THE CHLORINATION OF SULFATE LIGNIN

by

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I. INTRODUCTION

Lignin, or woody substance, which comprises about 30 per cent of all cellulose growth, is the unused by-product of the paper industry. Every year the pulp mills either burn or run into the streams over two and a half million tons of this raw material.

In the sulfate industry for every 100 pounds of moisture free wood used in making pulp 55 pounds are either burned in the recovery process or lost in the effluents. Of immediate concern to the industry is the effluent, which is considered a pollution hazard. For at the present time there is a nation wide drive by state and federal agencies to decrease the pollution of streams in the heavily industrialized areas. There is also the conservation viewpoint since these millions of tons of lignin have potential value as a source of useful organic chemicals. As a result of these factors it has become urgent that major uses be found for lignin so as to make it economically feasible to recover. Investigators have made considerable progress, during the last few years, in research on the chemical nature and the utilization of lignin.

Recent work by D. F. Othmer on the chlorination of sawdust to produce a chlorinated lignin indicated that this product may have plastic value. However, lignin from softwood as produced by the sulfate process differs in structure and chemical properties from native lignin as used by Othmer. Experimentation is required to determine the effect of chlorination on the sulfate lignin. A study of the literature for previous data on chlorination of the different types of lignin indicates that data is needed on the solvent medium for chlorination, on the effect of temperature on the chlorination, on the effect of catalyst on chlorination, and the physical and chemical properties of the chlorinated product.

The object of this research is to study the chlorination reaction of sulfate lignin, and to determine the physical and chemical properties of the chlorinated product.

II. LITERATURE REVIEW

History. Botanists and plant physiologists have long known(28) that early in the development of the cell walls of woody tissues of vascular plants there occurs a change whereby cellulose is presumed to become hardened or what is generally described as lignified. The change consists in the addition to the cellulose of a substance or group of related substances which have been designated as lignin. The term lignin was introduced into scientific literature by the botanist and plant physiologist de Candolle in 1833.

The French chemist Anselme Payen(28) in 1838 first showed that wood was a heterogenous mixture and not a definite chemical substance. He treated wood with nitric acid, alkalies, alcohol and ether and obtained a substance which was relatively resistant to the action of these reagents. This substance Payen called cellulose, and the complex he removed from the cellulose he called the "true woody material".

E. Fremy in the 1860's considered that the residual material remaining after the treatment of wood with 72 per cent sulfuric acid was "ligneux" and this ligneux was chemically combined with the cellulose and not merely mechanically attached to it as was claimed by Payen.(28)

J. Erdmann(28) in 1866 pointed out that free cellulose dissolved in Schweizer's reagent, wood substance did not.

and he therefore assumed that the lignin was chemically combined with the cellulose and the other carbohydrates. By the degradation of wood with alkali, he obtained acetic and succinic acids and catechol. Purified cellulose, when similarly treated yielded no catechol and Erdmann accordingly suggested that the substance associated with the cellulose of the cell wall, had an aromatic nucleus and he designated it as "lignose".

Cross and Bevan(28) in 1903, as a result of many years of investigation on lignified and other plant tissues, concluded that lignin was chemically combined with the cellulose and called this substance "lignocellulose".

The use of alkali in the delignification of wood dates from the 1854 U. S. patents of Watt and Burgess.(20) In this process, known as the "soda process", the wood is cooked in a solution of caustic soda whereby the lignin and hemicelluloses are rendered soluble, and an impure cellulose pulp obtained in yields of 43 to 48 per cent by weight. Dahl(20) is credited with the modification of the "soda process" known as the "sulfate" or "kraft" process. He was issued a patent in 1884 suggesting the use of sodium sulfide in the cooking liquor to make up alkali losses.

<u>Lignin Isolation</u>. There are various methods described in the literature for the isolation of lignin,(28) these may be divided into two classes: (1) Those that depend on the

removal, by hydrolysis, of the cellulose and other components, leaving the lignin as an insoluble residue, and (2) those that depend on the removal of lignin from the cellulose and the other substances with which it is associated.

Much of the difficulty involved in determining the constitution of lignin can be attributed to the fact that, as yet, no method is known by which lignin can be isolated unchanged. Also, since lignin is amorphous, the usual criteria of purity, such as melting point, cannot be applied. Therefore, it is never certain if any particular lignin preparation is entirely free from contaminants.

Methods of Class I. The following methods of lignin isolation are some of the more used processes that depend upon the removal, by hydrolysis, of the cellulose and other components leaving the lignin as insoluble residue:

1. Sulfuric acid method.(28,25) Sulfuric or Klason(7) Lignin is produced from ground wood by the action of sulfuric acid. The wood is first extracted with ether and dried. Then for every gram of wood 50 ml. of 66 per cent sulfuric acid is employed and the mixture is allowed to stand for 48 hours then diluted to 3 per cent, heated and washed.
2. Fuming hydrochloric acid method. This method was first developed by Willstatter and Zechmeister.(7,28) These investigators found that 40 to 42 per cent hydrochloric acid readily dissolved cellulose, giving a

yield of from 25 to 28 per cent lignin. According to Hagglund(28) a portion of the lignin is dissolved by the fuming acid, and later separates out. Modifications of this method have been developed by Willstatter, Kalb, Lieser,(7,28) and Urban.

3. Method of Freudenberg. In this method(7,28) lignin is isolated by alternately hydrolyzing wood, previously degummed by digestion with cold 5 per cent aqueous sodium hydroxide solution, with boiling 1 per cent sulfuric acid and cuprammonium solution. Some of the lignin is dissolved by the cuprammonium solution and yields are around 16 per cent of the weight of the dried wood.

Methods of Class II. The following methods of lignin isolation depend on the removal of lignin from cellulose and the other substances with which it is associated:

1. Sulfite method. This is the method used in the "Sulfite" process of preparation of wood pulp. The delignification is brought about by heating wood with a solution of sulfurous acid and acid sulfites under pressure. Lignin is obtained in the form of water-soluble sulfonic acids.

2. Alkali method. The delignification of wood by sodium hydroxide solution or sodium hydroxide and sodium sulfide is commercially known as the "soda"

and the "sulfate" processes for manufacture of pulp. (7,20,28) These reagents form alkali soluble alkali-lignins and thio-lignins which are precipitated from the alkali salt solutions by acidification with mineral acid. Both thio-lignin and alkali-lignin are insoluble in water and can be precipitated from alkali salt solutions by lime water. A number of investigators have used aqueous and alcoholic sodium hydroxide, varying from 1.5 to 10.0 per cent sodium hydroxide and using temperatures as high as 160°C.

3. Separation of lignin by alcoholysis. Klason(28) in 1893 found that a portion of lignin was dissolved when spruce wood was heated with alcohol. This work was followed up in 1920 by Gruss.(28) In place of ethanol other alcohols such as methanol,butyl and amyl alcohols, benzyl alcohol, ethylene glycol and its monomethyl ether, glycerol oc-monochlorohydrin and dioxane may be used. In all cases a product is obtained containing the alkyl or aryl group, as the case may be, in combination with the lignin. The mechanism of the reaction between the hydroxy compound and lignin is not clear. It has been suggested by Hagglund(28) that a product in the nature of an acetal is formed. These reagents should be born in mind when chlorination of lignin is attempted in

different media. There are six or more procedures of isolation of lignin by this method. The ground wood is heated with alcohol from 10 hours to three days depending on the method used.

4. Extraction of lignin with phenols. The phenols like alcohols combine chemically with the lignin yielding the so called phenol lignin. According to Kalb and Schoeller(28) phenol lignin may be prepared by heating sawdust with phenol and hydroloric acid for 1 hour at 90°C. The reaction product is filtered, and the filtrate distilled in a current of steam to remove the excess phenol, leaving the lignin preparation in the distilling flask.

5. Other methods. Thioglycollic acid and hydrochloric heated with wood meal and the reaction extracted with 95 per cent ethanol. Friedrich (28) obtained a lignin preparation by treating wood meal with a mixture of glacial acetic acid and concentrated hydrochloric acid. Formic acid lignin is obtained by treating wood meal with 92 per cent formic acid after the wood has been alcohol extracted.

Physical Properties. X-ray studies mady by Harris(28) of sulfuric acid and methanol lignins, and their products of reactions showed a X-ray pattern typical of the crystal lattice of organic substances of high molecular weight.

The ultraviolet absorption spectra of lignin and lignin derivatives as determined by Herzog and others(28) indicate a benzenoid structure. Depending on the mode of isolation lignin is light to dark brown in color, insoluble in organic solvents, and morphological in structure. Lignin has a high refractive index. 1.61, which is indicative of aromatic structure, and its heat of combustion has been found as 6.277 Kg. Cal.

Constituent Groups. The different types of lignins(25) all have certain common chemical radicals. Methoxyl groups are always present. Both phenolic hydroxyls and aliphatic hydroxyls are present. It is now well established that lignin is built up almost entirely of building stones consisting essentially of an aromatic ring containing a three-carbon side chain, one or two methoxyl groups meta- to this side chain, and an oxygen bridge or phenolic group para- to the side chain. In addition, there may be carbon-to-carbon or carbon-to-oxygen bonds joining the aromatic ring to other portions of the structure.

Methoxyl Group (CH_3). The presence of the methoxyl group has been definitely established in the lignin preparations isolated from various sources and by different methods. The methoxyl content(9,7,28) of lignin from coniferous woods and straws is about 15 per cent and that from deciduous woods is about 21.5 per cent, varying somewhat with the method of isolation. Since methoxyl groups of lignin are not readily split off, it is inferred that they form an ether rather than an ester linkage. According to Freudenberg and co-workers, the methoxyl groups present in lignin are attached to aromatic nuclei. The methoxyl content of lignin varies somewhat with the source and the method employed in its isolation and is also effected by the age of the plant tissue from which the lignin is derived. When alcohols or phenols are used for the isolation of lignin, a product is obtained containing the alkyl or aryl groups, as the case may be. Depending on the nature of the combining groups, the percentage of methoxyl in the lignin may be either higher or lower than that found in alkali or acid lignins. Thus, for example, the percentage of alkoxyl, calculated as methoxyl in methanol and ethanol lignins are relatively high, because the alkyl groups arising from the alcohols used in the isolation of the lignin as well as the methoxyl groups naturally present in the lignin complex react with the hydriodic acid used in the Zeisel determination and thus give high methoxyl values.

Determination of Methoxyl. The first quantitative procedure(3,4,13) for the determination of the methoxyl group was proposed by Zeisel in 1865. The principle of this method depends upon the formation of methyl iodide when the unknown is heated with hydroic acid. The methoxyl iodide is removed with a current of carbon dioxide into absorption vessels where it is finally absorbed in a solution of alcoholic silver nitrate, the alkyl iodide being decomposed with the formation of silver iodide. The silver iodide is then recovered, weighed, and the methoxyl content is calculated.

Freeman(13) recommends the modification of this process which was proposed by Viebock and Brecher. The method depends upon the conversion of the alkoxyl groups to alkyl iodides with hydriodic acid, oxidation of the iodide to iodate, and iodometric determination of the iodate using potassium iodide an the standard thiosulfate. The alkyl iodide is absorbed in an acetic acid solution of potassium acetate to which a little bromine is added. The reactions taking place are as follows:

$\text{Wood-}(OCH_3)n + HI = CH_3I + \text{decompositions products}$

$CH_3I + Br_2 = CH_3Br + IBr$

$IBr + 2Br_2 + 3H_2O = HIO_3 + 5HBr$

$HIO_3 + 5KI + 5H = 3I_2 + 3H_2O + 5K$

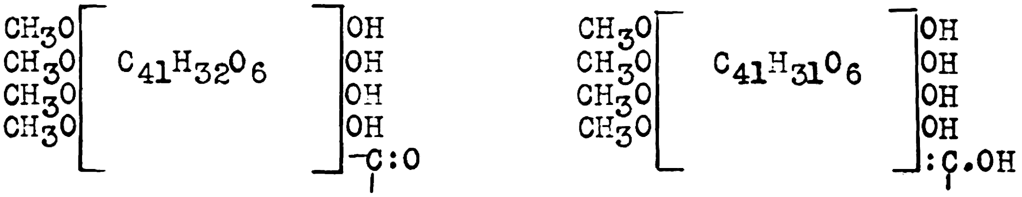
$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$

<u>Hydroxyl Groups</u>. The presence of hydroxyl groups(28) in lignin is indicated by the fact that it can be acetylated and alkylated. Complete methylation of the hydroxyl groups can be effected with dimethyl sulfate and alkali. However with diazomethane only a fraction of the hydroxyl groups can be methylated, from which it is inferred that

some of the hydroxyls groups are phenolic or enolic in character.

Acetyl Group. The fact that various lignified plant materials, when distilled with dilute sulfuric acid or digested in the cold with sodium hydroxide, yield acetic acid or sodium acetate, respectively. Whereas cellulose treated under similar conditions does not yield these products, has been accepted by certain investigators as evidence of the presence of the acetyl group in lignin. However, it has been recently demonstrated that, at least in the woods investigated, the acetyl group is associated with the carbohydrates and is not a part of the lignin complex.

Carbonyl Group. The evidence as to the presence of carbonyl group in lignin is rather inconclusive. Powell and Whittaker(29,30) found that their lignin preparations reduced Fehling's solution and concluded from this that an aldehydic group was present. Since, however, substances other than aldehydes can reduce Fehling's solution,(28) the claim of Powell and Whittaker must be accepted with considerable reserve. Brauns(28) found that isolated native lignin when treated with methyl alcohol-hydrochloric acid takes up two methoxyl groups and these are removed when treated with 72 per cent sulfuric acid. From this he concluded that a carbonyl group was present in the native lignin. Brauns also advanced a formulation for this native lignin, which is supported by clear cut analytical data, and involves a keto-enolic isomerism.



$$\begin{array}{l}CH_3O\\CH_3O\\CH_3O\\CH_3O\end{array}\left[\quad C_{41}H_{32}O_6 \quad\right]\begin{array}{l}OH\\OH\\OH\\OH\\-\underset{|}{C}:O\end{array} \qquad \begin{array}{l}CH_3O\\CH_3O\\CH_3O\\CH_3O\end{array}\left[\quad C_{41}H_{31}O_6 \quad\right]\begin{array}{l}OH\\OH\\OH\\OH\\:\underset{|}{C}.OH\end{array}$$

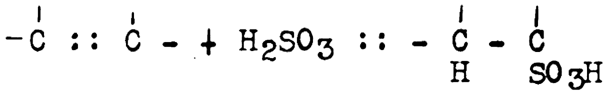
Brauns Empirical Structure For Native Lignin

The various methylated products are accounted for by this skeletal formula with a high degree of accuracy. This formula offers a measuring rod for use in evaluating formulas suggested by other workers. These results apply to the native lignin of spruce and western hemlock.

However, isolated native lignin represents only about 8 to 10 per cent of the total lignin content. Hagglund has advanced the fact that lignosulfonic acids from condensation products with aromatic amines and also that these acids contain a portion of this sulfur in the form of loosely bound sulfurous acid as evidence of the presence of active carbonyl groups in lignin. However, lignosulfonic acids are obtained as a result of the reaction of lignin with bisulfite and sulfurous acid at relatively high temperatures. Under these conditions, drastic changes in the structure of lignin undoubtedly take place, so that even if it is assumed that carbonyl groups are present in lignosulfonic acids, it does not necessarily follow that these groups are actually present in the lignin itself.

Methylenedioxy Group ($-O-CH_2-O-$). Freudenberg(28) found that lignin isolated from wood by Urban's method when distilled with 12 per cent hydrochloric acid yields formaldehyde. From this evidence Freudenberg advanced the hypothesis that the formaldehyde arises from a methylenedioxy group present in the lignin molecule, as compounds containing this group are known to yield formaldehyde when they are distilled with hydrochloric or dilute sulfuric acid. All investigators agree that certain isolated lignin when distilled with dilute hydrochloric or sulfuric acids yield some formaldehyde (0.5 to 4 per cent). There is however a disagreement as to whether this can be accepted as evidence of the presence of the methylenedioxy group in lignin.

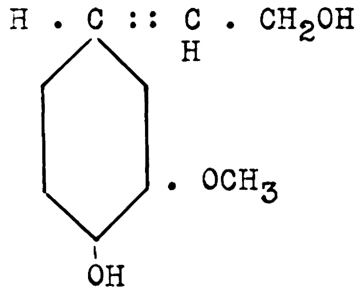
Ethylene Bond. The presence of the ethylenic bond in lignin has not been definitely established and the data are rather contradictory. This lack of agreement may perhaps be explained by the fact that lignins isolated by various methods behave differently with the reagents commonly used for detection and estimation of unsaturated groups. Klason assumed that an ethylenic bond was present in lignin and that the formation of the stable sulfonic takes place as follows:



$$-\overset{|}{C} :: \overset{|}{C} - + H_2SO_3 :: -\underset{H}{\overset{|}{C}} - \underset{SO_3H}{\overset{|}{C}}$$

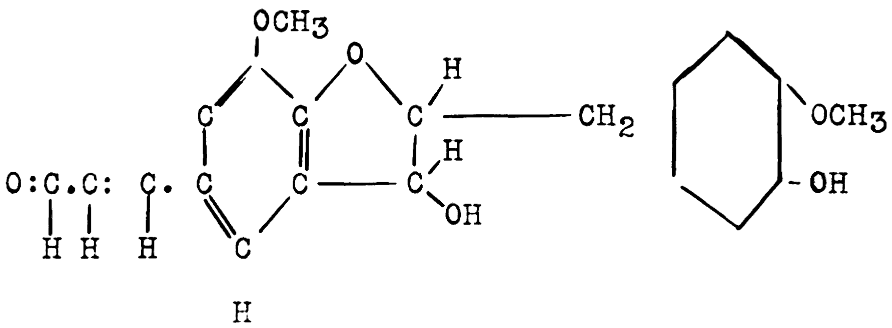
Formation of Sulfonic Acid

<u>Structure of Lignin</u>. Phillips(28) states that it cannot be emphasized too strongly that it is entirely premature to propose any constitutional formula for lignin considering the incomplete knowledge of the chemistry of this substance. However, in view of the fact that all proposed structures of lignin are based on experimental work and have foundation and aid in the interpretation of experimental work, several of the proposals of the leading investigators are presented. Several investigators have proposed that lignin is essentially a condensation polymer of simple units. Klason(28) first suggested an aromatic structure of lignin and considered that it is essentially a polymer, or condensation product of coniferyl alcohol or coniferyl aldehyde and oxyconiferyl alcohol. This concept of the structure is in harmony with the hypothesis, now accepted by several investigators, that lignin is essentially a condensation polymer of simple units.

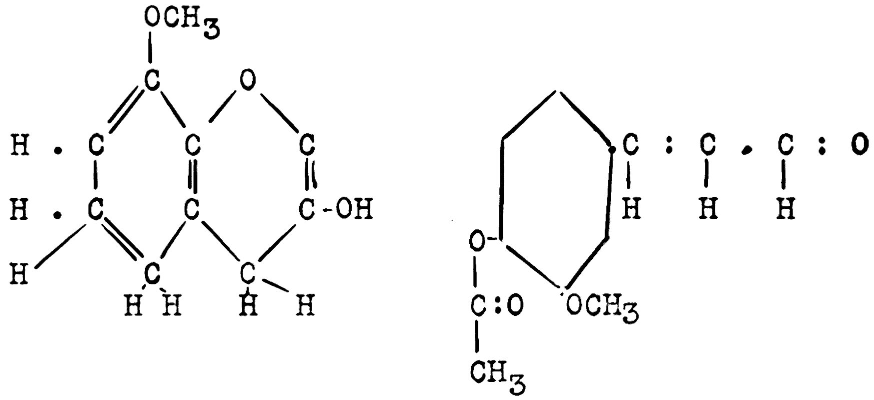


Coniferyl Alcohol

Klason proposed in 1923 the following two possible structures for lignin, which he precipitated from sulfite waste liquor with calcium chloride.



Formula A

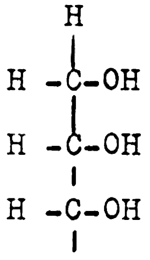


Formula B

Klason considered that the lignin precipitated was a condensation product of coniferyl aldehyde.

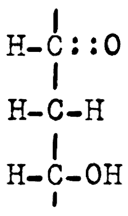
Probably the most significant discovery regarding the nature of the nucleus was that of Phillips,(6) who distilled alkali lignin from corncobs with zinc dust in an atmosphere of hydrogen at a temperature not exceeding 400°C and first identified among the phenolic products 1-propyl-3-methoxy-4-hydroxybenzene, as well as catechol and guaiacol. A neutral fraction was also obtained, which yielded anisic acid ($p-CH_3OC_6H_4CO_2H$) when oxidized with potassium permangnate. These results suggested the presence in lignin of one aromatic nucleus having a side chain of three carbon atoms, in addition to a methoxy group and a hydroxyl group in the meta and para positions, respectively, to the side chain and of a second neucleus with a methoxyl group para to the side chain $-C_6H_4OMe$.

Proposed Mechanism of Lignin Formation. Freudenberg and co-workers have presented a theory of building units combining to form several possible structures for lignin. Freudenberg considers that the three carbon side chain in the lignin molecule may be either I, II, or III as shown below:



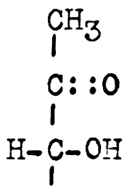
$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \end{array}$$

I



$$\begin{array}{c} | \\ H-C::O \\ | \\ H-C-H \\ | \\ H-C-OH \\ | \end{array}$$

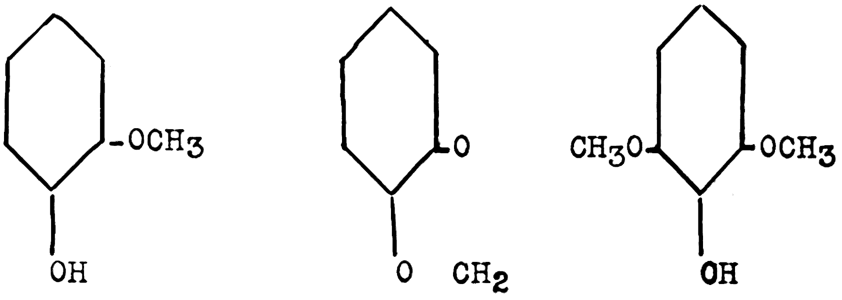
II



$$\begin{array}{c} CH_3 \\ | \\ C::O \\ | \\ H-C-OH \\ | \end{array}$$

III

These side chains are attached to aromatic nuclei IV, V and VI which are shown below:



IV. V. VI.

Aromatic Nuclei

Lignin may be regarded as a product resulting from the etherification and subsequent condensation of the above mentioned building units, the etherification taking place through a phenolic hydroxyl group and an alcoholic hydroxyl group of the side chain. One of the reactions believed to take place is represented in Fig. 1.

Such condensation products may undergo further etherification and condensation with other building units in a similar manner to that illustrated in Fig. 1., and complex products of high molecular weight may be formed. Similarly in place of building units containing the aromatic nuceleus IV, other units containing the aromatic nuclei, V and VI with side chains II and III may undergo etherification and condensation in an analogous manner to that illustrated.

