe Cl number
  - **T3-35**
    S in L = 3.59%(-23%)
    S in BL = 4.07%
    S in BR = 4.06%
    - 20° C. Ext'n.
      - **T3-35-20**
        S in L = 3.18%
        S in BL = 3.70%
    - 80° C. Ext'n
      - **T3-35-80**
        S in L = 3.34%
        S in BL = 4.11%
- 75% of Roe Cl number
  - **T3-75**
    S in L = 2.21%(-53%)
    S in BL = 3.30%
    S in BR = 3.08%
    - 20° C. Ext'n.
      - **T3-75-20**
        S in L = 3.19%
        S in BL = 3.21%
    - 80° C. Ext'n.
      - **T3-75-80**
        S in L = 3.24%
        S in BL = 3.04%

Legend

S = Sulfur
L = Klason lignin from pulps
BL = Benzidine lignin from liquors
BR = Benzidine lignin from caustic-treated residues of chlorination liquors

With a chlorine consumption of 35 per cent for Pulp T2, the sulfur content of the lignin is decreased 13.4 per cent in spite of the entrance of only 2.7 per cent chlorine, and with the 75 per cent, the decrease is 41 per cent with only an increase of chlorine of 6.3 per cent (Chart II). This is even greater for Pulp T3 which shows that the entrance of the chlorine into the lignin unit, thus increasing the molecular weight, was not the only reason for the decrease in sulfur content. The results show that the lignins in the chlorination liquors have lower sulfur contents than those from the original pulps, which indicates that chlorine splits off sulfur from the lignin during the chlorination process.

In the chlorination treatment the entrance of chlorine into the lignin makes the sulfur so labile that it is split off during the lignin isolation since sulfur contents of the lignins from the chlorinated pulps are all lower than those of the lignins isolated from the solution or from the original pulp.

It is interesting to note the statement of Noll (45) that "no sulfur could be found in lignin from a sulfite pulp when the lignin had been isolated using 78 per cent sulfuric acid and dimethylaniline", which shows that the method of Noll is much more drastic in splitting off sulfur than the Willstätter and Klason methods of lignin isolation.

3. Methoxyl Content. Various investigators (14, 16, 24, 25) have reported that chlorination of lignin splits off methoxyl groups. This is definitely borne out by the results tabulated in Chart IV.

CHART IV

METHOXYL CONTENT OF LIGNINS

(All Values are Corrected to Chlorine-, Benzidine-, Ash-, and Sulfonate-Free Basis)

T2
(MeO in L = 13.2%)

- 35% of Roe Cl number → **T2-35**
  - MeO in L = 10.55%
  - MeO in BL = 5.40%
  - MeO in BR = 5.46%
  - 20° C. Ext'n. → **T2-35-20**
    - MeO in L = 12.49%
    - MeO in BL = -----
  - 80° C. Ext'n. → **T2-35-80**
    - MeO in L = 12.43%
    - MeO in BL = 10.69%
- 75% of Roe Cl number → **T2-75**
  - MeO in L = 7.38%
  - MeO in BL = 3.81%
  - MeO in BR = 3.38%
  - 20° C. Ext'n. → **T2-75-20**
    - MeO in L = 9.11%
    - MeO in BL = -----
  - 80° C. Ext'n. → **T2-75-80**
    - MeO in L = 8.72%
    - MeO in BL = -----

T3
(MeO in L = 15.1%)

- 35% of Roe Cl number → **T3-35**
  - MeO in L = 12.29%
  - MeO in BL = 6.39%
  - MeO in BR = 6.59%
  - 20° C. Ext'n. → **T3-35-20**
    - MeO in L = 14.11%
    - MeO in BL = 6.98%
  - 80° C. Ext'n. → **T3-35-80**
    - MeO in L = 13.91%
    - MeO in BL = 8.96%
- 75% of Roe Cl number → **T3-75**
  - MeO in L = 7.21%
  - MeO in BL = 3.46%
  - MeO in BR = 3.04%
  - 20° C. Ext'n. → **T3-75-20**
    - MeO in L = 13.28%
    - MeO in BL = 4.63%
  - 80° C. Ext'n. → **T3-75-80**
    - MeO in L = 13.21%
    - MeO in BL = 5.25%