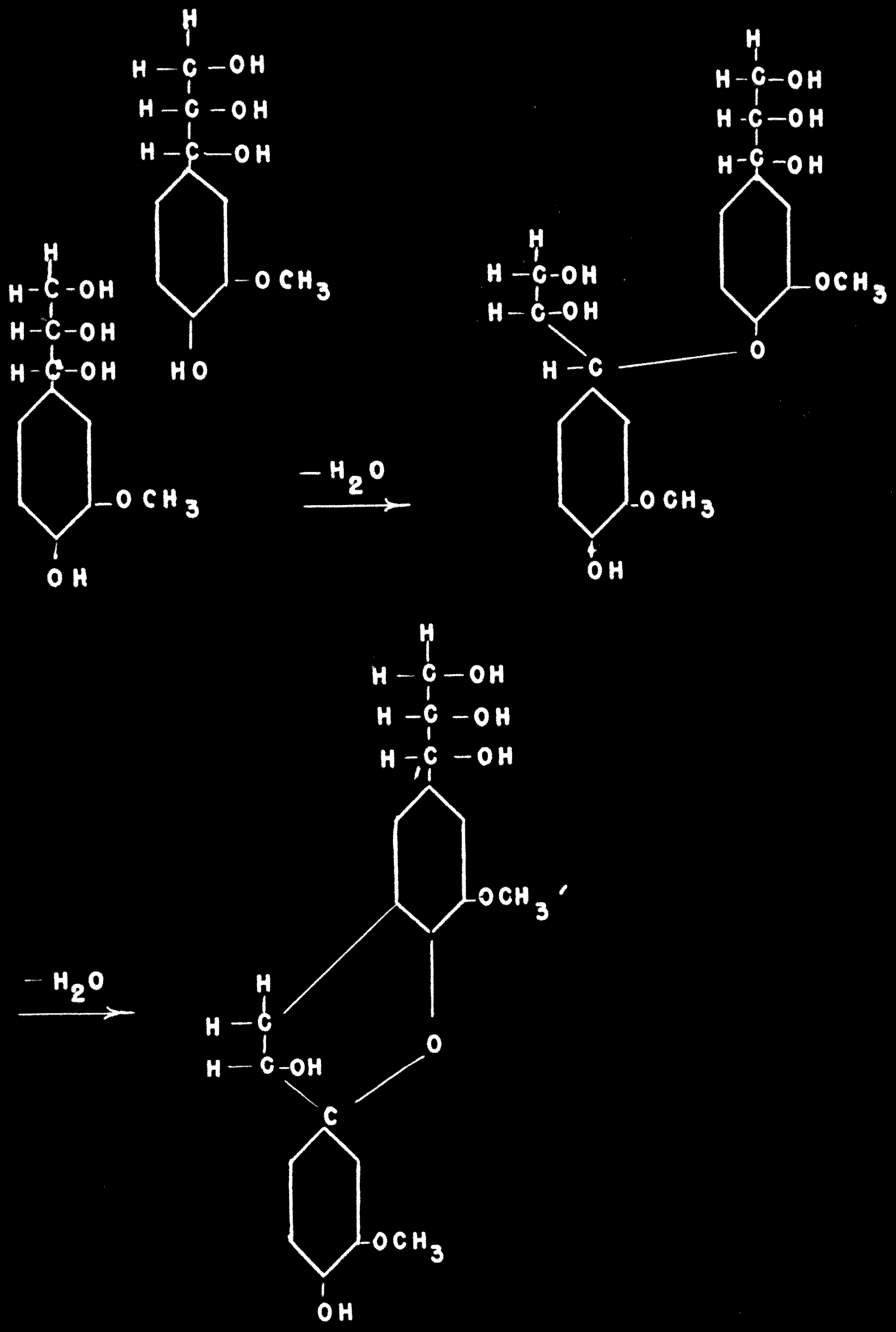


FIG. I

Freudenberg theory of condensation of aromatic building units to form lignin (20)

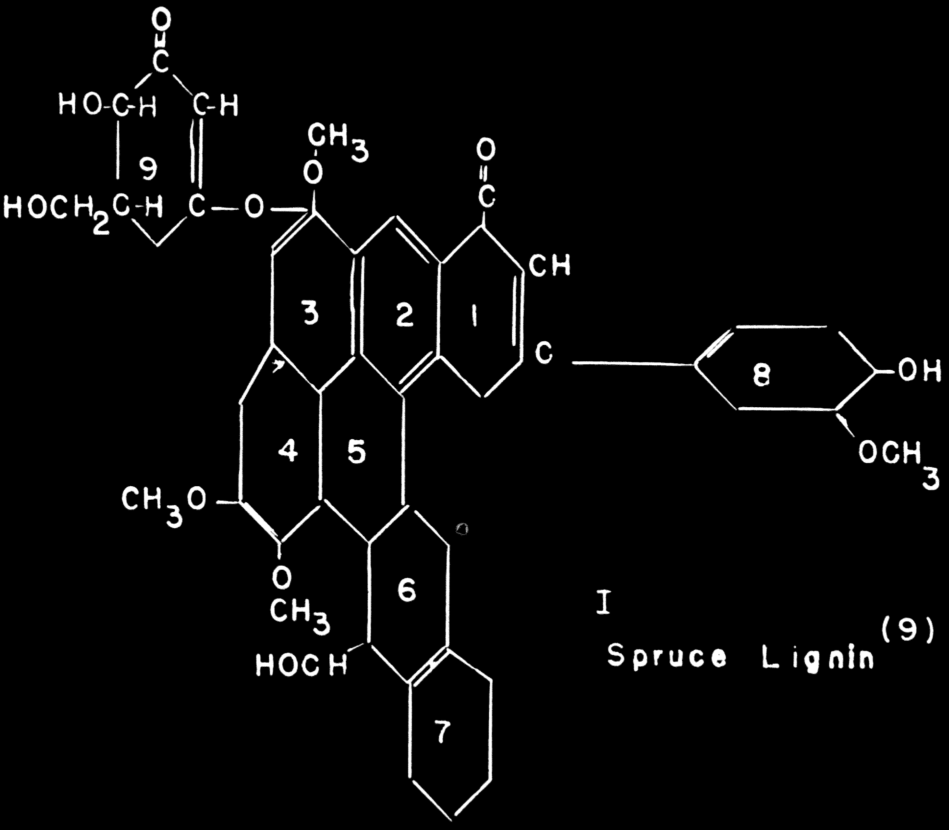
Phenol Lignin. The various lignins react with phenols by a mechanism not too clearly defined. This reaction(25) which occurs in the presence of acid as a catalyst may take place more often than has been proven by investigations when certain types of lignified tissue containing either tannin or coloring matter are treated with acidified solvents.

Phenol lignins can be prepared by heating sawdust with phenol and hydrochloric acid for 1 hour at 90°C. Buckland(28) prepared phenol-lignin from sawdust and obtained a yield of phenol lignin which amounted to 67 per cent of the weight of the original wood meal taken. The residual dark-brown tarry solid which results from the reaction is dissolved in methyl alcohol and the lignin is precipitated by adding this solution dropwise to distilled water. Attempts have been made to fractionate phenol lignin and use it in studies on the structure of lignin. However, lignin is itself of complex structure and when it is heated with phenol at elevated temperatures a complex mixture of various condensation products is formed and it is practically impossible to interpret results obtained from such a mixture in terms of the original lignin.

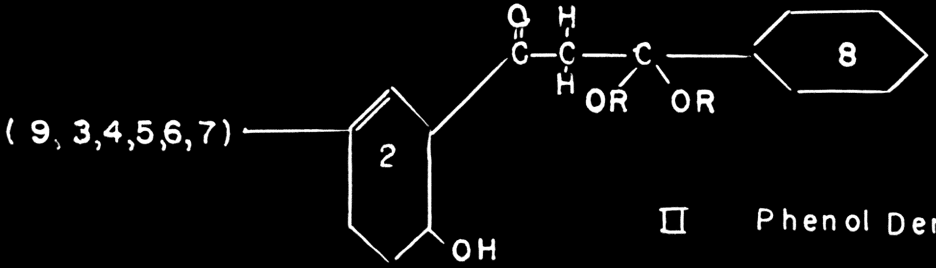
When(28) alcohols or phenols are used for the isolation of lignin a product is obtained containing the alkyl group or the aryl group as the case may be. Depending on the nature of the combining group, the percentage of metholyl in the lignin may be either higher or lower than that found in alkali or acid lignins. Thus for example the percentages of alkoxyl, calculated as methoxyl in methanol and ethanol are relatively high because the alkyl arising from the alcohols used in the isolation of lignin, as well as the methoxyl groups naturally present in the lignin complex react with the hydriodic acid used in the Zeisel determination, and thus give high methoxyl values. On the other hand, the percentages of methoxyl in phenol lignin is less than native lignin or Willstatter lignins, because the phenol groups which have combined with the lignin yield no alkali iodide under the conditions prevailing in the Zeisel determination. Moreover, by condensing lignin with phenol, the molecular complexity of the resulting product is increased and the relative proportions of methoxyl naturally present in lignin is correspondingly decreased.

Fuchs(14)experimented with phenol as a delignifing agent with spruce wood. He achieved definite results in breaking the phenol lignin bond in phenol lignin. Hagglund(14)was unable to achieve a cleavage of the phenol introduced into phenol lignin and therefore assumed an essentical difference between phenol lignin and the various aryl lignins. This assumption according to Fuchs, is erroneous. The phenol introduced into phenol lignin may be split off, at least in part, by heating the substance with a mixture of acetic acid and hydrobromic or hydriodic acid preferably in the presence of small amounts of reducing agents, such as phosphorous or hydrophosphorous acid. The cleavage of the phenol lignin definitely proves, at least for the phenol split off, either an acetal linkage as previously postulated or an ether linkage as assumed by Hibbert(9).

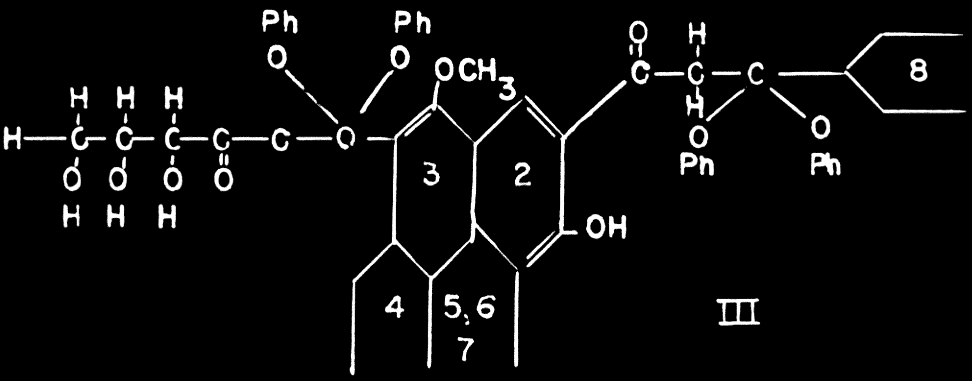
Fuchs(14) has suggested the formulation of a hypothetical substance, the properties of which are consistant with what is known as spruce lignin and its fusion products. This formulation is represented in Fig. 2. The analytical data agree fairly well with formula I, formulas II and III reported possibilities concerning the formulation of phenol and methoxyl derivatives. In this respect the following contradication is observed: acetals of simple substances are easily formed and easily decomposed, ethers are more difficult to obtain and harder to hydrolize. Since the products in question are obtained easily, but not easily decomposed, both possibilities are apparently conceivable; in Fuchs opinion, however, the evidence



I
Spruce Lignin (9)



II Phenol Derivatives



III

FIG. 2

for acetal formation by ring splitting is stronger. As to break down experiments, catechol derivatives may be traced to ring 8, phenol derivatives to ring 2, and benzene derivatives to the system comprising rings 5, 2, 3, 4, and 6. This formula was presented as a means of summing up the results obtained by Fuchs and others in their investigations, and of expressing new experimental procedures.

Alkaline Delignification. The soda process for delignification of wood is the cooking of wood in a solution of caustic soda and rendering soluble the lignin and hemicelluloses. The "sulfate" or "kraft" process is the soda process modified by the addition of sodium sulfide to the cooking liquor. Sodium sulfate is added to the liquor to make up alkali losses: the sodium sulfate is reduced to sodium sulfide during the process of alkali recovery. The "sulfate" process has proved superior to the "soda" process from the standpoint of pulp yield, quality and cost, and is of much greater industrial importance. The sulfate pulp was over 4,428,000 tons in 1941(25) as compared to 2,890,000 tons of sulfite pulp and 609,000 tons of soda pulp produced in 1941. This tonnage of sulfate pulp was made by a total of 39 mills(2) through out the country, which at the same time produced between 1,500,000 and 2,000,000 tons of lignin.

This lignin was used as a fuel since it was recovered when the black liquors from the process were evaporated for alkali recovery. These Kraft mills are located predominantly in the south, 24 of the 39 mills being located in this section of the country, so as to utilize the large tracts of southern pine. Typically sulfate pulp(5) is made from pine which includes the longleaf, shortleaf, loblolly, pond, and slash species; however the sulfate process is applicable to almost any wood since resins and and other extraneous materials do not interfere as they do in the sulfite process. The pulp from these coniferous woods has the longest wood fibers. For this reason, and because the sulfate process does not attack the fibers so harshly as in the acid or soda process the sulphate pulp has high strength.

Types of Alkali Lignins. Although alkaline pulping has been practiced for many years the chemical reactions involved are largely unknown.(20) Study of the action of alkali on wood is extremely difficult, due to the heterogeneous nature of the reactions involved and the fact that both carbohydrates and lignin decompose in the presence of alkali at elevated temperatures. Brauns and Hibbert(18) have shown that two different lignin derivatives are obtained, by acid precipitation, from the black liquor obtained on soda pulping of spruce wood. These two fractions, called alkali lignin A and alkali lignin B vary in their solubility in dioxine-ether and in their ratios of acidic hydroxyl to methoxyl groups as shown by methylation experiments.

	Methoxyl Groups	Acetic Hydroxyl Groups
Lignin (from methanol lignin)	12	2.5
Alkali lignin A	8	4.0
Alkali lignin B	9	8.0

From these data it appears that the single phenolic enolic hydroxyl group in the highly polymerized lignin complex is not sufficient to bring about solution in sodium hydroxide, but under conditions prevailing in alkaline pulping, new hydroxyl groups are formed. Such new hydroxyl groups, according to Brauns and Grimes,(20) may be formed either by the hydrolysis of a methoxyl group (phenolic, enolic or acidic) with the simultaneous formation of methanol by the opening of a furan or pyran ring, or by the combination of both reactions. The reaction involving the hydrolysis of methoxyl groups with the formation of methanol appears probable, since methanol is found as a by-product of the soda process and the methoxyl content of alkali is less than that of native lignin. Decrease in methoxyl content is approximately equivalent to one methoxyl per lignin building unit of 850 molecular weight, and if the hydroxyl formed on splitting off methanol is acidic in character, it would produce the ratio of methoxyl to acetic hydroxyl of 8:4 experimentally found in the case of alkali lignin A. However this is probably not the only change which takes place in the lignin, because all of the hydroxyl groups cannot be derived from existing methoxyl groups, and some of the hydroxyls must come from other reactions as yet unknown.

Effect of Sulfur on Alkaline Delignification. Presence of sulfur in the cooking liquor in the form of sodium sulfide results in a distinct acceleration in the rate of solution of lignin. However, the chemistry involved in this process has been little investigated, with the result that less is known concerning the role of sulfur than is known of the action of caustic soda.

In the sulfate process,(20)sodium hydrosulfide is derived from hydrolysis of sodium sulfide. According to Bray, Swartz, and Fong sodium hydrosulfide hydrolyses rapidly on contact with water giving Na_2S, NaOH, and H_2S. However, Hanson(20)states that spruce wood may be pulped by cooking with a pure solution of sodium hydrosulfide. The sulfur content of lignin approaches 10 per cent as a maximum, equivalent to the introduction of three atoms of sulfur per lignin building unit of 850 molecular weight.

The work of Ahlm as reported by Brauns indicates that lignin of spruce wood, cooked in sodium sulfide, forms a thiolignin containing 3.7 per cent sulfur, equivalent to one sulfur atom per lignin building unit. Such thiolignin, methylated with hydrochloric acid and methanol, adds only one methoxyl unit, whereas if it is methylated with diazomethane, three methoxyl units are introduced. On the basis of this evidence it may be postulated that sodium hydro-sulfide reacts with a carbonyl group in the lignin, with the formation of a mercapto-group. There are thus three groups in the lignin capable of forming sodium salts, namely one mercapto-group and two hydroxyl groups. Sodium hydroxide in the cooking liquor aids in the dissolution of lignin by the formation of sodium salts with the hydroxyls, solubility of the lignin being increased by the presence of sulfur.

Mechanism of Alkaline Delignification. The mechanism of alkaline delignification appears to involve three separate stages:

1. Absorption of alkali at the lignin-liquor interface by acidic phenolic groups in the lignin complex. This interface is in saturated equilibrium with alkali in the liquid phase, since it has been shown that the diffusion of alkali to this interface is rapid and does not influence the reaction rate.

2. Following absorption of alkali, a chemical combination takes place between the lignin and the absorbed alkali.

3. In the final stage, chemical hydrolysis takes place and the alkali lignin complex separates from the lignin surface and enters the liquid. The energy calculated to be necessary for the solution of one alkali-lignin complex is of the order $5.3/10^{-20}$ calories.

Variables of Alkaline Delignification. Delignification of wood by alkali is affected by several variables in addition to the variations inherent in the types and quality of wood used. These process variables are:

1. Time of Digestion.

2. Maximum Temperature of Digestion. Bray(20) has shown that the physical characteristics of pulps from the sulfate process are not changed by varying the temperature from 160 to 180 degrees Centigrade, pulp being compared at the same yield. However, Lewis and Laughin found that cooking at 200°C by the soda process destroys both cellulose and lignin, and that the residue insoluble in 72 per cent sulfuric acid (ie: the lignin) increases on prolonged cooking at this temperature. It was suggested that such high temperatures bring about the

formation of a cellulose-lignin condensation product, which is insoluble in 72 per cent sulfuric acid, and this appears as lignin on analysis.

3. Amount of Active Alkali Used. In the case of the sulfate process, it is the sum of sodium hydroxide and sodium sulfide. Bray, Martin, and Schwartz found that increasing the amount of chemical in the sulfate process from 15 to 25 per cent increased the amount of lignin in the waste. The same investigators found that above 25 per cent chemical, based on wood weight, does not increase delignification of pulp but does have a destructive effect on the cellulose.

4. Concentration of Active Alkali in the Cooking Liquor. The rate of delignification increases with the concentration of the liquor. The rate at which alkali lignin is dissolved is substantially inversely proportional to the logarithm of the alkali concentration. On the basis of their experiment with concentrated alkali, Machlin and Maass suggest that delignification takes place in two distinct steps; in the first, lignin is obtained in a colloidally soluble form; and in the second, this alkali lignin is dispersed or peptized in solution. The formation of alkali lignin proceeds very rapidly in high concentrations of sodium hydroxide but, due to a salting out effect, this changed lignin does not enter

solution except as the lignin micelles are broken down into smaller particles. At concentrations below 20 per cent of sodium hydroxide, solution of the lignin proceeds normally as it reacts with the alkali. The action of high concentration alkali on the cellulose is unfavorable, since it has been found that the pulp obtained is of low viscosity and alpha-cellulose content, indicating that solution of such high concentration tend to produce fission of the cellulose chain.

5. Sulfidity of the Cooking Liquor. Sulfidity, which is the sodium sulfide present in the cooking liquor expressed as a percentage of the sum of the sodium sulfide and sodium hydroxide present. In the sulfate process, losses in alkali are replaced by addition of sodium sulfide in the recovery system, such sodium sulfide being reduced to sodium sulfide during the burning and smelting of the black liquor solids. Bray, Martin, and Schwartz state that sodium sulfite in the cooking liquor hydrolyze according to the following equation:

$$Na_2S + H_2O :: NaOH + NaSH$$

They assumed that this hydrolysis was complete in the sulfate cooking liquor, and that sodium hydroxide was the active delignifying agent, and that on this basis, calculated that only 51.3 per cent of the sulfide added to the cooking liquor would be available as active cooking agent. A series of cooks were made in which the sum of the sodium hydroxide added as such and the sodium hydroxide formed, according to the equation above, was held constant and the sulfidity varied from zero to 100 per cent. Results showed that sodium sulfide has a specific effect in pulping in addition to its contribution to the content of caustic soda in the cooking liquor, made available through hydrolysis, and that sodium hydrosulfide formed in the cooking liquor acts mainly through its high reactivity with lignin. The major part of the changes brought about by increasing sulfidity are obtained through use of sulfidities up to 25 per cent.

Sodium Sulfide as a Pulping Agent. Aronovsky and Gorthner(6) ran a series of wood cooks using only sodium sulfide as a pulping agent. This being one of the two main ingredients of the cooking liquor for sulfate pulp. The following equations show some of the reactions which undoubtedly take place during the cooking process.

$$2Na_2S + 3O_2 :: 2Na_2SO_3$$

$$Na_2S + 2H_2O :: 2NaOH + H_2S$$

$$2H_2S + O_2 :: 2H_2O + 2S$$

$$Na_2SO_3 + 2H_2O :: 2NaOH + H_2SO_3$$

$$H_2SO_3 \rightleftharpoons H_2O + SO_2$$

$$2H_2S + SO_2 :: 2H_2O + 3S$$

$$Na_2SO_3 + S :: Na_2S_2O_3$$

They also found that the amounts of lignin in the liquor increased with increasing concentration of sodium sulfide in the cooking liquors, but an increase in time and temperature of cooking had little effect on this substance. The amounts of sulfur chemically combined with the lignin increased with the increase in sodium sulfide used in cooking. The time and temperature of cooking had very little effect upon the sulfur content of the lignin. It appears that the percentages of lignin-sulfur compounds formed were dependent, not on the amounts of lignin present, but on the quantities of sodium sulfide used in the cooking liquor.

Summary of Alkaline Delignification. Brauns(7) summarizes the process of alkaline delignification. He states in the sulfate process the lignin is rendered soluble by digesting the wood with a mixture of one part sodium sulfide and two parts of sodium hydroxide in a 5 per cent solution at 160 - 180°C. From the black liquor lignin is thrown out together with some hemicelluloses by acidification with mineral acid, and is obtained, after purification, as a light-brown powder consisting of a mixture of thiolignin and alkali lignin. The exact mechanism of the reaction between sodium sulfide and lignin is not yet known but there is little doubt that because of the partial hydrolysis of the sulfide a mercapto group is formed in the lignin molecule. Alkali lignin from the soda process has been the subject of various investigations but the results vary widely, because the lignin is more or less drastically attacked by the alkaline cooking liquor. In both the sulfate and soda pulps the residual lignin is chemically changed.