<u>Legend</u>

MeO = Methoxyl
L = Klason lignin from pulps
BL = Benzidine lignin from liquors
BR = Benzidine lignin from caustic-treated residues of chlorination liquors

It is shown definitely that the greater the degree of chlorination, the greater the loss of methoxyl. Caustic treatment of the residues of the chlorination liquors apparently has no effect on the methoxyl content, but caustic extraction of the pulps tends to remove the lignin with the lowest methoxyl content. In every case the methoxyl content of the lignins from the chlorinated pulps are lower than for the caustic-extracted pulps. The methoxyl content of the lignins in the caustic solutions are considerably lower than from the caustic-treated pulps but higher than the lignins from the chlorination liquors.

8. DISTRIBUTION OF METHOXYL IN PULP

The question is often raised as to the amount of methoxyl in wood that is not accounted for in the lignin. Ritter and co-workers (46) and, more recently, Hagglund and Sandelin (47) have found that about 0.5 per cent of the total methoxyl in sprucewood (4.56 per cent) is attached to carbohydrate material. Table XXIII is an attempt to show the distribution of methoxyl in pulp and to determine if there are any changes in distribution during the various processes.

The pulps from T2 show that the amount of methoxyl not accounted for in the lignin is nearly constant for the different treatments. In general, the more drastic the treatment, the less the percentage of methoxyl that is accounted for in the lignin. For T3 pulp samples, there seems to be less methoxyl not accounted for in the lignin as the drasticity of treatment is increased. The percentage of methoxyl in the lignin seems to change very little on caustic treatment. It is also interesting to

TABLE XXIII

DISTRIBUTION OF METHOXYL IN PULPS

	MeO in 100 g. of Pulp (g.)	MeO in Lignin from 100 g. of Pulp (g.)	MeO in Carbohydrates from 100 g. of Pulp (g.)	MeO in Lignin (%)
T2	0.74	0.45	0.29	61
T2-35	0.57	0.19	0.38	33
T2-75	0.29	0.09	0.20	31
T2-35-20	0.49	0.21	0.28	43
T2-35-80	0.46	0.19	0.27	41
T2-75-20	0.29	0.06	0.23	21
T2-75-80	0.30	0.05	0.25	17
T3	2.78	2.01	0.77	72
T3-35	1.66	0.94	0.72	56
T3-75	0.99	0.35	0.64	35
T3-35-20	1.54	0.85	0.69	55
T3-35-80	1.46	0.75	0.71	51
T3-75-20	1.02	0.54	0.48	53
T3-75-80	0.94	0.47	0.47	50

note that the methoxyl not connected with lignin is greater in the pulp with the greater lignin content. For all the pulps analysed the average percentage of methoxyl not accounted for in the lignin is 0.46 per cent, which is close to the value given by Hagglund for wood and shows that the carbohydrate methoxyl is very stable.

H. CARBON DIOXIDE EVOLUTION ON CHLORINATION

Inasmuch as a certain amount of oxidation occurs on chlorination and the extent of the reaction seems to depend on the percentage of the chlorine demand used (18, 21, 22), it appeared logical to make carbon dioxide determinations during chlorination experiments on pulps with various percentages of the chlorine demand. The values obtained in this investigation are given in Table XII.

As is evident from the values given in Table XII, the quantity of carbon dioxide evolved when pulp is chlorinated is very small, and the increase percentage, if any, owing to the increase of chlorine demand, is also very small. This would lead one to believe that, if chlorine exerts an oxidising effect upon the lignin in the pulp, the action is not severe enough to result in the formation of carbon dioxide.

I. CHANGE OF pH DURING CHLORINATION

Figure 4 shows clearly that the lowering of pH on chlorination is very rapid at first and that the curve finally smoothes out to a nearly constant value. The pH lowering is greater when larger quantities of chlorine are used. There is, however, a definite and noticeable difference between the pH of the chlorine water and the final chlorination liquor, which indicates that more hydrochloric acid is evolved during the chlorination process than is formed by the hydrolysis of chlorine gas:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

Figure 6 is a plot of chlorine water versus pH; from this curve it is evident that in the above equation the reaction is shifted to the right with increased concentration of chlorine.