Alcoholysis. In the isolation of lignin from wood by alcoholysis, the reaction mixture obtained after heating the wood with an alcohol and catalyst is filtered, the filtrate concentrated, and poured in an excess of water, whereupon the lignin is precipitated. This wood has been previously extracted with alcohol-benzene solution and degummed with a five per cent sodium hydroxide solution to remove the natural oils from the wood sample.

The filtrate from the isolation process contains important degradation products of lignin, which may be isolated by extraction of the filtrate with ether or benzene. The oily extract thus obtained was further extracted with 20 per cent sodium bisulfide solution, a saturated sodium bicarbonate solution, and 2 per cent sodium hydroxide solution. It was thus resolved into aldehydic or ketonic, acidic, phenolic, and neutral components. In the phenolic fraction of the oil from the ether oc-ethoxypropiovanillone was shown to be present. In the fraction of the oil soluble in the sodium bisulfide solution, vanillin, spyringaldehyde, and methyl 4-hydroxy-3, 5 dimethoxyphenyl diketone were identified.

It has been further found that ethanolysis of softwoods yields guaiacyl derivatives, whereas hardwoods yielded both guaiacyl and syringyl derivatives.

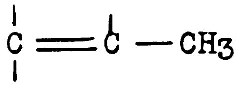
Alkylation and Halogenation. Harris and Sherrard(17,18) have studied the chemical reactions of lignin, using maple and spruce wood as the source of their lignin. These woods were chosen since it had been observed that hard woods differ from softwoods in lignin content. The investigators used 72 per cent sulfuric acid to dissolve the lignin, and produce a lignin free from carbohydrates. Their experiments with lignin prepared by the Hagglund and cuprammonium methods showed that the lignin was still combined with the carbohydrates. They found that lignin prepared by the Klason method produces charring, splits out acetic acid and also splits out formaldehyde, thus removing from the lignin the methylene oxide groups.

Methylation of Sulfuric Acid Lignin. The methylation, gromination and chlorination experiments of Harris and Sherrard(17,18) are related and will be discussed together. A unit molecular weight of 890 for the spruce lignin and approximately 1400 for the maple lignin were used to base the calculations of percentages of groups lost and added to the reactions. Spruce lignin as isolated contained

17 per cent methoxyl and when methylated with 1 per cent alkali (the authors do not state the reagent for methylation, Powell and Whittaker used methyl sulfate.(30)) the methoxyl derivative contained 21 per cent methoxyl, a second methylation with 5 per cent alkali gave a derivative with 24 per cent methoxyl and again with 15 per cent NaOH and obtained fully methylated lignin containing 32 per cent methoxyl. The 32 per cent was equivalent to 10 methoxyl groups in the unit. Maple lignin was fully methylated with 1 per cent NaOH and contained 32 per cent methoxyl. The authors state that this stepwise methylation indicated OH groups of different properties. The first hydroxyl group methylated indicated either a phenolic or an enolic grouping. When the lignins of both woods were chlorinated they lost their ability to be methylated and therefore must have lost all reactive groups. However, Harris in a latter investigation(16)found that during chlorination the lignin was also methylated. Phenolic hydroxyls are usually resistant to chlorinations while enolic or ethylenic linkage would be capable of being methylated easily and also be destroyed by chlorination.

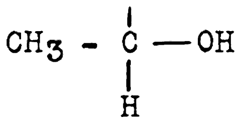
In comparing the two lignin on the basis of their methoxyl content it is noted that the fully methylated derivatives contain about the same amount of methoxy groups, this would indicate that both lignins have the same number of hydroxyl groups that can be methylated. In the original lignin the spruce showed half of the hydroxyls were methylated and the maple wood lignin showed 3/5 methylated, also in the ease of methylation there is a difference in the two lignins, Maple lignin can be methylated in a per cent sodium hydroxide solution while spruce lignin required a concentration of over 15 per cent alkali. The reactivity of the last hydroxyls of spruce lignin corresponds to primary and secondary alcohols.

Chlorination of Sulfuric Acid Lignin. The bromine and chlorine reactions were about the same in results. Both reagents showed the property of removing some of the methyoxyl groups. Bromine combines with less ease than chlorine and its products were less definite. Therefore, the authors used the chlorination reaction for better study. The products obtained from the chlorination of spruce lignin differed. The chlorination was carried out by bubbling dry chlorine through a solution of lignin suspended in carbon tetrachloride. The spruce lignin combined with about twice as much chlorine as the maple lignin. The spruce lignin reaction was mostly addition demonstrated by analysis and the fact that very little HCl was released. If the principal reaction of chlorine on spruce lignin in a dry solvent is addition, the loss of methoxyls can be accounted for if they are attached to unsaturated groups such as shown below:



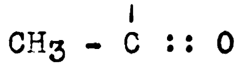
$$\mathrm{C{=}C{-}CH_3}$$

When chlorine is added to such a group, the addition compound, due to the accumulation of negative groups on one carbon, loses the methyl group and forms a compound containing the carbonyl group. The authors further state that when the chlorination takes place in water the final amount of chlorine introduced is about the same as when carbon tetrachloride was used, but the reaction was quite different, oxidation, substitution and addition takes place. This reaction splits off not only the methoxyls attached to groupings that required oxidation as well as chlorination to split the ether linkage. The substitution reactions in this case were favored, the reaction being similar to that which occurs when ethyl ether is chlorinated in the presence of moisture. If this were a primary or secondary alcohol grouping chlorination in water would produce carbonyl groups. Ritter and Seaborg(7) have reported the presence of carbonyl groups in chlorinated lignin. Another type grouping to which the methoxyl was attached did not lose chlorine, the authors suspect an aromatic or some other tertiary carbon which is not susceptable to oxidation. The lignin produces iodoform and chloroform when treated with alkaline solutions of iodine and chlorine. This reaction suggests a group of either:



$CH_3 - \overset{|}{\underset{\underset{H}{|}}{C}} — OH$

or



$CH_3 - \overset{|}{C} :: O$

Comparison of Chlorination of Natural and Extracted Lignins. In a comparison of the percentages of combined chlorine in the three forms of maple lignin if was found that lignin chlorinated in the wood added 37 per cent chlorine, while extracted lignin added only 23 per cent. When extracted lignin was methylated and then chlorinated the chlorine percentage was increased to 35 per cent. This indicates more unsaturated groups of lignin form in the wood and that the unsaturation is again obtained by methylation. This same observation was made by Ritter and Seaborg,(29) that the reaction of chlorine with lignin is similar whether the substance has been isolated or is still in the wood.

Harris and Sherrard determined the chlorine content of the lignin by first extracting the hydrochloric acid and determining the HCl formed by titration of the washings, then digesting the lignin with nitric acid and silver nitrate and titrating the excess silver.

Alkali Chloro-lignin. Powell and Whittaker(29)(30) used flax, pine, spruce, ash, birch and poplar lignin in attacking the problem of the constitution of lignin.

The lignin was prepared by the digestion of the flax and wood chips in a caustic solution at 140°C from 6 to 10 hours. The alkali lignin was chlorinated by suspending it in a solution of carbon tetrachloride and passing through a slow stream of dry chlorine. The color of the lignin changed from dark brown to bright red with the evolution of much hydrogen chloride. This chloro-lignin was precipitated as a bright red solid, soluble in cold alkali. The chloro-lignin forms acetyl derivitives on treatment with acetic anhydride. Analysis showed that the chloro-lignin had a methoxyl content of 5.2 and a chlorine content of 35.1. The bromo-lignin was prepared in the same manner and was a dark red solid soluble in alkali. The reactions were at ordinary temperature and in the absence of sunlight. Both bromo-lignins and chloro-lignins contained twelve halogen atoms, and analysis, together with the fact that considerable evolution of halogen acid takes place during halogenation, shows that substitution as well as possible addition occurs. The halogen acid reacts with the methylated hydroxyl groups of the lignin. The bromo-lignin contains one methoxyl group while the chloro-lignin contains two. Both bromo-lignins and chloro-lignins are soluble in caustic soda, acetone, and acetic acid. These halogenated lignins are not nitrated or oxidized by nitric acid;

on acetylation with acetic anhydride five acetyl derivitives are very readly hydrolyzed.

From their results Powell and Whittaker drew the conclusions that flax lignin molecule contains five methoxyl groups and five hydroxyl groups capable of acetylation. And that three of the hydroxyl groups are phenolic in nature shown by the fact that not more than three additional methoxyl groups can be readily introduced. The character of the remaining hydroxyl groups was not definite but they were unstable as indicated by their absence in the derivatives which were prepared from lignin. Thus chloro-lignin and bromo-lignin contain only seven hydroxyl groups some of which are methylated. One half of the chlorine present in chloro-lignin is readily eliminated by cold alkali, the remaining six atoms are firmly held and have probably substituted hydrogen atoms in the aromatic neculei present in the molecule.

Addition and Substitution Mechanism. Cross and Bevan first investigated the action of chlorine on lignified materials in 1890(10) and found that at least part of the chlorine does not revert to the chlorine ion as would be the case if oxidation alone were taking place. It is now well accepted that two types of chlorination take place:(20) addition and substitution. In the case of chlorination by direct addition, the chlorine enters an unsaturated bond without the formation of hydrochloric acid. In the case of substitution a chlorine atom displaces an organically bound hydrogen with the simultaneous production of hydrochloric acid. In this case half of the chlorine used in the reaction appears as hydrochloric acid in the liquid phase, the other half being organically bound. This reaction had been used to study the relative degree to which substitution and oxidation take place in the process of bleaching pulp. In the case of oxidation all chlorine is converted to the chloride ion and analysis of the bleaching liquors enables calculation of the relative amounts of chlorine which have been consumed in substitution and in oxidation. Experiments of this type indicate that at the beginning of bleaching of lignified materials with alkaline hypochlorites, the reaction is principally one of chlorination, oxidation being predominant in the later stages.

Pulp Bleaching. It has been shown(20) that there is one phenolic or enolic hydroxyl group in lignin which is very readily methylated, the influence on the bleaching of pulp with a chlorine solution has been investigated. When this hydroxyl group has been replaced with a methoxyl group, the pulp becomes much whiter and no longer gives the reactions of unbleached pulp. This free hydroxyl appears to play an important role in cleaching; when it is replaced by a methoxyl group the rate of reaction of lignin with a bleaching solution is greatly reduced. Further as bleaching proceeds, the methoxyl content of the pulp decreases approximately in proportion to the lignin removed.

Hibbert(20) studied the reactions of chlorine and chlorine solutions on isolated lignin, alkali and lignosulfonic acid, and on the residual lignin in unbleached soda and sulfate pulps. He found that all of these materials are simultaneously demethoxylated and chlorinated when treated with aqueous solution of chlorine. In neutral and acid solutions, the removal of one methoxy unit from the lignin building unit is accomplished by the introduction of one chlorine atom, up to the consumption of 25 to 30 equivalents of chlorine per kilogram of lignin. However, chlorination in an alkaline medium the organically bound chlorine is less than the methoxy lost due possibility to demethylation through oxidative cleavage by hypochlorous acid. The pH and the amount of chlorine reacting influence the degree of chlorination and demethylation. Chlorination occurs rapidly under acid conditions but also takes place at a slower rate under alkaline conditions. Hibbert states that the demethylation may be due to the primary action of molecular chlorine in phenols or their derivatives which are present in chlorine.

Reaction of Chlorine with lignin. The theory presented by Hibbert(20) to explain the reaction of chlorine with lignin is outlined as follows: he assumes the presence of guaiacyl nuclei in the lignin. Most, if not all, of the methoxyl groupings in lignin are probably attached to such nuclei, and, by analogy with known compounds, halogenation should occur in either the 6- or the 5- position, depending on whether or not the p-hydroxyl groupings are free. The presence of chlorine in the 6 or 5 position would include instability in the methoxyl groupings which would then cleave with the formation of quinone or diketone structures, which would yield further acidic groupings. Lignin, which is chlorinated under acid conditions, does not go into solution easily, but is made potentially soluble in alkali as a result of the formation of carboxyl groupings in the lignin at points from which the methoxyl was removed. Hibbert proposes the mechanism of the chlorination of lignin in bleaching liquors as shown in Fig. 3.

Chlorination of Lignin in an Alcohol Suspension. Janson and Bain(21) chlorinated spruce lignin that was suspended in methanol and obtained a cream colored chlorolignin. The lignin chloride was dissolved in the alcohol during the chlorination and subsequently precipitated by

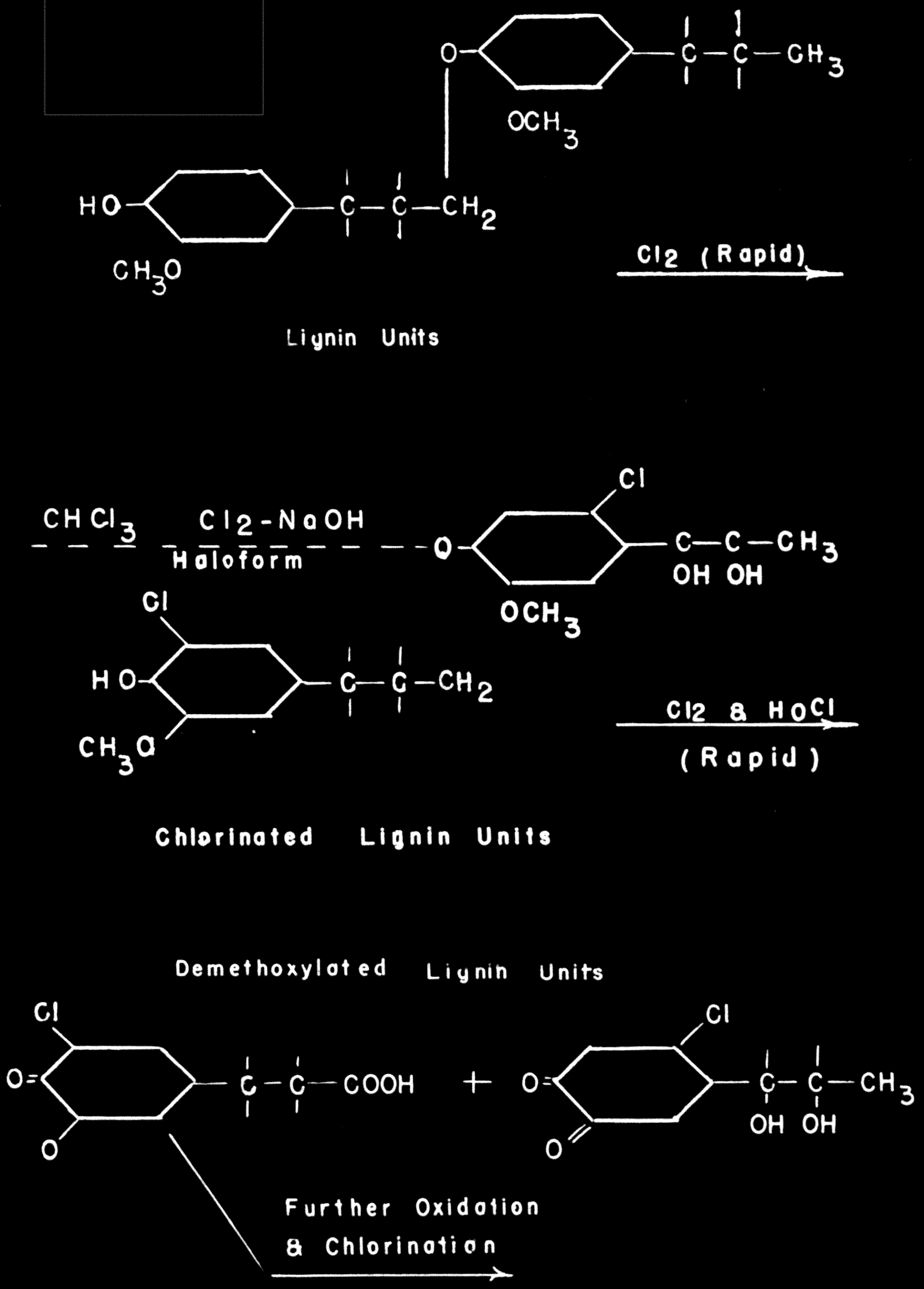


FIG. 3

Chlorination- Demethoxylation Reactions of Lignin.

addition of water. The empiricial formula of the chlorolignin was determined to be $C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$. This lignin was acelylated and two acetyl groups were introduced indicating the presence of two hydroxyl groups in this complex. Eleven of the chlorine atoms evidently replaced 10 H atoms and 1 OH group by simple substitution leaving two chlorine atoms which apparently entered to saturate a double bond. Seven of the chlorine atoms were shown to be readily removable when subjected to alkaline or acid reduction. The other six chlorine atoms, because of their stable union with the molecule, are assumed to be joined to an aromatic nucleus. Powell and Whittaker(29) have also found the same reactions with flax lignin.

In 1941 Harris and Lofdahl(16) studied the reaction between lignin and chlorine in a methanol suspension, and the interaction of lignin with methyl hypochloride. Chlorination and methylation were carried out with four different reagents, so as to determine the effect of the methyl hypochlorite on the chlorination reaction.

Chlorination of the sulfuric acid lignin was carried out under the following conditions:

1. Five grams of lignin suspended in methanol and chlorine passed through the suspension; the temperature was held at 10°C. The reaction carried out until no

further color change was evident. The lignin was precipitated by pouring the product on crushed ice, and dried under vacuum at room temperature.

2. The reaction of 5 grams of lignin with 200 grams of methanol with 25 grams of barium carbonate was carried out at in 1 above. The product was a light yellow powder.

3. Lignin was treated with dichlorourea in methanol solution, chlorination runs were made on a temperature range of 5 to 30°C.

4. Lignin was suspended in a methanol methyl hypochlorite solution and chlorinated. Product was recovered by evaporation under vacuum until the solution was concentrated to 50 cc, the concentrated solution was added to 1 liter of petroleum ether which precipitated the lignin as a flocculent powder.

The investigators made the following conclusions as a result of this work:

1. Lignin reacted with chlorine in methanol to produce compounds containing more methoxyl groups than did the starting material.

2. Methyl hypochlorite prepared in various ways reacts with maple lignin to produce compounds containing two methoxyl groups in excess of those in the starting maple lignin. (2 and 3 in the case of spruce lignin)

3. Addition of these methoxyl groups indicates the

presence of 2 ethylenic groups in maple, and 2 or 3 in spruce lignin, depending on the derivation.

4. A more highly chlorinated lignin was obtained by method 1 than by the other three methods of chlorination.

Effect of Water on Chlorination of Lignin. Kress and Voigtman(23)chlorinated lignin isolated from Canadian black spruce by three different methods. They also chlorinated lignosulfonic acids isolated from Mitscherlich sulfite blow-off liquor by dialyzing through parchment paper for two weeks. The chlorinations were carried out in the presence and absence of water. The results are given in the table I; it can be noted that the chlorine content of the chloro-lignin varied somewhat, depending on the method used for the isolation of the lignin. When the lignin was chlorinated in the absence of moisture, the chloro derivative contained a much greater percentage of chlorine than when chlorinated in the presence of water. In the case of the lignosulfonic acids, however the reverse is true.

Table I. Effect of Water on Chlorination of Lignin.

Material Chlorinated	Reaction Media	
	Anhydrous Cl%	Aqueous Cl%
Lignin A	29.0	18.6
Lignin B	32.5	18.2
Lignin C	33.0	20.1
Lignosulfonic acids	16.2	18.6

Methoxy Lignin Chlorides. Othmer(27)separates lignin from cellulose by suspending sawdust in methanol and chlorinating for five or six hours at the boiling point of the solvent. The author states that a new class of lignin derivatives has been obtained that show a higher degree of methylation and chlorination, combined than any similar derivatives previously obtained at lower temperatures. However several investigators have chlorinated lignin in methanol solution Harris(16)obtained a chlorinated product with a chlorine content of 33 to 34 per cent and a methoxyl content of 16 to 21 per cent.

The process was carried out by suspending sawdust in methanol raising the solvent to the boiling point at atmospheric pressure, and then bubbling in chlorine gas with provision for suitable agitation. Reaction was complete after the wood had passed through a series of color changes ranging from yellow to dark gray or purple and finally to light yellow.

The author states that small amounts of water present does not affect the course of the reaction, however Sherrard and Harris found that different reactions took place when lignin was chlorinated in water and when chlorinated in dry solvent. The methoxy lignin chloride was precipitated from the methanol solution by adding the solution to water. The precipitated lignin is of an ivory to light yellow color and is water insoluble but soluble in a number of organic solvents.

Othmer produced, by the same procedure, lignin from hardwoods, softwoods, and bagasse with very similar results. The methoxyl content varied from 16 to 24 per cent and the chlorine from 23 to 32 per cent for lignins produced from twelve different woods. In a later paper Othmer finds that increasing amounts of water resulted in a highly methylated product with correspondingly less chlorine combined with the lignin.

The chloro-lignins produced by the Othmer process have shown resinification properties. Preliminary work on a series of condensation resulting in ester formations of resinous and oily types, led to further and more extensive experimination of formation of methoxy lignin chloride phthalates. Resinification was carried out in methanol in an atmosphere of chlorine. The resins obtained were more thermosplastic than thermosetting in nature.

Polycondensation experiments with a catalyst using methoxy lignin chloride alone resulted in promising methanol insoluble resins.

III. EXPERIMENTAL

A. Purpose of Investigation

The purpose of this investigation is:

1. To determine the optimum time, temperature and concentration for the chlorination of sulfate lignin.
2. To determine the physical and chemical properties of the chlorinated sulfate lignin.

B. Plan of Investigation

The plan of this investigation is as follows:

1. A review of the literature will be made to obtain previous data that have been published on the chlorination of the various types of lignin.
2. Glassware equipment will be designed so that it will provide agitation of mixtures of lignin and the suspending medium, control of the rate of chlorine flow, control of the temperature of reaction, and a method for testing the progress of the reaction.
3. Chlorination tests will be made using methyl alcohol, phenol, and benzaldehyde as a medium for suspending lignin. The following points will be

determined:

a. The suspending medium which gives the best results for chlorination of lignin.

b. The optimum ratio of lignin to solvent.

c. The best procedure for the chlorination of of lignin.

d. Methods of separation of the chloro-lignin product from the suspending medium.

4. A series of chlorination tests will be made with the selected solvent to determine the following points:

a. The rate of each chlorination reaction as determined by an analysis of the unused chlorine gas passing from the reactor.

b. The degree of chlorination of lignin for each run as determined by an analysis for the chlorine content of the chloro-lignin.

c. A comparison of the reaction rates when the chlorination rate is doubled and the temperature held constant.

d. A comparison of the reaction rates when the temperature is raised from 25°C to the boiling point of the mixture and the rate of chlorine flow is held constant.

e. A comparison of the reaction rates with and without ferric chloride as a catalyst while the rate of chlorine flow and temperature are held constant.

f. A comparison of the rates of reaction with and without agitation of the mixture while the rate of chlorine flow and the temperature are held constant.