With the large percentage of chlorine which forms hydrochloric acid, as has been indicated in Table XVIII, and the low pH during the chlorination process, it is evident that the addition of hydrochloric acid to the chlorination mixture, as was pointed out in the historical review, would decrease the chlorine consumption or increase the degree of chlorination if the same amount of chlorine was added.

J. COLORIMETRIC DATA OF SOLUTIONS

The spectral transmission curves of the chlorination and caustic extraction liquors were taken after adjusting the solutions to a definite pH (1.20 to 1.49). Plots were made of wavelength versus $\log I_0/I = \log \frac{1}{T}$), but no definite conclusions could be drawn regarding the composition of the liquors; therefore, the data have not been considered.

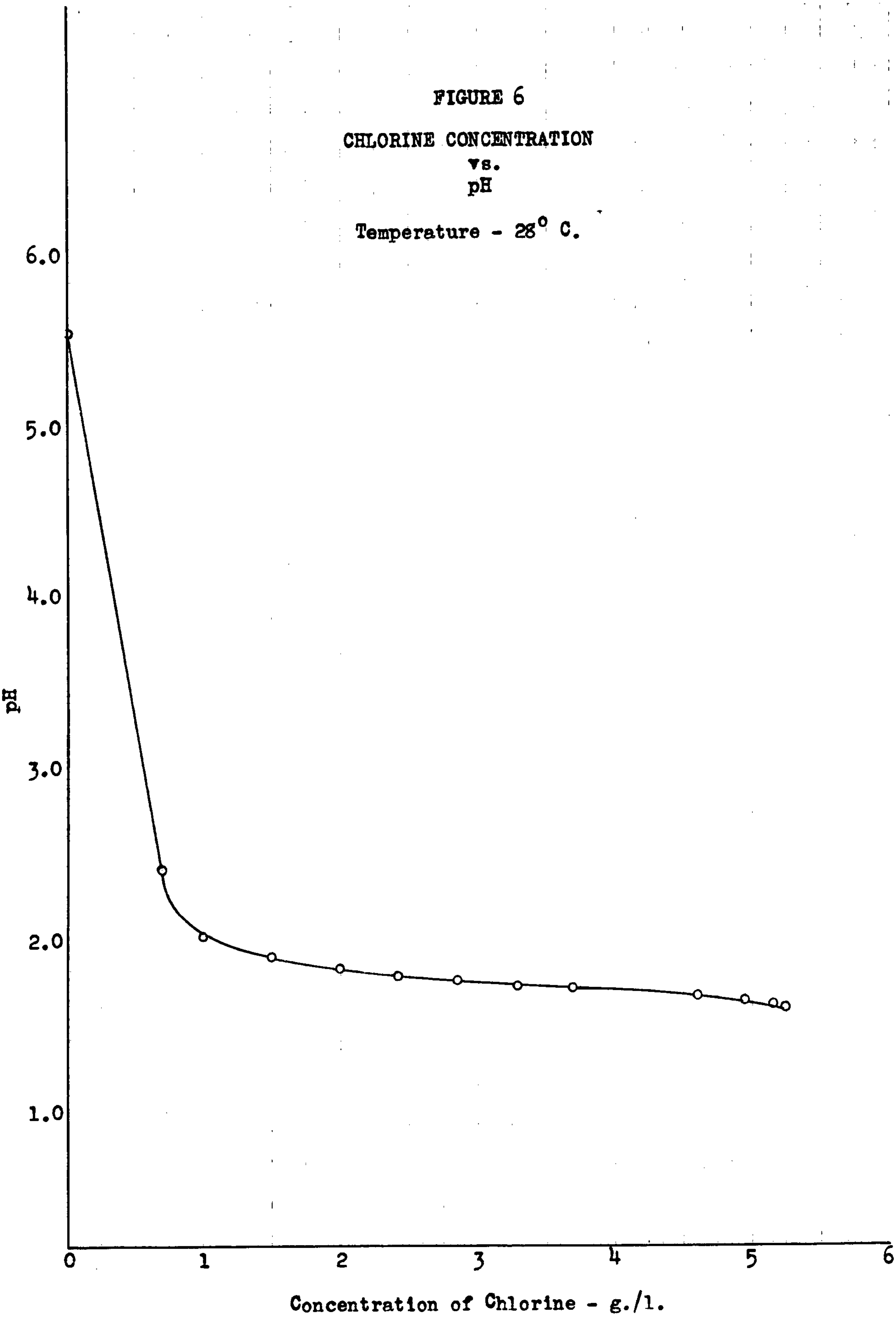


FIGURE 6
CHLORINE CONCENTRATION
vs.
pH
Temperature - 28° C.
6.0
5.0
4.0
3.0
2.0
1.0
pH
0
1
2
3
4
5
6
Concentration of Chlorine - g./l.