C. Materials

The following materials were used in the investigation:

Raw Materials

The following materials were used in the chlorination of sulfate lignin:

Indulin A. Sulfate pinewood lignin, Lot No. Z-823, obtained by acidification of black liquor. "Indulin(5) consists of about 65 per cent carbon, 5 per cent hydrogen, and 30 per cent oxygen. It is considered to be a polymer of many homogeneous units, having a unit weight of about 840 each, containing perhaps one carbonyl group. The solubility of Indulin in alkali is thought due to the phenolic character of one of the hydroxyl groups and to enolization of the carbonyl group." 100 pounds donated by the Development Laboratory, West Virginia Pulp and Paper Company, Charleston, South Carolina.

Alcohol, Methyl. 95 per cent technical, Lot 460722. (15 gal.) Used as a medium for chlorinating lignin. Obtained from Merck and Co., Inc. Rahway, N. J.

Phenol. (acid carbolic), U. S. P. Fused crystal, Lot No. 9845. Used as a medium for chlorinating lignin. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J.

Chlorine. 99.5 per cent purity, cylinder No. 1, 105 lb., 84 lb/in^2(569 cu.ft.) Used as halogenating agent for reaction with lignin. Obtained from Matheson Company, Inc., East Rutherford, N.J.

Caustic Soda. Commercial flake. Used to react with excess chlorine from reactor. Obtained from Phipps and Bird Company, Richmond, Va.

Chlorination Apparatus Materials

The following materials were used in constructing or operating the chlorination apparatus.

Sulfuric Acid. C..P., Special 95.5 per cent (Sp. Gr. 1.84) Lot No. 72645. Used in differential U-tube. Obtained from J.T. Baker Chemical Company., Phillipsburg,N.J.

Ammonia Hydroxide. 28 per cent solution. Used for detecting chlorine leaks in equipmemt, and for dissolving silver chloride. Obtained from Chemistry Department Stock Room.

Soda Lime. Used for canister filler gor gas mask. Obtained from Chemistry Department Stock Room.

Catalyst

The following chemical was used as a catalyst for chlorination of lignin:

Ferric Chloride. ($FeCl_3.6H_2O$), Lot No. 82045. Obtained from the Chemistry Department Stock Room.

Analytical Reagents

The following reagents were used to determine the excess chlorine from the reaction, and the percentage chlorine of the chlorinated lignin:

Sodium Hydroxide. Pellets, C.P., Lot No. 71646. Used as a test solution for reacting with excess chlorine. Obtained from J.T. Baker Chemcial Co., Phillipsburg, N.J.

Hydrogen Peroxide. U.S.P., 3 per cent solution. Used in chloride determination. Obtained from J.T. Baker Chemical Company, Phillipsburg, N.J.

Nitric Acid. Sp. Gr. 142, Lot 6146. Used in chloride determination. Obtained from General Chemical Company, New York.

Silver Nitrate. C.P., crystal, ACS Standard, Lot No. 1.1146. Used for chloride determination. Obtained from J.T. Baker Chemical Co., Phillipsburg, N.J.

Potassium Chromate. C.P, crystals, Lot No. 112743. Manufactured by the J.T. Baker Chemical Company, Phillipsburg, N.J.

Hydrochloric Acid. C.P., Sp.Gr. 1.19, Assay 37.0 per cent. Obtained from the J.T. Baker Chemical Company, Phillipsburg, N.J.

Sodium Chloride. C.P., Crystal, Lot No. 1342. Used in standardization of hydrochloric acid and silver nitrate solution. Obtained from the J,T. Baker Chemical Company, Phillipsburg, N.J.

Sodium Sulphite. Used for chlorine determination. Obtained from Phipps and Bird, Inc., Richmond, Va.

Sodium Bicarbonate. U.S.P. Used in chloride determination. Obtained from Church & Dwight Co., Inc., New York.

Ethyl Alcohol. Scientific grade. Obtained from Chemistry Department Stock Room.

Molding Materials.

The following materials were used in molding experiments:

Stearic Acid. U.S.P., powder, Lot No. 52741. Mold lubricant. Obtained from the J.T. Baker Chemical Co., Phillipsburg, N.J.

Wood Flour. Used as a filler. Obtained from the Chemical Engineering Department Stock Room.

Sawdust. white pine. Obtained from the Virginia Polytechnic Institute Wood Shop.

D. Apparatus

The following apparatus was used in the investigation:

Chlorination Apparatus

Flask, Wolff. (two 2000 ml., pyrex. Used for reaction flask for chlorination of lignin. Obtained from Phipps and Bird, Inc., Richmond, Va.

Condenser. (one) 600 mm., pyrex. Used for condensing vapors from reaction flask. Obtained from the Chemical Engineering Department Stock Room.

Flask, filtering. with side tube. (four) 1000 ml., pyrex. Used for traps and sodium hydroxide reaction flasks. Obtained from Chemical Engineering Department Stock Room.

Gage, U-tube differential. Three mm. glass tubing. Used in measuring chlorine flow to reactor. Made in Physical Chemistry Department.

Stirring Apparatus. motor driven, variable speed, rheostat controlled. Used to agitate solution in reactor flask during chlorination. No name plate. Obtained from Chemical Engineering Department Stock Room.

Stirring Apparatus. Fultorn Labmotor, 115 v., 350 r. p. m. Used to agitate solution in reactor flask during chlorination. Obtained from Fisher Scientific Company, Pittsburg, Pa.

Stopcocks. 8 mm., straight, pyrex glass, (six). Used to control and direct flow of chlorine in chlorination apparatus. Obtained from Chemistry Department Stock Room.

Mercury Seal Stirring Apparatus. Constructed in Chemical Engineering Department.

Valve. Non-automatic needle, No. 51. Constructed from cold rolled steel. Obtained from Matheson Company, East Rutherford, N. J.

Thermometers, Mercury Bulb, Filtering Flasks, Condenser Jacket, Glass Tubing, and Assorted Glassware. Obtained from Chemical Engineering Department Stock Room

Preparation and Recovery Apparatus

Aspirator (filter pump). Used for filtering lignin and silver chloride. Obtained from Chemical Engineering Department Stock Room.

Gage, Pressure-Vacuum. 0-30 lb. graduated in. and 1/2 lb. subdivisions. Manufactured by Ashcroft Manufacturing Company, New York.

Funnels. Buechner type, 115 mm. (two). Used for filtration of lignin. Obtained from E. H. Sargent & Co., Chicago, Ill.

Flask. filtering, pyrex, with side tube, 1000 ml., (two);500 ml. (two). Used for filtration of lignin.

Obtained from Chemical Engineering Department Stock Room.

Heaters. Electric, chromolox, 360 w., 120v. (two). Used for heating reactor and analytical work. Obtained from Edwin L. Wiegand Co., Pittsburg, Pa.

Beaker. 2000 ml., pyrex. Used for preparing lignin for chlorination. Obtained from Chemistry Department Stock Room.

Stirring Apparatus. Motor driven, variable speed, rheostat controlled. Used to prepare alcohol-lignin solution for chlorination. Obtained from Chemical Engineering Department Stock Room.

Thermometer. Mercury bulb, immersion type, 0-360°C. Used for temperature measurement of lignin-alcohol mixture. Obtained from Chemistry Department Stock Room.

Distilling, Flask. pyrex, 1000 ml. Used for distillation of chloro-alcohol-lignin solution. Obtained from the Chemical Engineering Department Stock Room.

Condenser. Pyrex glass, 450 mm. Used to condense distillate from chloro-alcohol-lignin solution. Obtained from Chemical Engineering Department Stock Room.

Balance. Torsion, large, capacity 4.5 Kg., No. B 72216. Used for weighing lignin samples. Manufactured by Torsion Balance Co., New York.

Analytical Apparatus

Oven. electric drying, 110 v. 600 watts, 35-180°C, thermostat controlled, No. 100-2761. Used for drying lignin samples. Obtained from Precision Scientific Co., Chicago, Ill.

Separatory Funnel. 250 ml. Used for generating carbon dioxide. Obtained from Chemical Engineering Department Stock Room.

Light. yellow, 60 w. Used for chloride determinations. Obtained from Chemical Engineering Department Stock Room.

Burette. 50 ml.(five). Used for titrations. Obtained from Chemistry Department Stock Room.

Oven. Electric drying, 110v. 660 w. Manufactured by E. H. Sargent & Co., Chicago, Ill.

Balance. Chainweight, No. 3X253 in 32, Manufactured by Seederer-Kohlbusch Inc., Jersey City, N. Y.

Microscope. Steroscopic, No. 29, 1.0x, 2.0x, 3.0x poised objectives and 9x, 12x poised eyepieces. Manufactured by the Spencer Lens Company, Buffalo, New York.

Volumetric Flasks, Funnels, Test Tubes, Gooch Crucibles, Bunsen Burner, and Desiccator. Obtained from the Chemical Engineering Department Stock Room.

Molding Equipment

Hydraulic Press. Pressure gage graduated in ram pounds, 0-20,000, No. 4905-20. Used to press lignin-sawdust samples. Manufactured by the Fred S. Carver Co., New York.

Cylindrical Steel Mold. Mold is cylindrical in shape, false bottom, 2 7/32 in. in diameter. Obtained from the Chemical Engineering Department Stock Room.

Heater Electric Mold. Used to heat cylindrical steel mold, temp. to 400°C. Built in Chemical Engineering Department.

Resistors, Electric. 660 w. (3). Used for controlling temperature of electric mold. Obtained from the Electrical Engineering Department.

Rheostat. Variable. 430 ohms, 1 Amp. Used to control temperature of electric mold. Manufactured by Rex Rheostat Co., Baldwin, N. Y.

Thermometer. Bi-metalic, 50 -500°F. Used to measure mold temperatures. Manufactured by Weston Electric Instrument Corp., Newark, N. J.

E. Method of Procedure

Construction of Chlorination Apparatus

The chlorination apparatus was constructed from glassware equipment using rubber tubing for connections, and was supported by a welded 1/2-in. pipe framework. The chlorine from the cylinder was piped through a needle valve and by rubber tubing to a liter filter flask. The flask served as a trap and expansion chamber, it was connected by the side tube to a 500 ml. filter flask, which was 2/3 filled with concentrated sulfuric acid. This flask was fitted with a one-hole stopper which contained a 3-ft. length of 8 mm. glass tubing, one end of which extended to the bottom of the flask and the other end open to the atmosphere. The purpose of this flask was to smooth out the small pressure changes of the gas from the cylinder.

Two chlorine glass tubes, each equipped with stopcocks, led from the expansion chamber. The chlorine could be passed directly along one tube, fitted with a chlorine outlet tube, to the reactor for use when quantitative high rate of flow chlorination runs were made. The second tube was fitted with a differential type U-tube for flow measurments. A trap was placed on each side of the U-tube to take care of sudden pressure changes. The U-tube orifices were made from 30 mm. lengths of capillary tubing which could be changed to allow a wide range of chlorine flow. Concentrated sulfuric acid was used as the liquid in the U-tube.

A tee was placed in the line between the U-tube gage and the reactor to provide a take-off line for test tube scale reactions. This line was fitted with a stopcock.

The chlorine outlet tube, 6 mm., was curved to fit the bottom of the reactor flask, and was fitted into a No. 7 two-hole stopped along with a thermometer for measuring reaction temperatures. A sliding joint was made for the outlet tube through the rubber stopper by having an outer 8 mm. glass tube through which the outlet tube passed. This sliding joint allowed the outlet tube to be raised above the reaction mixture for filling the system with chlorine. To prevent chlorine leaks the tubes are greased with silicone grease.

A variable speed electric motor was clamped to the piping framework above the reactor and was used to drive a mercury sealed glass agitator. The mercury seal was provided with a 6 mm. glass tube vent fitted with a short piece of rubber tube and a hose clamp. The vent provided a method to release pressure and prevent the mercury from being drawn into the reactor when the reaction was completed.

A 600 mm. condenser was fitted to the Wolff flask reactor to condense the volatile reaction products. The flanged end of the condenser was connected to a liter filter flask trap by 3-ft. of 8 mm. tubing. The glass tubing also acted as an air condenser. A thermometer was fitted through the two-hole stopper with the bulb even with the side tube outlet for obtaining gas temperatures.

Three glass tubes each fitted with a stopcock, were run from the trap. Two tubes lead to liter chlorine absorption bottles, the third was fitted with a gas sampling tube, and used to take gas samples during the chlorination runs.

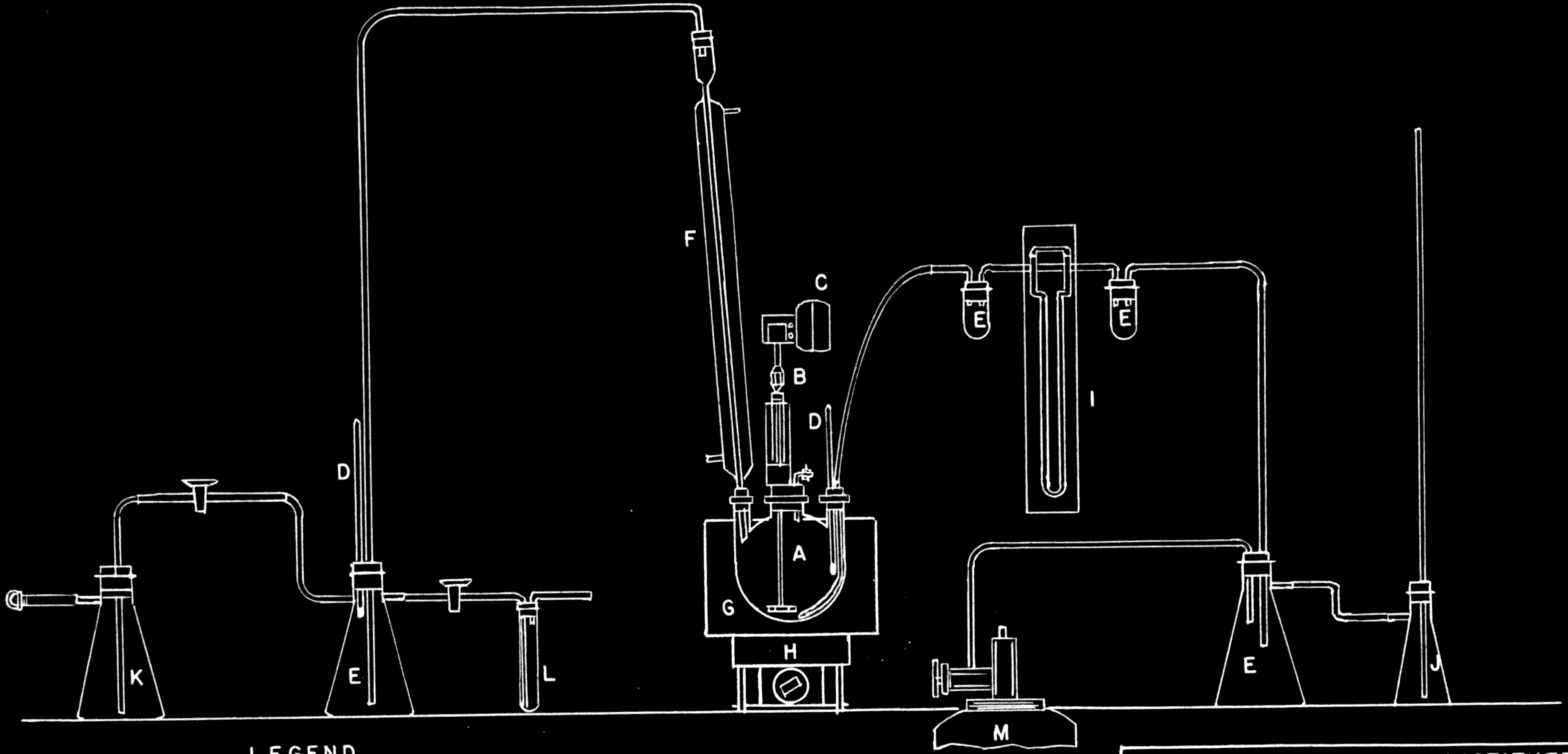
Excess chlorine from the absorption flask was carried to the atmosphere through a 1/4-in. iron pipe.

A schematic diagram of the chlorination apparatus is shown in Figure I, page 67.

Calibration of U-tube Flowmeter

Initial calibration of U-tube pressure gage was made to select the size orifice and filling liquid that would fit the following conditions:

1. Maximum chlorine flow would be below the velocity that would cause flooding in the condensing column.



LEGEND

A	Chlorination Flask
B	Stirring Apparatus
C	Stirrer Moter
D	Thermometer
E	Trap
F	Condenser
G	Water Bath
H	Hot Plate
I	U-Tube Gage
J	Exponsion Flask
K	NaOH Reactor
L	Gas Sampling Tube
M	Chlorine Tank

VIRGINIA POLYTECHNIC INSTITUTE
Department of Chemical Engineering
Blacksburg, Virginia

Schematic Diagram

LIGNIN CHLORINATION APPARATUS

Drawn by: B.a.s.
Checked: F.C.V.
Approved:

Case: PG
File No: 539
Date: 12-19-46

Fig. No. 4
Scale: 0.1" = 1"

2. A 100 per cent increase in chlorine flow, based on weight per cent, between maximum and minimum reading on the scale.
3. Selection of liquid for filling U-tube that would give maximum pressure difference and that would not react with chlorine. Mercury, petroleum, and concentrated sulfuric acid were tested.

The chlorine flow was determined by reacting the chlorine gas that passed through the system during a measured time with a solution of sodium hydroxide. Sodium hydroxide solutions of 0.5, 1.0 and 1.5 N. were used to determine the amount and strength of test solution. The chlorine outlet tube was drawn to a fine opening to decrease the diameter of the chlorine bubbles.

The following procedure was used in calibration of the U-tube pressure gage:

1. The U-tube was filled with sulfuric acid, Sp. Gr. 1.84, to the zero mark on the tube.
2. The orifice was cleaned with alcohol and carbon disulfide.
3. The needle valve was opened and the system allowed to fill with chlorine, and reach a constant pressure reading.
4. The pressure reading was adjusted to the required reading. The tests were made at readings of

2-in., 4-in., 6-in., and 8-in.

5. A 8-in. test tube containing 50 ml. of 1.5 sodium hydroxide solution was placed on the gas sampling outlet.

6. Gas was passed through the sodium hydroxide solution for 120 sec. Time was started with the first chlorine bubble that passed through the solution.

7. Check samples were made for each U-tube setting.

8. Samples were analyzed for chloride using the following procedure:

   a. Dilute the 50 ml. sample to 250 ml. in a volumetric flask.

   b. Measure a 50 ml. sample for analysis.

   c. Add an excess of hydrogen peroxide to destroy the sodium hypochlorite and boil to expell the excess peroxide.

   d. Neutralize the solution with (2:98) dilute nitric acid using phenolphthalein as an indicator.

   e. Add one gram of sodium bicarbonate to the solution to make it slightly alkaline and produce a clear end point.

   f. Titrate with standardized silver nitrate solution. 0.01 N. silver nitrate was used with low chloride samples, and 0.1 N. silver nitrate was used for samples requiring more than 100 ml. of the 0.01 N. solution. One ml. of 10 per cent potassium chromate solution used as an indicator.

g. All chloride tests were run with the room darkened and using a yellow bulb for light.

h. Samples were titrated consecutively so as to titrate them all to the same color end point.

The general procedure for chloride determination was taken from page 35 "Chlorine Handbook"(1).

A graph showing the calibration of the U-tube gage is shown on page 71.

Preliminary Experiments

The series of tests outlined under Preliminary Experiments were made in order to formulate procedures for the chlorination of lignin.

Specific Gravity of Alcohol-Lignin Solution. A series of specific gravity determinations using a 50 ml. pycnometer were made to find the solubility of lignin as a function of temperature. The procedure for the determination was taken from page 43 "Commercial Methods of Analysis" by Snell and Biffen. All determinations were made at 25°C.

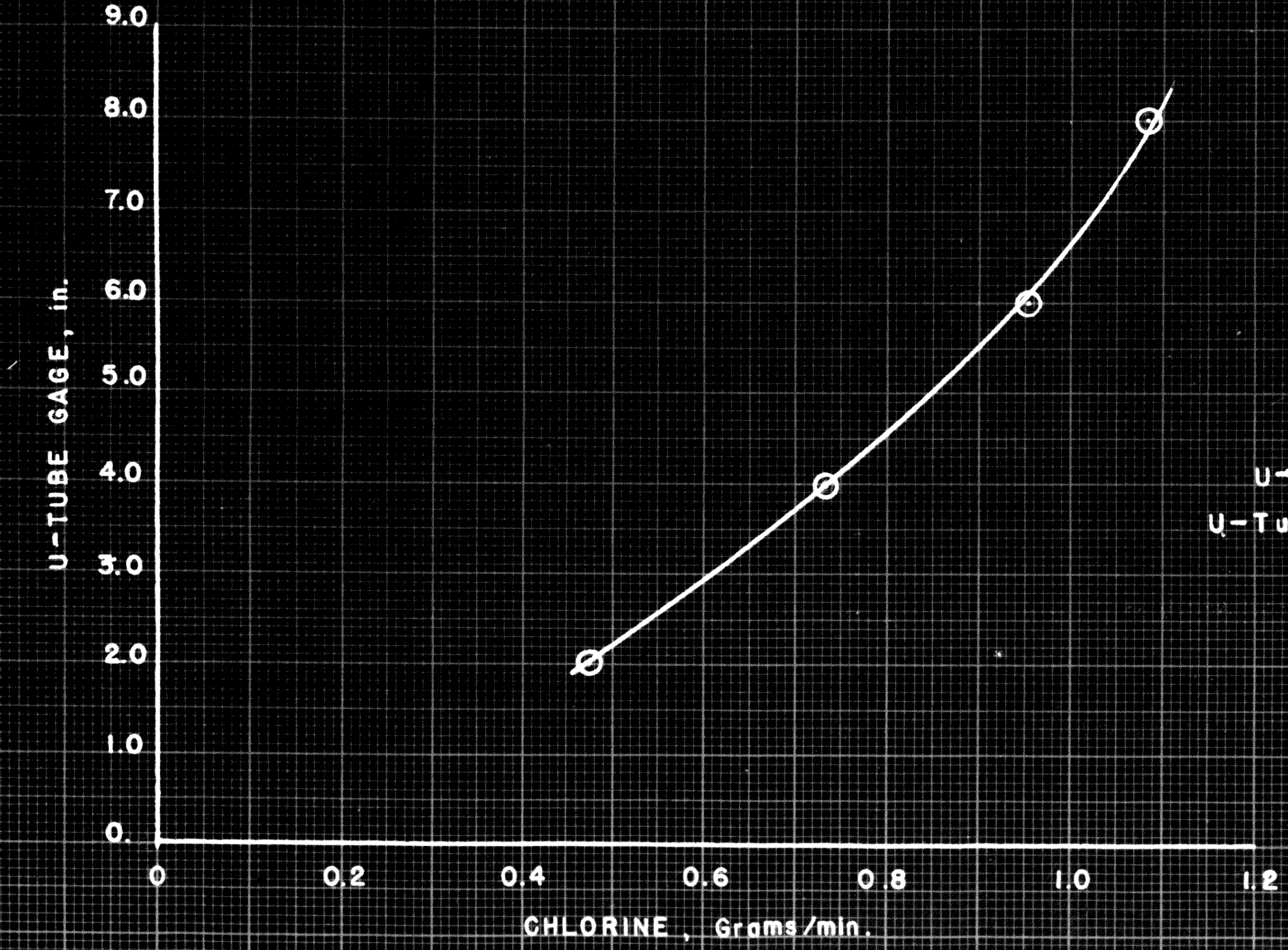


FIG. 5

Calibration Curve

for

U-Tube Differerntial Gage

U-Tube Gage-in. Vs Chlorine, gm/min.