K. ALKALI AND METHANOL LIGNINS FROM SULFITE AND CHLORINATED SULFITE PULP

The prime purpose in making a study of the methanol and alkali lignin from a sulfite and a chlorinated sulfite pulp was to study more closely the mechanism of the chlorination reaction on the lignin in the pulp. The lignins from the sulfite pulp were to furnish a means of comparison of these lignins with those from the chlorinated pulp. It was felt that the lignin isolated from the pulp by methanol would be changed to a less degree than by other methods of isolation. The alkali lignin from the chlorinated pulp was prepared to determine whether new hydroxyl groups (phenolic and acidic, or alphatic) were formed or lost by the removal of chlorine from the lignin by caustic.

Two methods were chosen to detect hydroxyl groups: methylation with diazomethane for phenolic or acidic, and acetylation for total hydroxyl groups.

In carrying out this study the lignins were methylated, acetylated, and analysed as previously described under Sections E and F of Part IV. The analyses are given in Table XIII.

1. Methoxyl Content. The lignins and lignin derivatives were recalculated to an ash-, sulfonate (SO_3H)-, and chlorine-free basis and tabulated in Table XXIV. The molecular weights and groupings given in the table are calculated from the formula of Brauns (48) for native lignin [$C_{42}H_{32}O_6(CH_3O)_4(OH)_4$-$\overset{|}{C}=O$], and methanol native lignin [$C_{42}H_{32}O_6(CH_3O)_4(OH)_4$-$\overset{|}{C}(OCH_3)_2$].

The two methanol lignin fractions, Samples T3-MeOH-A and T3-MeOH-B,

TABLE XXIV

METHANOL AND ALKALI LIGNINS

Lignin Derivative	Mol. Wt.	No. of MeO Groups	No. of OH or AcO Groups	Calcd. MeO	Found MeO	Calcd. AcO	Found AcO
Methanol N. L.	886	6	4 OH	21.0	20.9	——	——
T3-MeOH-A	872	5	5 OH	17.8	17.2	——	——
Methylated	900	7	3 OH	24.1	23.2	——	——
Acetylated	1066	5	5 AcO	14.5	13.7	20.2	18.7
T3-MeOH-B	840	4	5 OH	14.8	14.4	——	——
Methylated	854	5	4 OH	18.1	17.8	——	——
Acetylated	1050	4	5 AcO	11.8	11.8	20.5	21.6
T3-75-MeOH	826	3	6 OH	11.3	12.1	——	——
Methylated	840	4	5 OH	14.8	14.0	——	——
Acetylated	1062	3	6 AcO	8.8	8.8	24.3	26.2
T3-75-A	798 812	1 2	—— ——	3.9 7.7	5.4 5.4	—— ——	—— ——
T3-Na	840	4	5 OH	14.8	14.3	——	——
Methylated	868	6	3 OH	21.4	20.2	——	——
Acetylated	1050	4	5 AcO	11.8	11.2	20.5	21.1
T3-75-Na	826	3	5 OH	11.2	9.0	——	——
Methylated	854	5	3 OH	18.1	16.9	——	——
Acetylated	1036	3	5 AcO	9.0	7.2	20.8	19.9
T3-75-Na-D	826	3	——	11.2	9.1	——	——