20 grams of lignin was suspended in 200 ml. of methyl alcohol with mechanical stirring. The temperature of the solution was varied as follows:

Sample No.	Stirring Time	Temperature
1	10 min.	25°C
2	12 min.	25°C
3	5 min.	45°C
4	5 min.	65°C

Chlorination of a Methyl Alcohol Lignin Mixture.

To determine the effect of chlorine gas on a mixture of methyl alcohol and lignin an experiment was carried out under the following conditions:

1. 400 grams of lignin were mixed with 800 ml. of methyl alcohol.
2. The temperature of the alcohol was 25°C.
3. The mixture was placed in a reaction flask and placed in the chlorination system.
4. The mixture was agitated and chlorine at 5-in. gage was passed through the system for 76 minutes.
5. At the end of 76 minutes the excess methyl alcohol was poured from the reactor and chlorine gas passed over the lignin-alcohol mixture remaining in the reactor. Chlorine was passed for 50 minutes.
6. The product was examined to determine noticeable

physical changes.

Chlorination of Dry Lignin. Equipment was set up to chlorinate lignin in the dry powder state. The chlorinating vessel was the body of a 400 ml. condenser. A thermometer was fitted through one end of the condenser with the bulb in contact with and midway through the condenser tube. A rubber hose connected the chlorine tank to one water inlet and the excess chlorine was passed from the other water nipple to a flask containing sodium hydroxide solution.

Ten grams of lignin powder were placed in the tube so that the lignin had the maximum area exposed to the chlorine. Chlorine was passed through the tube at 1.5 in. gage for 30 minutes. Record was kept of the temperature and color change of the lignin. The chlorinated product was analyzed to determine the percentage chlorine added.

The chlorination was contitued to a definite excess by allowing chloine to flow through the reactor after there was no further apparent heat of reaction. The chlorination reactor was rotated during the run to expose fresh lignin surface to the chlorine.

The chlorinated lignin was dissolved in 1 N. sodium hydroxide solution and precipitated with 0.5N hydrochloric acid to observe any apparent physical change.

Chlorination of Lignin Wetted with Methyl Alcohol. Two grams of lignin were suspended in alcohol and filtered on a Buechner funnel. The filter paper was placed in a chlorination flask and chlorination was passed for 15 minutes. The product was examined under a microscope.

One gram of lignin was suspended in 10 ml. of methyl in a 8-in. test tube and chlorinated for 5 minutes. The run was repeated using one gram of lignin suspended in 20 ml. of alcohol. The two products were compared for relative chlorination.

Based on previous experiments a chlorination run was made to chlorinate lignin suspended in methyl alcohol. Eighty grams of lignin were suspended in 500 ml. of methyl alcohol by pouring the lignin slowly with stirring into the alcohol. To this suspension 500 ml. of alcohol was added making a total of 1000 ml. of alcohol.

The suspended lignin was chlorinated for two hours at 4-in. gage.

Data taken were time, temperature, color change, and observations of changes of physical properties of the lignin.

Chlorination of Lignin Suspended in Methyl Alcohol. A suspension of lignin in alcohol was prepared by adding 0.5 grams of lignin to 10 ml. of methyl alcohol in a 8-in. test tube. The test tube was shaken until the lignin was wetted and in suspension. Chlorine was passed through until no further color change was observed.

Optimum Lignin to Alcohol Ratio. Based on previous experiments tests were made using lignin to methyl alcohol ratios of 1:10, 1:15 and 1:20 to determine the optimum ratio for chlorination. The suspensions were prepared by adding the lignin to the alcohol by:

1. Dumping all lignin in the alcohol solution at once.
2. Adding the lignin slowly to the alcohol solution.

A mechanical stirrer was used to agitate the alcohol during the mixing operation.

Observations were made to select the optimum ratio and procedure for maximum suspension.

Chlorination of Lignin Dissolved in Sodium Hydroxide. 0.5 grams of dry-chlorinated lignin was dissolved in 10 ml. of 1.0 N. sodium hydroxide. The solution was chlorinated for 5 minutes, allowed to cool and 1:10 hydrochloric acid added to precipitate the lignin.

A comparison run was made leaving out the chlorination step.

In a third run 0.5 grams of lignin were dissolved in 10 ml. of chlorinated sodium hydroxide solution. Chlorine was passed through the sodium hydroxide for 10 minutes at 2-in. gage and this solution was used to dissolve the lignin. The solution was allowed to stand for 12 hours and the lignin then precipitated.

The lignin from the three runs was compared for structure and color change.

Chlorination of Lignin Suspended in Water. To determine the use of water as a suspending medium for lignin, 10 grams of lignin were suspended in 10 ml. of water. The suspension was chlorinated for 5 minutes. Color change of the lignin was noted.

Effect of Chlorinated Alcohol Solution on Lignin. One gram of lignin was suspended in 10 ml. of chlorinated alcohol and the suspension was brought to a boil over a bunsen burner. The lignin was studied for effect of chlorination.

Effect of Length of Chlorination on Lignin-Sodium Hydroxide Solution. A series of chlorinations with 1 gram of lignin dissolved in 25 ml. of 0.1 N. sodium hydroxide were run to determine the effect of time of chlorination on lignin. Chlorine was passed at 1.0-in. gage for 3, 5, and 10 minutes. The lignin was precipitated from solutions, when necessary, with 1:10 hydrochloric acid.

Effect of Sunlight on Chlorination Reactions. The effect of sunlight on the chlorination reaction was studied under the following conditions:

1. Three clear-glass one gallon containers were fitted with glass tubing for filling with chlorine.
2. The following three samples were prepared:
    a. 20 grams of dry lignin.
    b. 20 grams of lignin suspended in 350 ml. of methyl alcohol.
    c. 10 grams of lignin dissolved in 100 ml. of benzaldehyde.
3. Samples were placed in the containers and chlorine gas passed through to replace all air in the containers.
4. The containers were placed on the roof of the laboratory at night and left until the following night.
5. The containers were refilled with chlorine and placed in the sunlight immediately after refilling.

Chlorination of Lignin Suspended in Phenol and Benzaldehyde. Qualitative chlorinations of lignin suspended in phenol and benzaldehyde were made under the following conditions:

1. Five grams of lignin were dissolved in 10 cc of

phenol. Chlorine at 7-in. gage was passed through the mixture for 10 minutes.

2. Five grams of lignin was dissolved in 20 cc of benzaldehyde. Chlorine at 7-in. gage was passed through the mixture for 10 minutes.

Chlorination of Dissolved Lignin. The test sample was prepared by adding slowly with stirring 70 grams of lignin to 1400 ml. of methyl alcohol. The suspension was brought to 65°C on an electric heater. The solution was cooled and decanted removing all non-suspended lignin.

One-half of the alcohol lignin solution was placed in the reactor, the temperature raised to 65°C with a water bath and chlorine passed through at 8 in. gage for 30 minutes.

The remaining half of the solution was chlorinated with the temperature at 25°C.

The chloro-lignin precipitated by the reaction was separated by filtering and air dried. The filtrate was distilled under 12 to 16 inch vacuum to recover the dissolved lignin.

The distillation test was rerun at atmospheric pressure to determine the effect of temperature on the physical properties of the recovered lignin.

The specific gravity of the chloro-alcohol-solution was determined.

A check was made on the amount of dissolved lignin by precipitating the lignin from 50 ml. of chloro-alcohol-lignin solution by pouring into 50 ml. of water at 25°C. The lignin was dried at 35°C in an electric oven and weighed.

A boiling point determination was made on the chloro-alcohol-lignin solution. A 50 ml. distilling flask with a thermometer bulb at the level of the side neck and a condenser for collecting the distillate was heated by a bunsen burner. Observations were made of the time and temperature of the distillation.

Effect of Temperature on Suspended Lignin. The effect of temperature on suspended lignin was studied under the following conditions:

Ten grams of lignin was suspended with mechanical stirring in 200 ml. of methyl alcohol. The suspended lignin was decanted to remove the non-suspended lignin. The beaker containing the suspended lignin was placed in a water bath and the temperature was raised to 43°C with the mixture being agitated.

The experiment was repeated with the suspended lignin being prepared by the same procedure. The lignin suspension was agitated for 15 minutes at 25°C. The beaker was then placed in a water bath and the temperature raised to

60°C. Data were taken on the time and temperature and physical properties of the mixture.

A chlorination run based on the optimum conditions for suspending lignin was made. The lignin suspension was prepared by the same method and chlorine at 5-in. gage was passed through the suspension for 20 minutes.

Separation of Chloro-lignin from Alcohol. The following series of tests were run to determine a method for separation of dissolved chloro-lignin from alcohol. 10 ml. samples of chloro-alcohol-lignin were used for each test.

1. Air was sucked through the solution for two hours by use of the asperator.
2. A carbon dioxide generator was set up and carbon dioxide was passed through the solution for one hour.
3. Concentrated and 1:10 hydrochloric acid was added to the solution.
4. Concentrated sulfuric acid was added to the solution.
5. The test solution was poured into an equal volume of water at 25°C.

The results of all tests were compared to determine the method of separation to be used in future runs.

Molding Experiments. Molding experiments were made to determine the adhesive properties of the chloro-lignin. The following conditions were varied to find the optimum molding conditions:

1. Temperature: 80-270°C.
2. Time: 1 - 15 minutes.
3. Pressure: 500 - 4500 psi.
4. Percentage of chloro-lignin: 5 - 60%.
5. Types of chloro-lignin: Chloro-lignin, distilled chloro-lignin and precipitated chloro-lignin.
6. Filler: Sawdust and wood floor.
7. Plastizer: Water and chloro-alcohol distillate.

Tests were made using the precipitated chloro-lignin mixed with distillate to determine its gluing properties.

Chlorination of Suspended Lignin

The following outlined method of procedure was used for the chlorination of suspended lignin:

1. 70 grams of lignin were weighed out on the torsion balance.
2. 1000 ml. of methyl alcohol at 25°C were placed in a two-liter beaker.
3. The methyl alcohol was agitated by a glass stirrer driven by a variable speed motor.
4. The lignin was very slowly added to the agitated alcohol until it was all in suspension. Lignin must not be poured into the alcohol all at once since under these conditions it will lump together.
5. The lignin-alcohol suspension was decanted being careful to leave the non-suspended lignin in the bottom of the beaker.
6. 400 ml. of the methyl alcohol was added to the beaker and agitated. The alcohol-lignin suspension was decanted leaving only non-suspended lignin in the beaker.
7. The total volume of alcohol-lignin was measured, placed in a weighed reactor flask and weighed.
8. The non-suspended lignin was dried at 35°C and weighed.

9. The reaction flask was placed in the system, the agitator started and the system filled with chlorine. The reaction time was started when the system was filled with chlorine and the chlorine outlet was lowered to below the liquid level.

10. The reaction was continued to completion at constant chlorine flow.

11. The following data were taken during the run:

   a. Excess chlorine gas sample every 500 seconds.
   b. U-tube reading at 500 sec. interval.
   c. Reaction temperature every degree rise.
   d. Exit gas temperature.
   e. Color changes of reaction mixture.
   f. Time of each data taken.

12. The following steps were taken at the end of each run:

   a. The chlorine valve closed and the outlet tube raised above the reaction mixture to prevent clogging.
   b. Open the reactor to the atmosphere to prevent mercury from being drawn into the reactor.
   c. Cut off lines to sodium hydroxide reactors to prevent sodium hydroxide solution from being drawn into the gas lines.

d. Change sodium hydroxide solution.

e. Allow reactor to cool before removing from the system.

f. Clean mercuric chloride from mercury seal agitator.

g. Disassemble and clean needle valve.

h. Clean lines and traps.

13. The reaction flask was weighed; the alcohol-chloro-lignin solution separated on a Buechner funnel: the volume of alcohol-lignin solution measured and the chloro-lignin dried at 35°C in an electric oven and weighed.

Two experimental runs were made using this procedure. One run was made with a chlorine flow of five inches, the second run used a chlorine flow of eight inches. Both runs were started with the reaction mixture at 25°C.

Chlorination of Dissolved Lignin.

The chlorination procedure for chlorination of dissolved lignin was the same as for chlorination of suspended lignin with the following exceptions:

1. The dissolved alcohol-lignin solution was prepared as follows:

a. Add 1000 ml. of methyl alcohol to a two-liter beaker and bring to a boil at 65°C.

b. At the moment the alcohol reaches the boiling point add slowly with mechanical agitation 100 grams of lignin.

c. Agitate for 5 minutes.

d. Cover the beaker with a watch glass and place in a water bath.

e. Cool to 25°C.

f. Decant 735 ml. of alcohol-lignin solution.

g. Pour into a weighed reaction flask and weigh.

2. The reaction is carried out at temperatures of 25 and 65°C.

3. The reaction was heated to 65°C by a water bath maintained at 98°C by an electric heater. When the reaction temperature reached 65°C the chlorination was started.

4. The reaction was continued as outlined in the procedure for <u>Chlorination of Suspended Lignin</u>.

5. Ten runs were made chlorinating dissolved lignin under the following conditions:

No.	Temp. (Deg.C)	U-tube (in.)
1	25	2
1	25	8
2	65	2
6	65	8

Determination of Chlorine in Lignin

The method used for determination of chlorine in chlorinated lignin was suggested by Harris and Sherrard. The procedure follows in detail:

1. One gram sample of chloro-lignin was placed on a 4-in. filter funnel and washed until no test for chloride is obtained.
2. The washed sample was dried in the electric oven at 35°C for 12 hours.
3. A 0.25 gram sample was weighed on the analytical and brushed into a 600 ml. beaker.
4. Fifty ml. of hot 10 per cent sodium sulphite solution was added to the beaker and the mixture brought to a boil on a electric heater to dissolve the lignin.
5. The beaker and contents were allowed to cool to 40 - 50°C to prevent foaming and 15 ml. of 1:1 nitric acid was added to the solution.
6. The solution was heated to 80 - 90°C and enough 1 N. silver nitrate added to precipitate all the chlorine as silver chloride.
7. The solution was heated at 65 - 75°C for 20 minutes and allowed to cool and the precipitate to settle.
8. If the silver chloride was not filtered at once

the beaker was placed in a dark place to prevent the decomposition of silver chloride. (See page 288 "Inorganic Analysis" by Kolthoff and Sandell.)

9. The solution was filtered through a weighed gooch filter. The gooch was prepared for rapid filtering by placing a mat of glass wool flat on the filtering surface. A mat of ground, acid washed asbestos fiber was sucked on the glass wool under pressure and tamped. The gooch was dried at 150°C overnight in the electric oven and weighed.

10. The silver chloride was washed with 25 ml. of cold 1:1 nitric acid to dissolve any silver sulfide present. The precipitate was finally washed with 40 - 50 ml. of cold distilled water.

11. The Gooch crucible was dried at 150°C for twelve hours in the electric oven, desiccated, and weighed at once. Kollohoff and Sandell have shown that silver chloride loses weight on exposure to light.

12. The percentage chlorine based on the weighed sample was calculated.

13. A gelatinous precipitate will form in the filtrate and is not silver chloride but nitrated lignin.

14. The silver chloride precipitate is soluble in sodium sulphite and must not be washed with this reagent.

Separation of Lignin from Alcohol Solution

The chlorinated alcohol-lignin reaction product was first filtered on a buechner funnel to remove the suspended chloro-lignin. The chloro-lignin dissolved by the alcohol was recovered by three methods.

1. Distillation
2. Precipitation with water
3. Low temperature precipitation with ice.

Distillation Recovery was carried out by placing the filtrate in a 1000 ml. side neck distilling flask which was fitted with a mercury bulb thermometer whose bulb was even with the exit tube. A 400 ml. condenser was connected with the flask and the distillate was recovered in a 500 ml. filtering flask. The distillate flask was fitted with a hose connection to the vacuum line. Connections were sealed with rubber cement.

A vacuum of 10 inches was applied to the system and increased to 22 inches by increments of pressure change to prevent foaming. When the residue approached dryness the temperature was decreased to 25°C to prevent charing of the residue and the vacuum raised to 25 inches.

Water Precipitation. The dissolved lignin was precipitated from a measured alcohol solution by pouring with agitation into an equal volume of distilled water.

The water temperature was 25°C.

The precipitated chloro-lignin was allowed to settle and then was filtered on a Buechner funnel. The precipitated chloro-lignin was dried at 35°C in the electric oven and weighed. Calculations were made to determine the percentage of lignin per unit volume of solution.

Low Temperature Precipitation. Low temperature precipitation of chloro-lignin from alcohol solution was accomplished by pouring the solution over ice. The ice was crushed and placed in a liter beaker. A measured volume of chloro-alcohol-lignin solution was poured over the crushed ice. The precipitated lignin was allowed to settle to the bottom of the beaker and washed with ice water into a Büechner funnel.Successive washings of the ice with ice water removed all the precipitated lignin. Ice water was used to wash the pricipitate until no test was obtained for chlorides.

The funnel containing the lignin was dried at 35°C in the electric oven and weighed. The percentage chloro-lignin dissolved by the solution was calculated.

The filtrate was tested for further precipitation by pouring over crushed ice.

Molding Experiments

The molding equipment used in testing the adhesive properties of the various chloro-lignins were:

1. Hydraulic press, ram capacity 20,000 lbs.
2. Cylindrical steel mold, 2 1/4 in. diameter.
3. Electrical mold heater, temperature range 25-400°C.
4. Resistors.

The mold was placed in series with a bank of three 660 watt resistors and a variable 1 ohm resistor was placed in parallel across one of the fixed resistors. The temperature of the mold could be varied between 100 and 150°C by changing the variable resistor.

The heater was calibrated for temperature by placing a bimetallic thermometer on the inside wall of the mold; filling the body of the mold with asbestos and changing the position of the slide rheostat.

The mold was prepared by polishing the ram and inside walls with 00 emery paper and greasing with stearic acid. Excessive stearic acid was wiped from the mold before adding the molding mixture.

The following steps were used in preparing the lignin for molding:

a. Weigh the lignin on the torsion balance.

b. Reduce to a powder in a mortar and place in a

6-in. stoneware crock.

c. Add a weighed amount of filler and mix until the lignin is distributed evenly in the filler.

d. Add plasticizer, if used, and mix.

e. Heat molding powder in the electric oven, if required.

The prepared molding powder was quickly placed in the mold to prevent cooling and the mold and heater were placed in the press. The pressure was increased slowly to allow volatiles to excape, and maintained at the required pressure for the molding cycle.

The following conditions were varied for the molding experiments:

a. Type of chloro-lignin.

b. Percentage of chloro-lignin.

c. Temperature of mold.

d. Time of molding.

e. Plasticizer added.

f. Temperature of molding powder.

The pressed samples were tested for relative strength on a Civil Engineering Department impact tester.

F. Data and Results

Preliminary Experiments

In order to study the properties of lignin and to find the optimum methods for carrying on the chlorination studies, a series of Preliminary Experiments were made. The following data and results were obtained from these experiments:

Table No. I

Specific Gravity of Alcohol-Lignin Solutions.

Sample No.	Stirring Time min.	Temperature of Suspension °C	Specific Gravity
1	12	25	0.827
2	10	65	0.834
3	5	65	0.835
4	5	45	0.834

The specific gravities are averages of two or three determinations. Determinations varied due to the rapid evaporation of the solution.

Chlorination of a Methyl Alcohol-Lignin Mixture.

Conditions: 400 grams lignin
800 ml. methyl alcohol
5-in. gage
Temperature: 25°C
Chlorination Time: 76 min. (wet)
30 min. (dry)

Results: The methyl alcohol-lignin mixture forms a black viscous mass. After 76 minutes of chlorination the lignin sealed the tip of the chlorine outlet tube. There was no apparent change in color of the mass or any rise in temperature. The alcohol was poured from the reactor and after 30 minutes of chlorination a yellow crust formed on the surface of the lignin mixture. Five ml. of alcohol which were drained from the reactor had turned bright yellow.

Table No. II

Chlorination of Dry Lignin.

Test No.	Chlorination Time min.	Lignin grams	Gage in.	Temp Rise: °C	Results
1	30	10	3.0	23 to 41 in 7.5 min	Slight lightning of the brown color.
2	30	10	4.0	31 to 55 in 2.5 min	Reaction gas identified as $CHCl_3$. by three observers.
3	10	5	4.0	28 to 38	Slight lightning of brown color. Chlorine %: 4.5.

The chlorinated lignin from Test 1 was dissolved in a solution of 1.N sodium hydroxide and precipitated with a solution of 0.5N hydrochloric acid. The precipitate had a light cream brown color as compared with the dark brown color of the dry chlorinated lignin.

Chlorination of Lignin Wetted with Methyl Alcohol.

Conditions:	2 grams lignin
	Wet with methyl alcohol on a filter paper
	Chlorinate: 9 min.
	Air Dry: 12 hours

Results:

There was no noticable color change in the lignin immediately after removing it from the chlorinator. However, after 12 hours of air drying the surface of the lignin had turned light yellow. The lignin below the surface was unchanged.

Chlorination of Lignin Suspended in Methyl Alcohol.

Conditions:	0.5 grams lignin
Test No. 1	10 ml. methyl alcohol
	Shake in test tube
	Pass Cl_2 through the suspension at 25°C

Results:

The color of the suspension changed from dark brown to bright yellow with a slight rise in temperature.

Conditions:

Test No. 2:	1 gr. lignin suspended in 10 ml. of alc.
Test No. 3:	1 gr. lignin suspended in 20 ml. of alc.
No. 1 & 2 :	Chlorinated: 5 min.

Results:

Test No.	
2	Two fractions were formed: a. Bright yellow lignin suspended in methyl alcohol. b. A black unchlorinated fraction settled to the bottom of the test tube.
3	Two fractions were formed: a. Same as Test 2. b. A small amount of unchlorinated lignin settled out.
2 & 3	All lignin that was kept in suspension was chlorinated, and less unchlorinated lignin settled out when the lignin was slowly added to the alcohol solution.

Conditions: Test No. 4
80 grams lignin
1000 ml. methyl alcohol (Ratio 1:13)
Gage 4-in.
Temperature of reactants: 27°C
Time of reaction: 125 min.

Results:

Time min.	Observations
20	Stirring was difficult due to the lignin not in suspension fouling the glass stirrer. Color: dark brown
33	Color: dark red
60	Color: Orange, Temp. 132°F
100	Temperature: 133°F (maximum)
125	Temp: 124 Reaction product divided into three fractions: a. Methyl alcohol layer, dark red b. Precipitated chloro-lignin layer lignt yellow, granular powder c. Unreacted lignin, black.