are seen to have different compositions as regards methoxyl and hydroxyl groups, and both differ from the methanol lignin from the native lignin of Brauns in that Sample T3-MeOH-A has one and Sample T3-MeOH-B has two methoxyl groups less. Compared with native lignin, Sample T3-MeOH-A has one methoxyl group added, whereas Sample T3-MeOH-B has the same number of methoxyl groups. This indicates that the group in lignin which reacts with methanol in the presence of hydrochloric acid has already reacted in the sulfite cooking process, a fact which has already been pointed out by Brauns (48). The entrance of only one methoxyl group into lignosulfonic acid on treatment with methanol-hydrochloric acid was also found by King, Brauns, and Hibbert (49). The residual lignin in sulfite pulp reacts towards methanol-hydrochloric acid, at least in part, in the same way as isolated lignosulfonic acid. The blocking of the position for the entrance of another methoxyl group when treated with methanol is doubtless due to the sulfonic groups in the lignin. In Lignin T3-MeOH-B no new methoxyl group has been added and with diazomethane one hydroxyl is methylated; in Sample T3-MeOH-A two new methoxyl groups are introduced by this reagent. In the latter case, in addition to a phenolic hydroxyl group, the sulfonic acid group is probably esterified, but it cannot yet be decided what hydroxyl group has been methylated in Sample T3-MeOH-B.

The methanol lignin from the chlorinated pulp (Sample T3-75-MeOH) has two less methoxyl groups but one more hydroxyl group than Sample T3-MeOH-A and one less methoxyl group and one more hydroxyl group than Sample T3-MeOH-B. Methylation of Sample T3-75-MeOH with diazomethane adds one methoxyl group. The new hydroxyl group in Sample T3-75-MeOH apparently originates from the loss of a methoxyl group and may be alphatic in character. Since on treatment of the chlorinated lignin with methanol or of lignin with methanol-hydrochloric acid methylation usually takes place, it may be possible that the original lignin in Pulp T3-75 had a lower methoxyl content, which was increased first by the action of methanol-hydrochloric acid. This viewpoint is supported by the lower methoxyl content of Lignin T3-75-Na.

Since methanol lignins A and B were obtained in nearly equal amounts, the chlorination treatment must have removed most of fraction A or else altered the hydroxyl groups. This is borne out by the seven methoxyl groups of methylated methanol lignin A as compared with four methoxyl groups for the methanol lignin from the chlorinated pulp. The water-methanol-soluble lignin, T3-75-A, was probably a part of the lignin that had been attacked more severely. If this assumption is true, all the methoxyl could probably be split off by chlorination as was stated by Müller (87).

A comparison of Sample T3-Na and its acetylated product agrees very well with Sample T3-MeOH-B and its acetylated product; however, the methylated products are different. The methylation indicates the presence of two acidic or phenolic hydroxyl groups which is the same as Sample T3-MeOH-A. Again, the difference is probably due to the sulfonic group. The alkali lignin has one more hydroxyl group than native lignin. Although alkali lignin has not been prepared from native lignin, it is possible that the keto-enol group changes to a hydroxyl group.

The alkali lignin from the chlorinated pulp (Sample T3-75-Na) shows a loss of slightly more than one methoxyl group. Since methylation with diazomethane increases the number of methoxyl groups by two, and since the total number of methoxyl and hydroxyl groups is slightly less than eight, it can be concluded to be the same as alkali lignin with one less methoxyl group. The dioxane-soluble alkali lignin from the chlorinated pulp (Sample T3-75-Na-D) appears to be the same as Sample T3-75-Na as regards to methoxyl content. Since the sample was too small, methylation and acetylation experiments were not made.

2. Sulfur Content. The sulfur content of the alkali and methanol lignins and lignin derivatives were calculated on the basis of a lignin unit of 840 and to an ash- and chlorine-free basis. The results are taken from Table XIII and are tabulated in Table XXV.

TABLE XXV

SULFUR CONTENT OF METHANOL AND ALKALI LIGNINS AND DERIVATIVES

	Untreated Sample %	Methylated Sample %
T3-MeOH-A	4.44	4.38
T3-MeOH-B	3.88	3.82
T3-75-MeOH	3.14	2.78
T3-75-A	2.93	----
T3-Na	2.45	2.30
T3-75-Na	2.61	2.71
T3-75-Na-D	1.79	----

The sulfur content of the methanol lignins (average, 4.13 per cent) agree fairly well with the sulfur content of Klason and Willstätter lignins from Pulp T3 (4.79 and 4.85 per cent; see Table IV). The alkali lignin, Sample T3-Na, however, has a lower value (2.38 per cent), which shows further that alkali tends to split sulfur from the lignin. The chlorination treatment also splits off sulfur as can be seen from Sample T3-75-MeOH. The caustic treatment splits off as much sulfur in the unchlorinated as in the chlorinated sample (Samples T3-Na and T3-75-Na).

The sulfur content of a lignin unit of 840 containing one sulfonic group would be 3.4%, which corresponds fairly closely to the sulfur content for Sample T3-75-MeOH.

3. <u>Chlorine Content</u>. Table XXVI gives the chlorine content of the alkali and methanol lignins and their derivatives from chlorinated Pulp T3 calculated on the basis of a lignin unit of 840 to an ash- and sulfonate-free basis. The results are taken from Table XIII.

TABLE XXVI

CHLORINE CONTENT OF METHANOL AND ALKALI LIGNINS AND DERIVATIVES FROM CHLORINATED PULP T3

	Untreated Sample (%)	Methylated Sample (%)
T3-75-Na	3.7	3.4
T3-75-MeOH	15.8	15.7
T3-75-A	27.5	-----

The value for Sample T3-75-Na corresponds to about one chlorine atom per lignin molecule of 874 (4.05 per cent). The chlorine content of Sample T3-75-MeOH corresponds approximately to 4 chlorine atoms per lignin unit of 978 (14.6 per cent). This shows that the alkali splits off about 3 atoms of chlorine per lignin unit. The chlorine content of the water-methanol-soluble lignin, Sample T3-75-A, corresponds to 9 chlorine atoms in a lignin unit of 1151 (27.7 per cent).

VI. SUMMARY AND CONCLUSIONS

Two sulfite pulps (T2 and T3) with widely different lignin contents (3.85 and 15.2 per cent) were prepared in experimental sulfite digesters. Each pulp was chlorinated with 35 and 75 per cent of the chlorine demand (Roe chlorine number). The four chlorinated pulps were then extracted with cold and hot 2 per cent caustic (20° and 80° C.) at 10 per cent consistency. Material, chlorine, and sulfur balances were made in each case. The lignins of the original, chlorinated, and extracted pulps were isolated by the Klason method and analyzed. Analyses were also made on the chlorination and caustic waste liquors and on the solids obtained from the chlorination liquors. The original, chlorinated, and caustic extracted pulps were analyzed for bleachability (Roe chlorine number, permanganate number, and lignin content), sulfur, chlorine, and methoxyl content.

Methanol and alkali lignins were prepared from Pulp T3, and Pulp T3 chlorinated with 75 per cent of the chlorine demand. Analyses were made on the original, methylated, and acetylated products.

The following conclusions were drawn from the work carried out:

The residual lignin in sulfite pulps is present as a sulfonated lignin (solid lignosulfonic acid) with an average sulfur content of 4.75 per cent for Klason and Willstätter lignin and 4.13 per cent for methanol lignin.

On chlorination of a normal sulfite pulp (T2), lignin appears to be about the only product removed; however, for a rawer pulp (T3), a considerable amount of carbohydrate material is removed, and the greater the percentage of chlorine demand used, the greater the quantity of carbohydrate material dissolved from the pulp.

When chlorinated pulps are extracted with caustic, lignin is also the chief product removed, but some carbohydrate material is also dissolved. For pulps with a low lignin content (T2) the ratio of the carbohydrate material removed to the lignin removed is greater than for the rawer pulps (T3).

From 87 to 92 per cent of the chlorine added in chlorination can be recovered in the chlorination waste liquor; from 56 to 66 per cent of the total is found as hydrochloric acid. The amount of hydrochloric acid formed was greater when a greater percentage of the chlorine demand was used, which indicates that the first chlorine is utilized by substitution followed by an oxidation reaction.

A part of the chlorine remaining in a chlorinated pulp is held loosely and is removed during the process of drying.

A part of the chlorine in the chlorinated pulp is so labile that it is split off during its isolation by the Klason method.

The chlorine in the solids of the chlorination waste liquors is relatively stable to heat and drying.

On chlorination of a sulfite pulp a part of the sulfur is split from the lignin and another part rendered labile, so that it is removed from the chlorinated lignin during isolation by the Klason method.