Optimum Lignin to Alcohol Ratio.

Conditions:

Test No.	Ratio gr. lignin to ml. alcohol	Procedure
1	1:10	Pour lignin into alcohol with mechanical stirring.
2	1:15	
3	1:20	

Results: In all tests some of the lignin formed a thick viscous mass with the alcohol that settled out of solution. This mass could not be suspended by stirring in excess alcohol. A ratio of between 1:15 and 1:20 suspended the greater proportion of the lignin and was suitable for chlorinating. Less lignin settled out when the lignin was added slowly to the alcohol solution with stirring.

Chlorination of Lignin Dissolved in Sodium Hydroxide.

Conditions:

Test No.	
1	One-half gram of dry chlorinated lignin dissolved in 10 ml. of 1.0N. NaOH; Chlorinated 5 minutes and precipitated with 1:10 HCl.
2	One-half gram of dry chlorinated lignin dissolved in 10 ml. of 1.0 NaOH and precipitated with 1:10 HCl.
3	One gram of dry chlorinated lignin dissolved in 1.0 NaOH which has been chlorinated for 10 minutes. Allow to stand 12 hours and precipitate with 1:10 HCl.

Results:

Test No. 1 Gelatinous light yellow lignin.

2 Gelatinous dark brown lignin.

3 Gelatinous dark brown lignin.

Table No. III

Effect of Time of Chlorination on Lignin Sodium Hydroxide Solutions.

Test No.	Lignin Grams	NaOH 0.1N. ml.	Gage in.	Time of Chlorination min.	Results
1	1	25	2	3	HCl precipitates dark brown lignin
2	1	25	2	5	Same as 1
3	1	25	2	10	Solution turns acid and precipitates light brown lignin.

Chlorination of Lignin Suspended in Water Solution and in Chlorinated Alcohol Solution.

Conditions and Results:

Test No. 1 One gram of lignin was suspended in 10 ml. of water and chlorinated for 10 minutes. The lignin showed no evidence of chlorination.

Test No. 2 One gram of lignin was suspended in 10 ml. of methyl alcohol that had been chlorinated for 30 minutes. The suspension was heated to boiling for 10 minutes. Lignin showed no sign of chlorination.

Table No. IV

Effect of Sunlight on Chlorination Reaction.

Test No.	Constituents	Procedure	Results
1	20 gr. lignin	All test samples are placed in 1 gal. containers and filled with Cl_2. Placed in the sunlight for 12 hours with one refilling of Cl_2	For all test samples there was no apparent reaction as evidenced by any change in color or physical appearance.
2	20 gr. lignin suspended in 350 ml. CH_3OH		
3	10 gr. lignin dissolved in 100 ml. benzaldehyde		

Table No. V

Chlorination of Lignin Suspended in Phenol and Benzaldehyde.

Test No.	Lignin grams	Solvent ml.	Gage in.	Time min.	Results
1	5	10 ml. phenol	7	10	No noticable change of color or physical properties.
2	5	20 ml. benzaldehyde	7	10	Solution turned bright red. Lignin could not be precipitated by acid or water.

Table No. VI

Chlorination of Dissolved Lignin.

Conditions: A lignin solution was prepared for chlorination by adding the lignin slowly with mechanical stirring to 1400 ml. of methyl alcohol. The suspension was brought to 65°C, cooled and the alcohol lignin solution was decanted removing all non-dissolved lignin. The solution was divided and chlorinated.

Test No.	Temp. °C	Gage in.	Time min.	Results
1	65	8	30	Both test solutions gave an orange chloro-lignin precipitate, and a clear red chloro-alcohol-lignin solution. Sp. Gr. Test No. 2: 0.861. Neither solution gave a boiling point test. The temperature increaced from 60 to 96°C with a clear distillate and from 96 to 102°C with a yellow distillate.
2	25	8	30	

The chloro-alcohol-lignin solution from test No. 1 was distilled under vacuum and at atmospheric pressure. The lignin residue from the vacuum distillation was bright red in color and was easy to remove from the distilling flask. The lignin residue from the atmospheric distillation was dark red in color and had fused to the distilling flask.

Table No. VII

Effect of Temperature on Suspended Lignin.

Conditions: 10 grams lignin
200 ml. methyl alcohol
Suspend with stirring at 25°C

Results: The suspension was placed in a water bath and the temperature was raised to 43°C. At this temperature the lignin formed a plastic mass and settle to the bottom of the beaker.

Read No.	Time sec.	Temperature Alc-lignin Suspension °C.	Observations
1	0	22	Lignin in suspension.
2	160	25	Same.
3	430	30	Same.
4	660	35	Some lignin sticks to the side of the beaker.
5	890	40	Sides of beaker coated with lignin.
6	1110	45	Lignin coagulates and settles to the bottom of the beaker.

Separation of Chloro-lignin from Alcohol.

Conditions and Results:

Test No.

1 Air at 25°C was passed through a chloro-alcohol-lignin solution for 2 hours. A partial precipitation of light yellow lignin took place.

2 Carbon dioxide was passed through the solution for 1 hour. A partial precipitation took place.

3 A rapid precipitation resulted with the addition of concentrated and 1:10 HCl. The lignin was bright yellow.

4 Same for concentrated sulfuric acid as Test 3.

5 An immediate precipitation of bright yellow lignin was obtained when the solution was added to an equal volume of water. The filtrate from this mixture was red in color suggesting that lignin was still in solution. However, the addition of acid and centrifuging did not remove any additional lignin.

Table No. VIII

Molding Tests using Chloro-lignin as a Binder.

Test No.	Mold Time min.	Temp. °C	Pressure lb/in^2	Lignin			Filler		Remarks
				Type	Wt. gms	%	Type	Wt. gms	
1	4	270	1400	DL	8	50	WF	8	Moist with alcohol mixture ran from mold.
2	5	85	1800	DL	8	50	WF	8	Firm yellow cake.
3	10	155	2850	DL	5.5	40	SD	7.5	Uneven bond Some char.
4	10	160	3600	DL	5.5	40	SD	7.5	Thick dark cake.
5	13	155	2850	CL	5.5	40	SD	7.5	Not well bonded.
6	1	150	1400	DL	10	40	SD	15	One side bond One side char.
7	6	148	2850	CL	10	40	SD	15	Mixture ran.
8	10	104	2100	CL	10	40	SD	15	Good bond yellow cake.
9	10	104	2100	DL	10	40	SD	15	Dense, dark well bond.
10	7	113	1400	DL	10	100	--	--	Mixture ran.
11	11	113	700	CL	10	40	SD	15	Light brown good bond.
12	10	107	700	DL	10	40	SD	15	2 ml. dist. dark color Good bond.
13	8	113	700	CL	5.5	40	SD	7.5	Bright yellow No bond.
14	8	113	3600	CL	5.5	40	SD	7.5	Good bond Light yellow.
15	5	121	1400	CL	5.5	40	SD	7.5	Good bond Light yellow add trace of water.

Legend:
DL: Distilled chloro-lignin
CL: Chloro-lignin
SD: Sawdust
WF: Wood Flour

Chlorination Experiments.

The experimental data and results obtained from chlorination experiments are presented in the following tables and graphs.

Chlorination of Suspended Lignin. Tables IX and X present the data obtained from tests of chlorinating lignin suspended in methyl alcohol at 25°C to determine the effect of rate of chlorine flow on the reaction. The rate of flow for test No. 1 was 0.85 grams of chlorine per minute and 1.084 gm/min for Test No. 2. All other conditions were held constant. The remarks section indicates the color change of the reactants.

Figure 6 curves A and B plots unreacted chlorine in grams per minute against reaction time in seconds for Tests 1 and 2.

Chlorination of Dissolved Lignin. Tables XI and XII present the data obtained form tests of chlorinating lignin dissolved in methyl alcohol at starting temperatures of 25°C.

Figure 7 shows plots of reaction data for chlorine rates of 0.472 and 1.084 grams of chlorine per minute. All other conditions were held constant.

Tables XIII through XIX are data compiled from chlorination tests of dissolved lignin chlorinated at 65°C.

Figure 8 represents the chlorine consumption of seven chlorination tests. Curve A presents the data for chlorination at 0.472 gm./min. chlorine rate; all other curves are for chlorinations with a chlorination rate of 1.084 gm./min. With the following exceptions chlorination conditions were maintained constant: Curve B represents a test with out stirring, and curve G represents a test using $FeCl_3$ as a calalyst.

The data in table XX are a compilation of 11 chlorination runs. The data in column 6 are the weights of the alcohol insoluble chloro-lignin precipitated by the reaction. Column 7 lists the amount of chloro-lignin that was precipitated from chloro-alcohol solution by the ice precipitation method. The chlorine percentages in column 9 were determined by the method of Harris and Sherrard(17). The precipitated chloro-lignin of Test 13 was obtained by water precipitation. Test 13 was a quantitative test using an excess of chlorine.

Table No. IX

Chlorination of Suspended Lignin.

Chlorination Test No. 1 Conditions:
Wt. Suspended Lignin: 55.0 gm. 70 gm. Lignin
Per Cent Suspended Lignin: 78.6 1400 ml. CH_3OH
Wt. Alc-lignin Sol.: 1161.0 gm. Start Temp: 28°C
Wt. Chloro-alc-lignin Sol.:1332g 5-in. Gage Cl_2
Sp. Gr. Chloro-lignin Sol.:0.960 Stirrer On.

Read No.	Time sec.	React Temp. °C	Gas Samples Time sec.	Gas Samples $AgNO_3$ 0.1N ml.	Gas Samples Cl_2 gms.	Remarks
1	181		515	4.6	.0086	Dark Brown Sol.
2	412	30				
3	1010	36.7				
4	1204	38.9				
5	1605	43.3				No lignin settles
6	1904	47.8	576	6.4	.0118	Dark brown solution
7	2167	47.8				Dark redish brown
8	2880	51.7				Light red-brown
9	3500	54.4				Dull orange
10	4150	55.6	450	4.3	.0108	Medium Orange
11	4780	57.2				Orange
12	5004	57.8				
13	5706	60				
14	6400	60.5	200	22.3	.0951	Orange
15	8100	60.5	300	40.3	.143	
16	9990	59.5				Stop run repair gage
17	0	50.0				restart timer
18	1800	52.8	200	53.9	.287	
19	2370	55.0				
20	2991	55.6				
21	4824	55.6				
22	5000	55.0	300	64.4	.228	Orange
23	7800	55.3	300	64.9	.231	
24	9999	50.0				Timer starts over
25	150	50.0	360	72.8	.214	
26	2450	48.9	200	83.1	.433	
27	6500	45.6	250	83.4	.355	
28	6800	45.6				End Test Total time: 7 hr 26 m.

Table No. X

Chlorination of Suspended Lignin.

Chlorination Test No. 2	Conditions:
Wt.Suspended Lignin:56.8gm.	70gm.Lignin
Percent Suspended Lignin:81.3	1400ml.CH_3OH
Wt.Alc-lignin Sol.:1136.6 gm.	Start Temp:24°C
Wt.Chloro-alc-lignin Sol:1265.5g.	8-in gage Cl_2
Vol.Chloro-alc-lignin Sol:1135ml	Stirrer on

Read No.	Time	React Temp	Exit Gas	Gas Samples			Remarks
	sec.	°C	°C	Time sec.	0.1N. $AgNO_3$ ml.	Cl_2 gms.	
1	0	23.9	27				Start Test.
2	500	35.0	27				Dark brown sol.
3	1000	40.6	27				Air Temp:24°C
4	2106	48.9	26	200	2.05	.0109	Dark red sol. lignin film on flask.
5	3107	54.4	26	300	3.44	.0122	Medium orange-red
6	4222	58.9	26	200	27.6	.147	Orange-red sol.
7	5017	60.0	26	100	29.4	.313	
8	6015	6010	26	100	28.4	.303	
9	7019	60.0	32	100	*26.4	.225	Orange Sol. lignin film chlorinated.
10	8010	5819	34	100	27.2	.289	
11	9018	5819	40	100	40.6	.432	$CHCl_3$ odor. in exit gas.
12	0	57.8	40				Timer repeats
13	18	57.8	40	100	*36.5	.311	
14	1011	57.2	42	100	34.1	.363	
15	2014	56.7	43	100	32.9	.349	
16	3008	56.5	43	100	35.0	.372	
17	4008	55.6	44	100	35.2	.375	
18	5008	55.5	44	100	42.1	.447	End Test:
19	5169	55.5	44				Time: 4 hr. 11 min.

* Sample diluted to 200 ml.

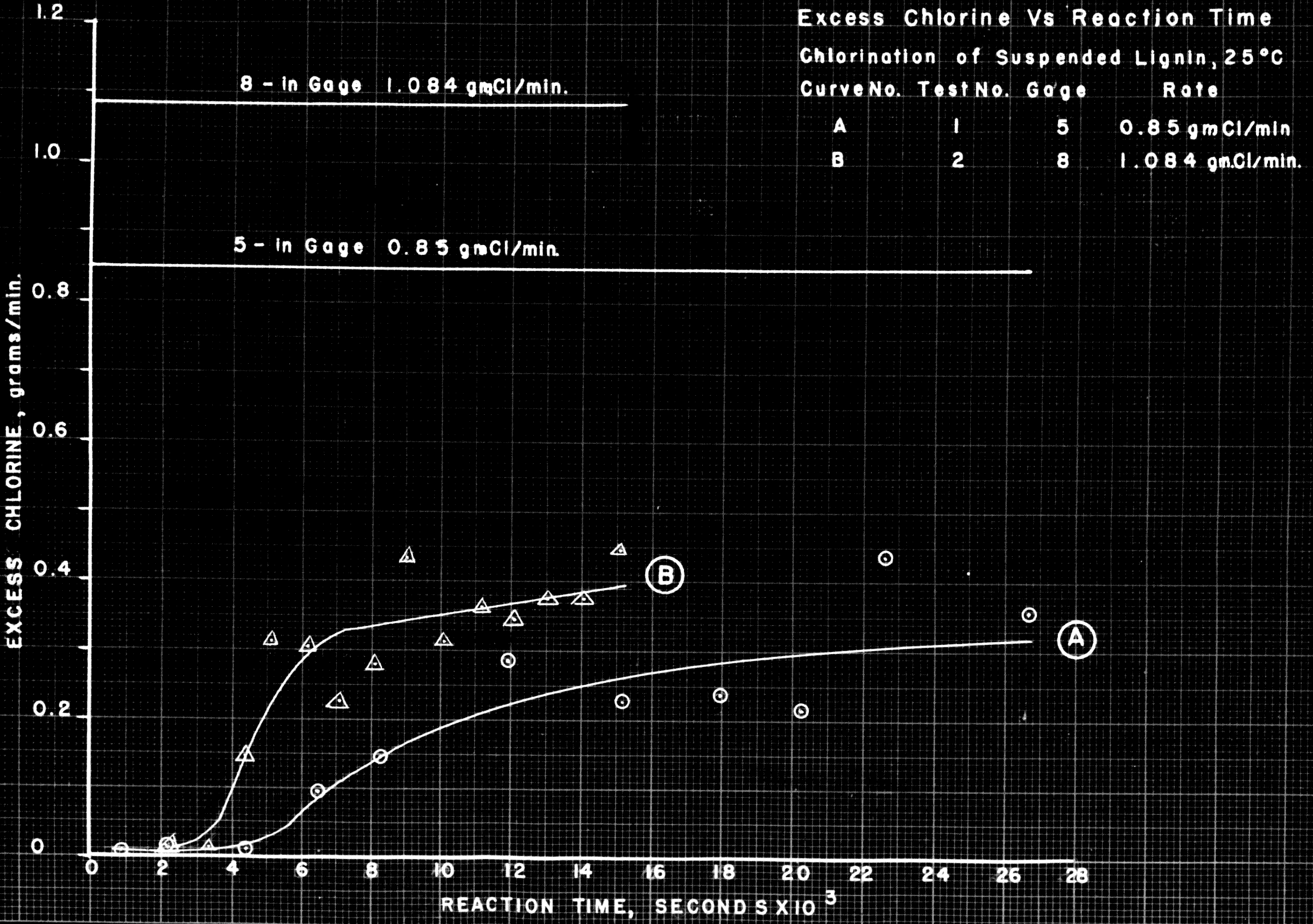


FIG. 6

Excess Chlorine Vs Reaction Time

Chlorination of Suspended Lignin, 25 °C

Curve No.	Test No.	Gage	Rate
A	1	5	0.85 gmCl/min
B	2	8	1.084 gmCl/min.

Table No. XI
Chlorination of Dissolved Lignin.

Chlorination Test No: 3
Wt.Dissolved Lignin:44.3 gm.
Percent Dissolved Lignin:44.3
Vol.Alc-lignin Sol: 735 ml.
Wt.Alc-lignin Sol: 602.6 gm.
Vol.Chloro-alc-lignin Sol:632 ml.

Conditions:
100 gm.Lignin
1000ml CH_3OH
Start Temp:26°C
2-in gage Cl_2
Stirrer On

Read No.	Time	React Temp.	Exit Gas Temp	Gas Samples Time	AgNO$_3$ 0.1N.	Cl$_2$	Remarks
	sec.	°C	°C	sec.	ml	grams	
1	0	26.7	27	100	1.54	.0163	Start test, shade
2	100	31.7	27				down; Air temp.
3	800	37.8	27				26.5°C; Dark brown
4	1212	40.0	27	88	2.6	.0314	sol. color
5	1600	43.3	27				
6	2121	45.0	27	100	2.28	.0243	
7	2600	47.3	27				
8	3370	47.8	27	100	1.84	.0196	Red foam
9	3800	48.4	27				Dark red sol.
10	4201	48.4	27				Cl$_2$ tube stopped
11	0	29.4	29				Start test 6hr.
12	1107	37.2	29.5	100	5.02	.0534	
13	2090	38.9	30	100	4.65	.0495	
14	2250	39.4	30				Red-orange color
15	3250	42.2	30				
16	4151	44.5	30	100	4.12	.0448	
17	5050	50.0	29.5	100	5.0	.0533	
18	5730	55.0	29.5	100	7.5	.0798	
19	6000	55.0	29.5				Medium-red sol.
20	6350	55.5	29.5	100	11.8	.1255	
21	7035	55.5	29.5	100	9.2	.0978	
22	8054	55.0	30	100	8.6	.0915	Medium-red sol.
23	8800	54.4	31.5				Stirrer heated
24	9000	53.3	32	100	12.8	.0136	
25	9100	52.8	33				End test. Time:3hr 41min

Table No. XII

Chlorination of Dissolved Lignin.

Chlorination Test No: 4
Wt.Dissolved Lignin: 41 gm.
Percent Dissolved Lignin: 41
Vol.Alc-lignin sol: 733 ml
Wt.Alc-lignin Sol: 602 gm.
Vol.Chloro-alc-lignin: 672ml

Conditions:
100 gm.Lignin
1000 ml CH_3OH
Start Temp: 30°C
8-in gage Cl_2
Stirrer On

Read No.	Time sec.	React Temp. °C	Exit Gas Temp °C	Gas Samples Time sec.	$AgNO_3$ 0.1N. ml	Cl_2 grams	Remarks
1	0	31.7	25.5				Start test
2	100	32.8	25.5	100	4.58	.0389	Shade down Air temp 25°C
3	700	46.1	26				Dark red-brown
4	1000	52.2	26	100	1.94	.0237	Dark brown-red
5	2000	60.0	27	100	2.5	.0265	Medium red sol.
6	3100	58.9	26	100	10.7	.1134	Red sol.
7	4000	58.9	33	100	28.0	.2979	NaOH cool
8	5000	58.3	41	100	25.2	.2682	
9	6000			100	26.3	.2799	
10	6200	57.2					
11	6800	56.7	40				
12	7100	56.7	40	100	27.4	.2916	
13	8000	55.2	39	100	24.6	.2619	Red sol.
14	8540	55.0	42				End test. Total time: 2 hr 20 min.

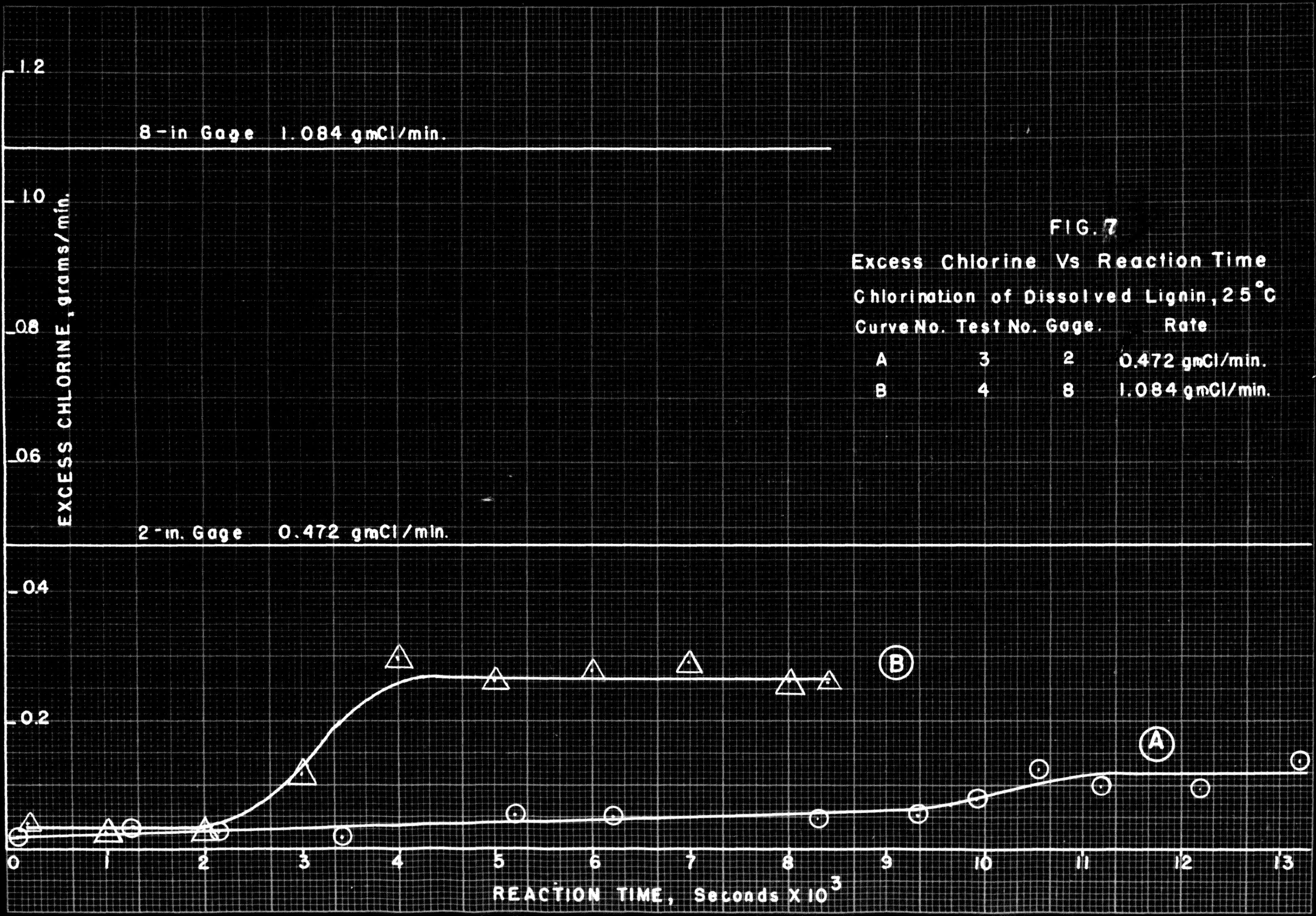


FIG. 7

Excess Chlorine Vs Reaction Time

Chlorination of Dissolved Lignin, 25 °C

Curve No.	Test No.	Gage.	Rate
A	3	2	0.472 gmCl/min.
B	4	8	1.084 gmCl/min.