Chlorination of pulps with 75 per cent of the chlorine demand reduces bleachability values only about one and a half times that of 35 per cent of the chlorine demand, even though over twice the quantity of chlorine is used, indicating that a part of the chlorine is consumed by the already chlorinated lignin.

Hot caustic extraction (2 per cent at 80° C.) is about 10 per cent more effective in lowering bleachability values of chlorinated pulps than cold extractions (20° C.). For the total bleachability lowerings (chlorination plus extractions), the hot process is 3 to 4 per cent more effective than the cold.

Bleachabilities are reduced considerably more by chlorination alone than by caustic extraction after chlorination. The bleachability lowering for cold extraction was about one fourth of that for the 35 per cent chlorination and one third of that for the 75 per cent chlorinations. The lowerings for hot extractions were about one half of that for the chlorinations.

Chlorine is split from chlorinated lignins on treatment with caustic. The chlorine content of Klason lignins from caustic-extracted pulps are lower than from chlorinated pulps, which indicates that caustic soda tends to remove some chlorine from the lignin not removed by the strong acid during the lignin isolation.

Chlorination of pulps splits methoxyl groups from the lignin; the greater the degree of chlorination, the greater the loss of methoxyl. Indications are given that all methoxyl groups might be split off by chlorination.

Methanol lignin from chlorinated sulfite pulp (Sample T3-75-MeOH) indicates a replacement of one methoxyl group by an alphatic hydroxyl group in a lignin unit during the chlorination of the pulp and subsequent isolation of the lignin.

Caustic extraction of the residues from chlorination waste liquors has apparently no effect on the methoxyl content, but when chlorinated pulps are extracted, the lignin with the lowest methoxyl content is removed. Alkali lignin from a chlorinated pulp (Sample T3-75-Na) indicates a loss of slightly more than one methoxyl group from the lignin unit.

The oxidation reaction of chlorine on lignin in sulfite pulps is not severe enough to form appreciable amounts of carbon dioxide, even when 140 per cent of the chlorine demand is used.

The pH lowering on chlorination is very rapid at first and soon becomes nearly constant. The lowering is greater for greater amounts of chlorine added per unit volume of stock.

VII. BIBLIOGRAPHY

1. Bixler, A. L. M., Paper Trade J. 107, no. 15:29-40(Oct. 13, 1938).

2. Payen, A. Compt. rend., 9:149(1839); quoted by Schorger, A. W. "The chemistry of cellulose and wood." 1st ed. especially p. 101. New York, McGraw-Hill, 1926. 596 p.

3. Fremy, E. and Terreil, Bull. soc. chim. 9:439(1868); quoted by Schorger, A. W. "The chemistry of cellulose and wood." 1st ed. especially p. 101. New York, McGraw-Hill, 1926. 596 p.

4. Cross, C. F., and Bevan, E. J. "Cellulose." London, Longmans, Green, 1910. 328 p.

5. de Vains, A. R., British patent 189,561(1921); 198,975(1922); quoted by Schorger, A. W. "The chemistry of cellulose and wood." 1st ed. especially p. 413. New York, McGraw-Hill, 1926. 596 p.

6. Cataldi, B., British patent 101,475(Sept. 11, 1916); C. A. 11:209-210 (1917).

7. Schmidt-Nielsen, S., Papir-J. 26:83-85, 94-97(1938).

8. Hirschkind, W., Pac. Pulp Paper Ind. 10, no. 4:7-8(April, 1936).

9. Strong, Howard W., J. Soc. Chem. Ind. 47:196T-198(1928).

10. Strong, Howard W., J. Soc. Chem. Ind. 47:87T-90(1928).

11. Heuser, Emil, and Sieber, Rudolf, Z. angew. Chem. 26:801-806(1913).

12. Heuser, Emil, and Haug, Alfons, Z. angew. Chem. 31:99-100, 103-104(1918).

13. Waentig, P., Z. angew. Chem. 41:493-498, 977-980, 1001-1005(1928).

14. Müller, Oskar A., Papier-Fabr. 32:329-332, 338-342, 347-351, 354-358(1934).

15. Müller, O. A., and Stalder, F., Papier-Fabr. 36:81-88, 89-93(1938).

16. Jansen, G. V., and Bain, J. W., Can. J. Research B15:279-294(1937).

17. Brauns, Fritz, and Hibbert, Harold, Pulp Paper Mag. Can. 34:187-188(1933).

18. Fotiev, S. A., Pulp Paper Mag. Can. 39:749-752(1938).

19. Freudenberg, K. "Tannin cellulose lignin." Especially p. 139-146. Berlin, Julius Springer, 1933. 165 p.

20. Opfermann, Erich, and Hochberger, Ernst. "Die Bleiche des Zellstoffs." vol. 3, part 2, especially p. 167-182. Berlin, Elsner, 1936. 416 p.