Table No. XIII

Chlorination of Dissolved Lignin.

Chlorination Test No: 5
Wt.Dissolved Lignin: 41.5 gm.
Percent Dissolved Lignin:41.5
Wt.Alc-lignin Sol: 610.8 gm.
Vol. Alc-lignin Sol: 742 ml
Vol.Chloro-alc- lignin Sol:625ml

Conditions:
100 gm.Lignin
1000 ml CH_3OH
Start Temp:65°C
2-in Gage Cl_2
Stirrer On

Read No.	Time	React Temp.	Exit Gas Temp	Gas Samples Time	$AgNO_3$ 0.1N.	Cl_2	Remarks
	sec.	°C	°C	sec.	ml	grams	
1	0	65.2	30				Start test Dark brown sol.
2	260	65.6	30	100	0.29	.003	Shade down
3	1250	65.6	30	100	1.22	.0129	
4	2260	65.6	30	100	1.35	.0144	Reflux white
5	2750	65.6	30				Dark red-brown
6	3260	65.6	31	100	3.14	.0334	
7	4260	65.6	31.5	100	3.5	.0372	Reflux white
8	5260	65.6	32	100	6.2	.0695	Color dark red
9	6100	66.7	33	100	3.4	.0352	Red sol. Reflux white
10	7100	66.7	35	100	6.2	.066	Bright red sol.
11	8100	66.7	36	100	28.9	.308	Reflux white
12	9100	66.7	36	100	38.8	.413	
13	0	67	52.5				Timer repeats
14	100	67	52.5	100	44.0	.467	
15	1100	67.8	58	100	41.4	.441	
16	2100	67.8	55	100	41.0	.431	
17	2285	67.8					End test. Total time: 4 hr 44 min

Table No. XIV

Chlorination of Dissolved Lignin.

Chlorination Test No: 7
Wt. Dissolved Lignin: 42.5 gm.
Percent Dissolved Lignin: 42.5
Wt. Alc-lignin Sol: 660.3 gm.
Wt. Chloro-alc-lignin Sol: 688.5 gm
Vol Alc-lignin Sol: 810 ml
Vol Chloro-alc-lignin Sol: 692 ml
Sp.Gr. Chloro-alc-lignin Sol: 0.885

Conditions:
100 gm. Lignin
1000 ml CH_3OH
Start temp: 65°C
8-in gage Cl_2
Stirrer Not On.

Read No.	Time sec.	React Temp. °C	Gas Samples Time sec.	Gas Samples $AgNO_3$ 0.1N. ml	Gas Samples Cl_2 grams	Remarks
1	0	64.4				Start run.
2	100	64.4	100	1.95	.0207	
3	900	65.0	100	4.35	.0463	
4	1900	65.0	100	15.7	.1661	
5	2900	65.0	100	27.2	.29	
6	3100	65.0				Dark red.
7	3300	65.0				Bright red color
8	3900	65.0	100	63.15	.671	
9	4500	63.3				
10	5000					Explosion stopped run.

Table No. XV

Chlorination of Dissolved Lignin.

Chlorination Test No: 8
Wt Dissolved Lignin: 39.5 gm.
Percent Dissolved Lignin:39.5
Wt Alc-lignin Sol: 632.5 gm.
Wt Chloro-alc-lignin Sol:678.3gm.
Vol Alc-lignin Sol: 768 ml
Vol Chloro-alc-lignin Sol:665ml

Conditions:
100 gm. Lignin
1000 ml CH_3OH
Start Temp:65°C
8-in Gage, Cl_2
Stirrer On

Read No.	Time sec.	React Temp. °C	Exit Gas Temp °C	Gas Samples Time sec.	Gas Samples $AgNO_3$ 0.1N. ml	Gas Samples Cl_2 grams	Remarks
1	0	64.4					Start run.
2	100	64.4		100	0.56	.0059	Dark brown sol.
3	350	65.6	29				Stirrer slow to
4	900	65.6	29	100	1.83	.0195	cut entrainment
5	1200	65.6	29				No.ppt.lignin
6	1400	65.6	29.5				Cond.Liquid
7	1450	65.6	30				yellow Dark-brown-red
8	1900	65.6	30.5	100	6.29	.0736	Ent.3/4 cond.
9	2180	65.6	31				Cond.liquid Y. Dark red sol.
10	2300	65.6	31				Dark red sol.
11	2700	65.6	31.5				Cond.liq.yellow
12	2900	65.6	31.5	100	28.8	.3061	Bright red sol.
13	3100	65.6	31.5				Ent.½ cond.
14	3900	65.6		100	65.0	.681	
15	4300	65.6	34				
16	4900	65.6		100	98.6	1.05	
17	5000	65.6					Bright red sol.
18	5300	65.6	38				
19	5362	65.6					Explosion stopped run. Total time: 1 hr 29 min.

Table No. XVI

Chlorination of Dissolved Lignin.

Chlorination Test No: 9
Wt Dissolved Lignin: 46.5 gm.
Wt Alc-lignin Sol: 603.3 gm.
Vol Alc-lignin Sol: 735 ml
Vol Chloro-alc-lignin Sol: 547 ml.

Conditions:
100 gm. Lignin
1000 ml CH_3OH
Start Temp: 65°C
8-in Gage Cl_2

Read No.	Time	React Temp	Exit Gas Temp	Gas Samples			Remarks
				Time	$AgNO_3$ 0.1N.	Cl_2	
	sec.	°C	°C	sec.	ml	grams	
1	0	64.4	30				Start run.
2	210	64.4	30	90	0.87	.0103	Dark brown sol.
3	1070	65.0	30	130	2.76	.0235	Reflux white
4	1700	65.6	30				Dark red brown
5	2005	65.6	30	95	9.23	.1034	
6	2300	65.6	30				Dark red
7	2700	65.6	31				Medium-red
8	3100	65.6	32.5	100	51.0	.543	Light-med-red reflux yellow Ent. 1/3 cond.
9	3250	65.6	37				Light red sol.
10	3400	65.6	45				Reflux yellow
11	3700	65.6	55	100	49.4	.525	
12	4000	65.6	59.5	100	55.5	.590	Change NaOH
13	4600	65.6	68				Reflux ½ cond.
14	4850	65.6	60				
15	5200	65.6	54	100	94.5	1.004	Light red sol.
16	6000	66	57	100	*89.7	.761	
17	6295	65	56				Cl_2 tube stopped
18	6295	65.6	30				Start run.
19	7200	66	66	100	41.2	.438	Reflux yellow
20	8400	68	57	100	53.8	.573	
21	9000	68	62	100	56.4	.60	$CHCl_3$ odor.
22	0	68.9	65	100	78.0	.830	Timer repeats
23	1000	69.5	68	100	78.8	.84	Collect gas
24	2000	71.0	68	125	123	1.048	Reflux yellow
25	3000	69	69.5	100	99.6	1.058	
26	3100	69	69.5				Light red sol. End run. Total time: 3 hr 38 min.

* Sample diluted to 200 ml.

Table No. XVII

Chlorination of Dissolved Lignin.

Chlorination Test No: 10
Wt Dissolved Lignin: 40.5 gm.
Percent Dissolved Lignin:40.5
Vol Alc-lignin Sol: 735 ml
Vol Chloro-alc-lignin: 650ml
Sol. Stirred:10 min.

Conditions:
100 gm Lignin
1000 ml CH_3OH
Start Temp:65°C
8-in Gage Cl_2
Stirrer On

Read No.	Time sec/	React Temp °C	Exit Gas Temp °C	Gas Samples Time sec.	Gas Samples $AgNO_3$ 0.1N. ml	Gas Samples Cl_2 grams	Remarks
1	0	65	26				Dark brown sol. Start test.
2	229	65	26	100	0.76	.0065	
3	1100	65.6	26				Red-brown
4	2111	65.6	26	119	15.0	.134	Dark red sol.
5	2510	65.6	26	108	19.3	.2055	Reflux white Med.red sol.
6	3009	66.7	26.4	100	27.7	.295	Bright red sol. Reflux white
7	3200						Ppt. Lignin sticks to Cl_2 outlet tube
8	3505	65.6	28	100	54.0	.69	
9	4000						Test stopped due to explosion in NaOH trap.
10	0	66.7	21				Start run
11	532	66.7	24	100	8.0	.085	Reflux yellow
12	1003	66.7	32	100	34.5	.366	
13	1505	66.7		100	39.0	.415	
14	2006	66.7	48	112	89.2	.848	
15	2504	66.7	52	100	84.3	.896	
16	3252	66.7	44	100	80.6	.859	Reflux white
17	3504	66.7	54	100	80.6	.859	Orange-red sol.
18	3943	66.7					End run. Time:2hr 12min.

Table No. XVIII

Chlorination of Dissolved Lignin.

Chlorination Test No: 11	Conditions:
Wt Dissolved Lignin: 41;2 gm.	100 gm.Lignin
Percent Dissolved Lignin:41.2	1000 ml CH_3OH
Wt Alc-lignin sol: 677.5 gm.	Start Temp:65°C
Wt Chloro-alc-lignin Sol:695gm	8-in Gage Cl_2
Vol Chloro-alc-lignin Sol:560ml	Stirrer On
Stirring Time: 10 min.	

Read No.	Time	React Temp.	Exit Gas Temp	Gas Samples			Remarks
				Time	$AgNO_3$ 0.1N.	Cl_2	
	sec.	°C	°C	sec.	ml	grams	
1	0	65	34				Dark brown
2	539	65	29	100	6.66	.0567	Time:8:30
3	1065	65	28.5	114	15.8	.147	Dark brown
4	1520	65	28.5	110	22.4	.216	Dark red-brown
5	2044	65	28.5	100	26.9	.286	Dark red
6	2514	65	28	100	29.9	.318	Med.dark red
7	3010	64.4	27	100	36.3	.386	Medium red
8	3509	65.6	27.5	100	53.1	.565	Medium red
9	4007	65.6	29	100	59.6	.635	Med(light)red
10	4100	65.6	33	1			Red
11	4508	65.6	33	100	67.0	.714	Red
12	5005	65.6	36	100	56.1	.597	Red
13	5506	65.6	38	100	57.3	.61	
14	6006	65.6	41	125	89.0	.606	
15	6517	65.6	45	100	59.0	.629	
16	7004	65.6	47	100	57.4	.61	
17	7504	67	49	100	59.1	.629	
18	8063	67	49	100	59.1	.629	Chloro-alc.cond.
19	8505	68	52	100	61.3	.653	in traps
20	9004	68	55	100	62.4	.663	
21	4	68.5	56	100	63.9	.68	Timer starts
22	1000	69	59	100	72.7	.773	over
23	2000	71	60	105	77.2	.772	
24	2110	71	60				Red. End run. Total Time: 3 hr 22 min.

Table No. XIX

Chlorination of Dissolved Lignin.

Chlorination Test No: 12	Conditions:
Wt Alc-lignin Sol: 603.7 gm.	100 gm.Lignin
Wt Chloro-alc-lignin Sol:611.8gm.	1000 ml CH$_3$OH
Vol Alc-lignin 735 ml	Start Temp:65°C
Wt FeCl$_3$6H$_2$O: 40 gm.	8-in Gage Cl$_2$
Vol Chloro-alc-lignin Sol:585ml	Stirrer On

Read No	Time	React Temp	Exit Gas Temp	Gas Samples			Remarks
	sec.	°C	°C	Time sec.	AgNO$_3$ 0.1N. ml	Cl$_2$ grams	
1	0	65.5	32				Start run.
			32				Shade down
2	475	65.5	32	105*	4.28	.0348	Dark brown sol.
3	500	66.7	32.5				Air temp:28.5°C
4	1019	66.7	34.5	100	3.68	.0392	Brown-red sol. Reflux white
5	1500	66.7	34.5				Dark red sol. Reflux white
6	1800	66.7	36	100	6.7	.0712	
7	2400	66.7	39				Medium red sol.
8	2645	66.7		100	1.66	.0176	
9	3000	66.7	59				Red sol.
10	3207	66.7		100	2.76	.0294	Light red sol.
11	3700	66.7	42				Reflux white
12	4050	66.7		100	5.28	.0562	
13	4400	65.6	47				
14	4406	65.6		100	36.9	.392	Bright red sol.
15	4600	65.6	56				Undond. liquid collects in trap
16	4700	65.6					Stirrer off
17	5300	66.7	41				Stirrer on
18	5600	68	48	100	79.4	.846	
19	6505	69.9	66.5	100	69.5	.740	Change NaOH
20	7200	69.9	36.5	100	96.2	1.022	Reflux yellow
21	8100	71	55	100	89.8	.955	Reflux ½ cond.
22	9005	71	57	100	96.5	1.038	
23	9720	71	57.4	100	95.1	1.01	Reflux ¼ cond.
24	700	71	58	100	117.9	.966	Noreflux
25	1500	71	57	100	93.4	.995	
26	2112	71	59				End test. Total time: 3 hr 21 min

* Sample diluted to 200 ml

Table No. XX

Summary of Conditions and Results of Chlorination Tests.

Test No.	Conditions Temp °C	Gage in	Type	Total Time sec.	Chloro Lignin grams	Ppt. Lignin Chloro grams	Chloro Lignin %	Ppt. Chloro Lignin %
1	30	5	Sus	26780	64		25.0	
2	30	8	Sus	15169	57.7	70.3	25.3	23.3
3	30	2	Dis	13300	31.1	31.5	20.95 27.7	25.2
4	30	8	Dis	8540	27.0	30.95	27.0	28.0
5	65	2	Dis	12285	35.0	32.8	28.3	27.3
6	65	2	Dis	5360	17.5	26.7		20.25
7	65	8	Dis	5000	26.0		21.7	
8	65	8	Dis	5360	28.0	34.8	20.8	24.45
9	65	8	Dis	13100	35.3	24.15	29.4	28.45
10	65	8	Dis	7940	27.2		25.43	
11	65	8	Dis	12105	37.5		24.93	
12	65	8	Cat. Dis	11500	32.5	26.2	29.25	25.4
13			Dis					29.1

Legned: Dis :: Dissolved Lignin
sus: : Suspended Lignin
Cat :: Catalyst

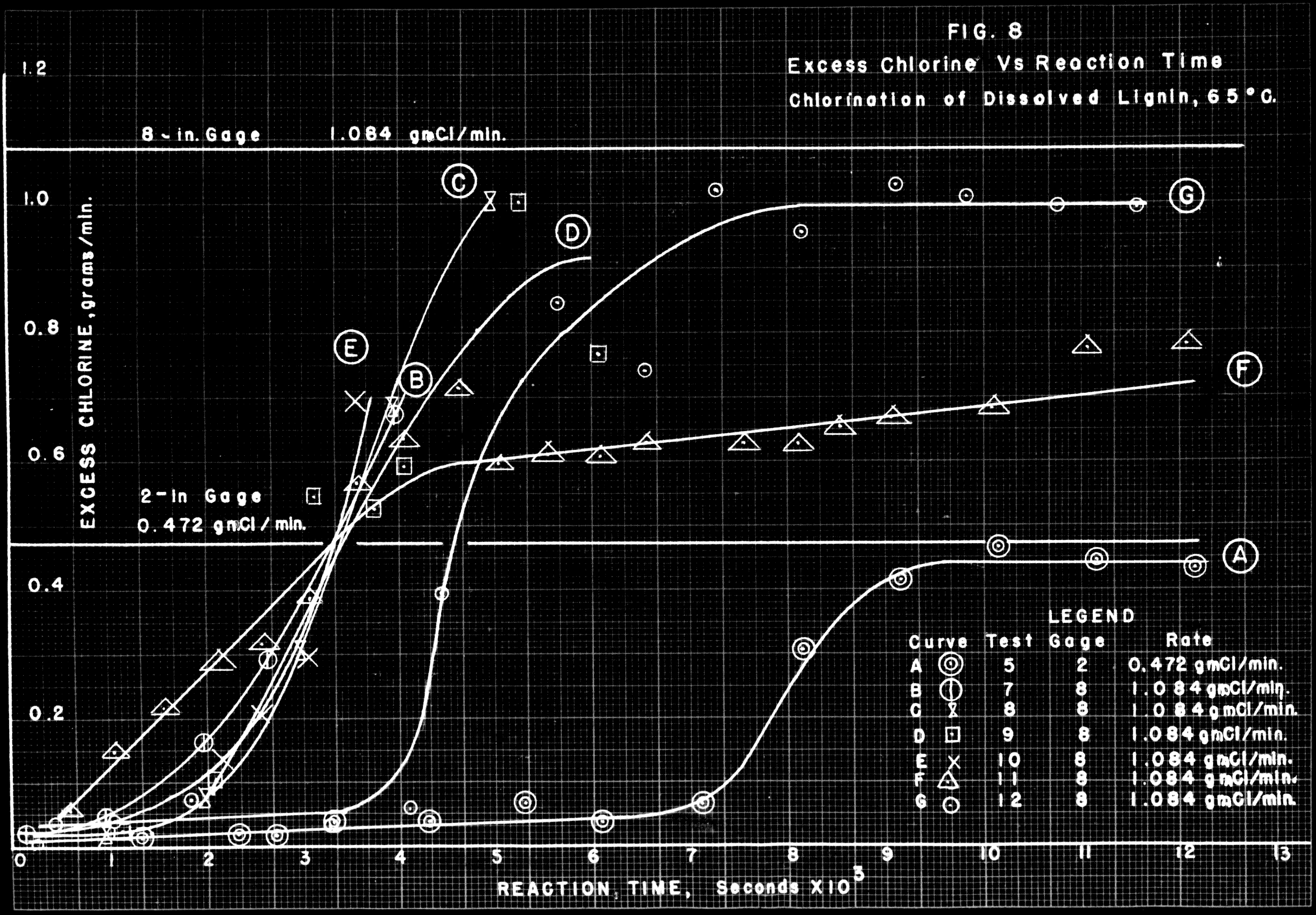


FIG. 8

Excess Chlorine Vs Reaction Time

Chlorination of Dissolved Lignin, 65 °C.

Molding Experiments.

Molding Conditions. Table XXI summarizes the conditions of the chloro-lignin molding tests. The term chloro-lignin refers to the lignin precipitated from the chloro-alcohol-lignin solution during chlorination. Precipitated chloro-lignin refers to the ice precipitated chloro-lignin. Distilled lignin refers to the lignin free solution condensed from the distilled lignin recovery. The white pine sawdust filler was unscreened sawdust as obtained from the Virginia Polytechnic Institute Wood Shop.

Impact Testing. Table XXII lists the results of testing the molded lignin samples with an impact tester. The term fracture used in describing the failing point of the sample indicates that the sample has cracked but not broken. The cake color refers to the color of the sample with the surface darkening, caused by the mold lubricant, removed.

Table No. XXI

Conditions for Molding Chloro-lignin.

Legend:
CL: Chloro-lignin
PL: Precipitated Chloro-lignin
DL Distilled Chloro-lignin

Constant Conditions:
Molding Temp: 112°C
Filler: White Pine Sawdust
Plastizer: Distillate Chloro-lignin

Test	Lignin			Filler	Plast	Thick	Press	Time
No.	Type	Wt gms	%	Wt gms	-izer ml	in	lb/in^2	min
1	CL	8	40	12	15	0.246	2600	10
2	PL	8	40	12	-	0.189	3400	10
3	PL	4	20	16	25	0.243	3500	10
4	PL	1	5	19	25	0.287	3500	10
5	PL	2	10	18	25	0.260	3500	10
6	PL	4	20	16	25	0.250	3500	10
7	PL	4	20	16	6	0.296	4300	10
8	PL	4	20	16	-	0.30	4300	10
9	CL	8	40	12	10	0.231	4300	10
10	CL	4	20	16	10	0.275	4300	10
11	PL	8	40	12	-	0.253	4300	10
12	CL	10	100	-	-	0.15	4300	10
13	PL	10	100		10			
14				20	25		4300	10
15	DL	10	40	15	2	0.292	750	10 @ 107°C

Table No. XXII

Impact Testing of Chloro-lignin Plastics.

The impact numbers were determined on an International Impact Testing Machine for rock toughness. The impact number is the drop in cm. of a five kilogram weight required to fracture the sample. Samples that required more than one maximum impact were prefixed by the number of drops required for fracture.

Test No.	Impact No. cm.	Remarks
1	30	Dark yellow cake, fair bond, sample dented then fractured.
2	16	Light brown cake, fair bond, sample dented slightly. Cake hard.
3	40	Brown cake, good bond. Sample dented then fractured.
4	50	Light tan cake, good bond. Sample dented then fractured.
5	60	Light tan cake, hard cake, good bond. Sample dents then fractures.
6	50	Light tan cake, hard cake, good bond. Sample dents then fractures.
7	3R60	Yellow, hard cake. Good bond. Sample dents then fractures. Weight dropped three times from maximum height before fracturing.
8	5R60	Yellow, hard cake, good bond, sample dented. Weight dropped maximum height fove times with no fracture.
9	10	Red-brown, hard, brittle, flaky cake. Poor bond. Dents and fractures on impact.
10	35	Yellow, flaky, fair bond cake. Dents then fractures.
11	35	Light yellow, flake formation, hard. Poor bond. Dents slightly then breaks.
15	20	Red-brown, hard, crumbly cake. Water resistant. Does not dent. Breaks at 20 cm.

IV. DISCUSSION

A. Discussion of Results

Definition of Terms. The lignin was recovered as a by-product of the "sulfate" process for paper making; short leaf southern pine was the basic raw material. Since this process acts drastically(20) on the lignin structure the results can only be interpreted as applicable to the sulfate-type lignin.

The types of chlorinated lignin are described as follows:

1. Chloro-lignin will be used to refer to the lignin which is thrown out of solution by the chlorination reaction.
2. Precipitated chloro-lignin will be used to refer to the lignin which is recovered from alcohol solution by precipitation in the presence of ice.
3. Distilled chloro-lignin will be used to refer to the lignin which is recovered from alcohol solution by distillation.

Suspension of Lignin in Methyl Alcohol. The lignin-alcohol suspension for controlled chlorination tests was prepared by adding 70 grams of dry lignin to 1400 ml. of methyl alcohol with mechanical agitation. The temperature of the methyl alcohol solution to which the lignin was added was kept at 25°C. The temperature and method of adding lignin to alcohol proved to be critical factors in preparing a suspension.