21. Bye, L., Papier-Fabr. 26:256-260, 269-275, 288-289(1928).

22. Rauchberg, Herbert, Papier-Fabr. 29:490-497, 516-524, 535-541(1931).

23. Kress, Otto, and Voigtman, Edward H., Paper Trade J. 97, no. 7:29-44 (Aug. 17, 1933).

24. Harris, E. E., Sherrard, E. C., and Mitchell, R. L., J. Am. Chem. Soc. 56:889-893(1934).

25. Roberts, Martin Joseph. "A study of the action of chlorine on spruce wood and of the isolated chlorolignin." Master's Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1936. 33 p.

26. Friedrich, A. and Pelikan, B., Biochem. Z. 239:461-472(1931).

27. Müller, O. A., Papier-Fabr. 37:237-240(1939).

28. Sarkar, P. B., J. Indian Chem. Soc. 11:777-785(1934); C. A. 29:2514(1935).

29. Powell, Walter James, and Whittaker, Henry, J. Chem. Soc. 125:357-364 (1924).

30. Powell, Walter James, and Whittaker, Henry, J. Chem. Soc. 127:132-137 (1925).

31. Hibbert, Harold, and Sankey, Charles A., Can. J. Research 4:110-118(1931).

32. Hibbert, Harold, and Taylor, K. Austin, Can. J. Research 4:240-253(1931).

33. Fuchs, Walter, and Horn, Otto, Ber. 61:2197-2202(1928); 62:1691-1693 (1929).

34. Pomilio, Umberto, Papier 27:195-210(1924).

35. Rassow, B. and Zickmann, P., J. prakt. Chem. 123:189-234(1929); C. A. 24:721(1930).

36. Freudenberg, Karl, Belz, Walter, and Niemann, Christian, Ber. 62:1554-1561 (1929).

37. Roe, Ralph B., Ind. Eng. Chem. 16:808-811(1924).

38. Kingstedt, F. W., Z. anal. Chem. 112:101-103(1938); C. A. 32:4103(1938).

39. Pregl, Fritz. "Quantitative organic microanalysis." Translated from the 3rd German edition by Ernest Fyleman. 2nd ed. Philadelphia, Blakiston, 1930. 237 p.

40. Freudenberg, Karl, Harder, M., and Cohn, E., Ann. 433:230-237(1923).

41. McElhinney, T. R., Whittemore, E. R., and Lynch, D. F. J., Paper Trade J. 106, no. 10:37-41(March 10, 1938).

42. Rassow, B., and Kraft, H., Papier-Fabr. 27:489-495, 508-514, 524-527 (1929).

43. Palmrose, G. V., Paper Trade J. 100, no. 3:38-39(Jan. 17, 1935).

44. Weidner, John Prestin. "An investigation of the nature of chlorinated kraft lignin." Master's Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1936. 41 p.

45. Noll, A., Zellstoff u. Papier 11:409-411(1931).

46. Kurth, E. F., and Ritter, Geo. J., J. Am. Chem. Soc. 56:2720-2723(1934); Ritter, Geo. J., and Barbour, James H., Ind. Eng. Chem., Anal. Ed., 7:238-240(1935); Harris, E. E., Sherrard, E. C., and Mitchell, R. L., J. Am. Chem. Soc. 56:889-893(1934).

47. Hägglund, Erik, and Sandelin, Olle, Svensk Kem. Tid. 46:83-87(1934).

48. Brauns, F. E., J. Am. Chem. Soc. 61:2120-2127(1939).

49. King, E. G., Brauns, Fritz, and Hibbert, Harold, Can. J. Research 13B:88-102(1935).