Experiments showed that lignin could not be kept in suspension above 45°C. At temperatures from 35 to 40°C lignin was deposited as an alcohol-insoluble black film on glassware. From temperatures of 43 to 45°C the lignin coalesces and settles to the bottom of the reactor. In this form the lignin can not be resuspended by heat or agitation and will foul moving parts of the equipment. During chlorination tests lignin in this form effectively sealed the chlorination outlet tube and stopped further chlorination. Relatively high rates of gas flow did not prevent the lignin from building up on the tube.

As a result of this property suspended lignin was chlorinated at the temperature level of the atmosphere.

A ratio of one part by weight of dry lignin to 20 parts by volume of methyl alcohol was found by tests to be satisfactory for suspending lignin in alcohol. A fraction of the lignin added to alcohol will form a plastic like black mass. The amount of formation varied depending on the method by which the suspension was prepared. Fifty to 75 per cent of the lignin when added in large amounts to methyl alcohol formed a non-suspendable mass. The per cent of non-suspended lignin varied depending on the conditions of stirring and temperature.

However, when comparable ratios of lignin and alcohol are mixed at 25°C by adding the lignin slowly with mechanical stirring to the alcohol up to 85 per cent of the lignin is suspended. The 1:20 ratio used was based on tests using ratios between 1:10 and 1:100. In every case some lignin was not suspended; however, the non-suspended amount decreased as the ratio increased. For ratios as high as 1:100 a small fraction of the lignin was not suspended. When the non-suspended fraction was dried, ground and resuspended, again the non-suspended and suspended fraction was formed. This property is interpreted as resulting from physical method of mixing and not due to the original lignin being of different constitution. In order to obtain enough chlorinated lignin from the experiments to make the necessary tests, the ratio of 1:20 was used.

Lignin Dissolved in Methyl Alcohol. The amount of lignin dissolved in methyl alcohol varied from 0.035 grams/ml. at 25°C to 0.043 grams/ml. at 65°C. Doubling the time of stirring had no effect on the specific gravity. The amount dissolved was the same when the tests were carried out at 45°C as for 65°C.

The dissolved lignin prepared for the experimental test varied from 39.5 to 46.5 per cent. The variation of amount dissolved was due, in part, to the method of preperation. In all cases the lignin was added with agitation to alcohol which had just reached 65°C. The mixture was mechanically stirred for five minutes then cooled in a water bath. However, under these conditions the amount of alcohol vaporized varied resulting in different amounts of lignin being dissolved. When the non-dissolved portion is air dried and ground it has a black color as compared with the dark brown color of the original lignin. This fraction will dissolve partially in alcohol, but the greater portion could not be dissolved on successive attempts. No quantitative data was obtained on the maximum lignin fraction which could be dissolved. The results indicate that the sulfate lignin has two physical forms: one that is methyl alcohol soluble, the other methyl alcohol insoluble.

Alcohol-lignin solutions on standing at 22 to 28°C will lose some of the dissolved lignin. This lignin comes out of solution in a black tarry mass.

When dissolved lignin is precipitated from alcohol solution by pouring into water the lignin precipitate is heavier than water and settles to the bottom of the flask. When the non-dissolved lignin is dried, ground and added to alcohol at 65°C the small amount that dissolves is lighter than water. This fact leads to the conclusion that the dissolved fraction was composed of lignin of different degrees of polymorization.

Separation of Chloro-lignin from Alcohol Solution. Chlorination of lignin dissolved in alcohol solution results in two chloro-lignin forms. The first was chloro-lignin which precipitated as the alcohol-lignin became chlorinated and the second was the chloro-lignin which remained in solution. The color of the precipitate resulting from this reaction was orange. The dissolved lignin when precipitated by ice water from solution was light yellow. These two forms differed in the amount of combined chlorine.

Tests of the chloro-alcohol solution have shown that lignin can be precipitated by acidifying the solution. Addition of dilute hydrochloric and sulfuric acid will immediately precipitate the chloro-lignin as a light yellow, flocculent powder. Passing carbon dioxide gas through the solution results in a partial precipitation. It is not clear why the hydrochloric acid formed by the reaction does not precipitate the dissolved chloro-lignin. It may be that the hydrochloric acid causes the precipitation of chloro-lignin during the reaction, but if so the precipitation is only partial. The chloro-lignin becomes insoluble in alcohol once it is precipitated. However, the dissolved chloro-lignin after being precipitated can be redissolved. This indicates that the chlorinated lignin is of two different chemical forms, probably resulting from the original lignin being comprised of two or more different physical or chemical structures.

The separation method, used for preparing dissolved lignin for testing, was precipitation by addition of a non-solvent to the solution. Addition of water will cause immediate precipitation if equal quantities of water and chloro-alcohol solution are used. It was noted that the filtrate from water precipitated lignin was still a red color indicating that all of the lignin was not removed. Adding water, acidifying and centrifugation did not remove this last fraction of dissolved chloro-lignin.

Harris(17)separated chloro-lignin from solution by precipitating with ice water. This method was used and lignin was removed from solution. Cragg and Hammerschlag, "Chemical Reviews" vol. 39, p. 102 (1946), point out that the precipitation point of a polymer-solvent-precipitant system depends very markedly on the temperature. The temperature dependence of solubility indicates that the chloro-lignin precipitated is a mixture of different weight lignins.

Some Phases of the Chemical Nature of Chlorinating Lignin. The number and effect of the different chemical reactions that took place during the chlorination reaction was not determined. That the methyl alcohol is necessary for the chlorination reaction was proven by chlorinating lignin in the dry state. The chlorinated dry lignin was 4.5 per cent chlorinated while the methyl alcohol lignin was chlorinated as much as 29 per cent.

Groggins(15) states that the chlorination of the side chain of aromatic compounds is favored by higher temperatures and lower temperatures favor the replacement of a nuclear hydrogen. The nuclear reaction is also greatly facilitated by the presence of a halogen carrier such as iron, aluminum or iodine. Thus during the chlorination test it is reasonable to assume that both side chain and nuclear chlorination takes place.

Hydrochloric acid was formed by chlorine substitution for a hydrogen of the lignin molecule. Hydrochloric acid will react with chlorine to form some methyl chloride. Since methyl chloride is a methylating agent it may have some effect during the chlorination.

Also some methyl hypochlorite will be formed by the action of chlorine on methyl alcohol. Harris has concluded that methyl hypochlorite adds to the ethylenic linkages of lignin and during chlorination more methoxyl groups are added to the lignin unit.

Gaseous products of the reaction included hydrogen chloride which was condensed in the trap. Chloroform was identified by odor. A dark red unidentified liquid was also condensed in the trap. A low boiling, white liquid, identified as a chlorinated unsaturated aldehyde was condensed by passing the reactant gases through an ice bath. Other gaseous products passed through uncondensed. Therefore, the total chlorine utilized is not all added to the lignin molecule.

Chlorination of Suspended Lignin. Figure 5 is a plot of excess chlorine in grams per minute against reaction time. Curve A is the plot using 0.85 grams of chlorine per minute and Curve B is a plot using 1.08 gm. Cl_2/min. The area under the curve represents the chlorine not used by the reaction. The area between the curve and the chlorine input line represents the chlorine being used in the reaction. A comparison of the curves for the two reactions shows an increased rate of reaction with a higher concentration. The time and temperature factors are constant. There was no known catalyst. And the possibility of photosynthesis was partially removed by runing the tests under artificial light. A study of the reaction curves shows for the period of the first 250 minutes for 0.85 gm. Cl_2/min. 87 per cent of the total chlorine was utilized in the reaction. For the higher rate of flow, 1.082 gm. Cl_2/min., 77 per cent of the total chlorine was reacted. The lower rate of flow favored the utilization of chlorine by 10 per cent. However, for the lower rate of flow 185 grams of chlorine were reacted in 250 minutes. The higher rate of flow resulted in the reaction of 208 grams of chlorine in 250 minutes. Thus the higher rate of chlorine flow gave an increase of 12.5 per cent over the lower in the weight of chlorine utilized over the same period of time. Then, for an increase in chlorine rate of 14.5 per cent, an increase in chlorine consumption of 12 per cent resulted.

The reaction progressed with the liberation of heat and a gradual change of color. The temperature of both tests rose to 60.6°C and a final solution color of orange. The suspension passed through the following color changes: original dark brown color, dark reddish brown, dark red, dull orange and finally orange. For the low rate of flow this change took place over 80 minutes and for the higher rate of flow the complete color change had taken place in 52 minutes. The color remained constant for the remainder of the test. For both reactions the final color was noticed at the point on the curve where a rapid decrease in chlorine consumption was indicated.

The lignin suspension of test No. 1 had 55 grams of lignin suspended and dissolved in the alcohol, test No. 2 had 56.8 grams dissolved. The total recovered chlorinated lignin from test No. 2 was 128 grams, of which 57.7 grams were chloro-lignin and 70.3 grams were precipitated chloro-lignin. The chloro-lignin was filtered to recover it from the reaction solution, but the filtrate was not washed to remove the combined reaction products such as HCl. Therefore, the dried chloro-lignin weight cannot be taken as exact.

The percentage combined chlorine of the chloro-lignin for test No. 1 was 25.0 for test No. 2 was 25.3 per cent. The chlorine percentage for the precipitated chloro-lignin of test No. 2 was 23.3. Test No. 1 was run for 7 hours 26 minutes with no change in color after 1 hour 20 minutes and with a decrease in reaction temperature from 60.6 to 45.6°C. after 2 hours 15 minutes of reaction. The assumption is, therefore, made that for lignin chlorinated under these conditions the maximum percentage chlorination will be approximately 25 per cent.

It was noted that temperatures in excess of 43°C were reached, due to the exothermic reaction, with out causing the lignin to coagulate. This same temperature rise without chlorination caused the suspended lignin to coalesce and settle out. An assumption can therefore be made that after the first color change is noted in the reaction mixture the temperature of the mixture could be raised without causing coagulation of the suspended lignin.

Chlorination of Dissolved Lignin. Ten controlled tests were made chlorinating dissolved lignin. Two tests were made at starting temperatures of 25°C and eight tests were made at starting temperatures of the boiling point of the alcohol medium. These tests gave a comparison of the effect of rate of flow and of temperature on the chlorination. The chlorination tests at 65°C were carried out with and without $FeCl_3$ to determine the effect of a catalyst on the reaction.

Chlorination of Dissolved Lignin at 25°C. Figure 6 is a plot of excess chlorine in grams per minute against reaction time for starting temperatures of 25°C. Chlorine rates of 0.472 gr. Cl_2/min. for Curve A and 1.082 gr. Cl_2/min. for Curve B were used. The reactions were carried out under artificial light.

A study of the reaction curves show that for the reaction period of the first 117 minutes the higher rate of chlorination resulted in a higher percentage of the chlorine being reacted with the lignin.

For Curve B, 1.082 gm. Cl_2/min. 84.6 per cent of the total chlorine was utilized. For curve A, 0.472 gm. Cl_2/min. 96.7 per cent of the chlorine input was utilized. The lower rate of chlorine flow favored utilization by 12 per cent. During this period the higher rate of flow resulted in 109.4 grams of chlorine reacting. This gave a 102 per cent greater weight of chlorine reacting during the same time period. Again doubling the rate of flow doubled the chlorine consumption.

The exothermic reaction did not raise the temperature of the two tests the same amount. The lower rate of chlorination test reached a maximum temperature of 55.6°C in 106 minutes. The higher rate caused the temperature to increase to 60°C in 33 minutes. The color change of test No. 3 ranged from the orginal dark brown to a medium red color in 100 minutes. Test No. 4, 1.084 gm. Cl_2/min., changed to a final red color in 52 minutes. Both color changes took place as the rate of chlorination was decreasing rapidly as shown on curves A and B. The color of the final solution mirrored the chlorine percentages of the chlorinated product. For a chlorination rate of 0.472 gm. Cl_2/min., the percentage combined chlorine of the chloro-lignin was 25.2 per cent. However for the higher rate chlorination the lignin solution had a color change to red had a higher percentage of combined chlorine. The chloro-lignin for this test was 28.3 per cent chlorine and the precipitated chloro-lignin was 27.3 per cent chlorine.

Chlorination of Dissolved Lignin at 65°C. Figure 7 is a plot of excess chlorine in grams per minute against reaction time for starting temperatures of 65°C. Curve A is the plot using 0.472 gm. Cl_2/min. and curves B through G are plots of reaction using 1.082 grams of chlorine per minute. The curves show the rate of chlorination at constant temperature when varying the rate of chlorine flow. Curve G indicates the effect of catalyst on the reaction. Curve B is a plot of the chlorination reaction which was run with out mechanical stirring. It will be noted that no effect was had on the rate of chlorination. However, the lignin product from this test was unevenly chlorinated. Plots B, C, and E were not carried to completion due to chemical reactions in the system which stopped the runs. It is interesting to note that chlorination tests which are interrupted and continued after one to six hours have elapsed, have an apparent increase in reaction rate. This was the case even though the reaction temperature was maintained and the system was filled with chlorine when the test was restarted. Part of this large chlorine consumption can be explained by the absorption of chlorine in the chloro-alcohol solution.

With the exception of Test No. 11, Curve F, Test No. 12, using $FeCl_3$, as a catalyst, reacted with 26 per cent more chlorine than runs under the same conditions without a catalyst.

All tests using a chlorine rate of 1.082 gm. Cl_2/min., with the exception of No. 11, changed to bright red color between 50 and 51.5 minutes of reaction. Test No. 11 changed color after 67 minutes. For all other tests the color change was completed at the point in the reaction that the rate of chlorination was dropping sharply. Test 11 completed color change at the point the rate of chlorination had become constant after dropping sharply. Curve A, 0.472 gm. Cl_2/min., had completed color change to bright red after 118 minutes at the point the reaction rate dropped sharply. The final change in color cannot be taken as an indication of maximum chlorination. The percentage of combined chlorine for tests stopped after the chlorine rate dropped and the color change had been made, are as much as 8 per cent less than runs extend beyond this break in the chlorination curve.

The exit gas temperatures for all runs rose irregularly through the run. The final temperatures ranged from 55 to 69°C. This temperature increase would indicate a change in the boiling point of the vaporized reaction products and indicate that a varity of chlorinated products are resulting from side reactions.

The percentage combined chlorine of the chloro-lignin for test 5 was 28.3 after a reaction time of 284 minutes. Test 7 and 8, compared well, having combined chlorine percentages of 21.7 and 20.8 for reaction times of 83.4 and 89.5 minutes. Test 12, catalyst, had a high combined chlorine percentage of 29.25. Test 11 had the comparatively low percentage of 24.9. With the exception of Test 11 the percentages increased regularly with time of chlorination.

The conditions for Test 11 were maintained with one exception the same as other tests. The reasons for this tests variance from the normal of all other runs is not clear. One change was made in the chlorination procedure. The NaOH traps were emptied and the excess chlorine from the reaction instead of reacting with NaOH was passed to the atmosphere by an iron pipe line. The outlet of the pipe was placed under water to maintain the same overall pressure conditions as for previous tests. The excess gas combined vigerously with the water. This was attributed to the combination of gaseous hydrogen chloride and water. A calibration run was made with this change to check the chlorine flow and no change was found. The only explanation which can be offered is that the chlorine outlet line became coated with chloro-lignin and caused a false reading of the flow-gage.

A comparison of the percentage chlorine utilized and the weight of chlorine reacted is made for Test 5 curve A, Test 9 curve D and Test 12 curve G over the period of the first hour and 23 minutes of the runs. Test 5, curve A, utilizes 99.3 per cent of the total chlorine input a total of 39.07 grams of chlorine reacted. The utilization is high for this test since the rate was determined over the portion of the curve before the chlorination rate dropped. Curve D, 1.084 gm. Cl_2/min. utilizes 70.6 per cent of the chlorine and has reacted with 63.6 grams of chlorine. Curve G, 1.084 gm. Cl_2/min. with $FeCl_3$, utilizes 89.0 per cent of the input chlorine and reacted with 80.2 grams.

A comparison of the reaction rates of Test 4, 1.084 gm. Cl_2/min., at 30°C starting temperature and Test 9, 1.084 gm. Cl_2/min., at 65°C starting temperature indicate that for higher temperatures the chlorination rate decreases. This follows since the chlorination reaction is exothermic. The reaction rate of chlorination Test No. 4 was 0.934 grams per minute. The reaction rate of Test No. 9 is 0.758 grams per minute. The reaction rate for chlorination at 30°C is 23.2 per cent greater than that for 65°C.

Explosive Reactions during the Dissolved Lignin Tests. Chlorination tests 7, 8 and 10 were stopped due to a spontaneous chemical reaction which occured in the recovery system. The reaction took place violently accompanied by flame in the exit gas tube leading to the NaOH solution and in the NaOH solution itself. A black deposit was left on the glass equipment.

A series of tests were made to determine what factor was the cause of this reaction. The results indicated that the reaction took place only when the NaOH solution had reacted to completion and was acid to litmus. All of the explosions took place after the lignin mixture had passed through the final color change. The cause of the reaction was determined by using NaOH solution which had resulted in an explosion, and passing through the solution reaction gases from a chlorination test that was just being started. No reaction took place in a 30 minute test. To test the effect of chlorine alone, chlorine gas was passed into the NaOH solution which had previously reacted.

The test was made before any appreciable change in the temperature of solution took place. No reaction resulted. Chlorine was passed through heated alcohol for 40 minutes to the same NaOH solution with no reaction. When fresh NaOH was used following a reaction no further reactions took place. To summarize, the tests indicate that alcohol and chlorine vapors, chlorine alone, and the reactant gases during the early stages of the chlorination will not cause the spontaneous reaction to take place with the fully reacted NaOH solution.

The reaction will take place under the following conditions:

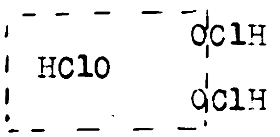
1. The NaOH solution must have reacted to completion with the chlorine.
2. The reaction gases passing through the NaOH solution must be from a chlorination test that has passed through its final color change.

The chemical nature of this decomposition reaction may be caused by the decomposition of one of the oxygen compounds of chlorine catalyzed by an organic compound given off by the reaction.

The original reaction was:

$2NaOH + Cl_2 \;;\; NaOCl + NaCl + H_2O$

Hydrochloric acid was liberated by the chlorination reaction and passes in the gaseous state through the NaOH solution. HOCl is formed when solutions of NaOCl are acidified. HOCl is a strongly endothermic compound and decomposes very easily. The decomposition may occur by the oxygen from two molecules of hypochlorite becoming attached to another molecule and thus forming chlorate.(11)



$$ClO + 2HClO :: ClO_3 + 2H + Cl$$

Also, on heating NaOCl dehydration may take place and the formation of chloride and chlorate results with explosive violence.

The evolution of oxygen from chlorates is an exothermic reaction and often takes place with explosive violence. If the oxygen given off is employed in an endothermic oxidation the decomposition of the chlorate is greatly accelerated, and the mass usually explodes.

Chlorates lose their oxidizing efficiency in neutral or alkaline solution, but when acidified the property appears again. Free chloric acid oxidizes with explosive violence when generated in the presence of organic matter.

Since the reaction may produce any of the discussed oxygen compounds of chlorine one of these reactions is likely the cause of the explosions.

Adhesive Properties of Chloro-lignin. All types of chlorinated lignin produced, when pressed at temperature of 100 to 115°C under pressures of 1000 to 5000 lb/in^2, showed definite adhesive properties.

The most promising results were obtained using precipitated chloro-lignin wetted with chloro-alcohol distillate. Impact test on samples with from 5 to 40 per cent precipitated chloro-lignin indicated that they had the best relative bond of all samples. They also exibited resistance to water absorption.

The precipitated chloro-lignin when wetted with the distillate formed a red plastic mass. This product is of thermoplastic nature. When this material is dried on glass at 35°C it forms a water and acid resistant yellow film. Some tests were made using this product as a glue. However, results were inconclusive. Wood blocks were placed under pressure using the chloro-lignin as a glue. One sample formed a good bond, while five other samples formed no bond.

Chloro-lignin samples broke easily on the impact tester. When these samples were placed in water all bonding properties were lost. Distilled chloro-lignin formed a very hard dense cake. These samples when placed in water showed no indication of water absorption.

B. Recommendations.

The following recommendations are made for future work on this subject:

1. Investigation of Bonding Properties of Chloro-Lignin. The bonding experiments of this investigation did not cover the effect of catalysts, hardeners, plasticizers and solvents on the chloro-lignin bonding material. Also only one filler and one lubricant were tested. It is recommended that further work be done with the chlorinated lignin as a binder to determine the effects of those variables on its bonding properties.

2. Condensation Reactions of Chloro-Lignin. Othmer(27) prepared chlorinated lignin products from sawdust and reported that a plastic was formed when the lignin was condensed with phthalic anhydride. It would thus appear that chloro-lignin can be made to form a copolymer. It is recommended that experiments be initiated to investigate the condensation reactions of chloro-lignin.

3. Film-forming Properties of Chloro-Lignin. Cragg and Hammerschlag, "Chemical Reviews" vol. 39, p. 102 (1946), reported that fractions of cellulose precipitated at low temperatures from an alcohol solution had valuable properties as a plastic film. These properties were not shown

in the cellulose precipitated at higher temperatures. Experimental tests on the bonded samples of this investigation indicated that the chloro-lignin which was precipitated from solution by ice had film-forming properties. The lignin precipitated during the reaction did not form a film. This film was acid and water resistant but did not have the toughness required of coating materials. It is recommended that a study be made to improve the properties of this lignin film.

4. Chlorination of Sulfate Lignin. Harris (17) states that lignin chlorinated in an alcohol solution adds methyoxyl groups to the ethylenic linkages. The methylation was due to the action of the methyl hypochlorite which is formed when chlorine reacts with methyl alcohol. By analogy another suspending or dissolving medium might add groups to the lignin molecule during chlorination. Preliminary experiments indicated that lignin is chlorinated when dissolved in benzaldehyde. Lewis (25) states that plastic properties of lignin should be improved by the addition of phenolic hydroxyl groups. It is recommended that other suspending media for chlorination be investigated with the purpose of adding other groups to the lignin molecule to improve its plastic nature.

5. Chlorination of Lignin and Sawdust Mixture. Sherrard and Othmer have produced bondable materials by chlorinating sawdust in methyl alcohol, and attribute the bonding effect to the chlorinated lignin. It is recommendated that a mixture of sawdust and sulfate lignin by chlorinated in a suspending medium to investigate the effect of additional chloro-lignin on its bonding properties.

6. Investigation of Reaction Gases. The reaction gases from this investigation contain a number of chlorinated products which appear to have been split off the lignin molecule. An analytical approach to these products may give information as to the structure of the sulfate lignin molecule.

V. CONCLUSIONS

From the results of this investigation the following conclusions were drawn:

1. Suspension of 80 per cent of sulfate lignin can be accomplished using the following procedure:

   a. Add one part by weight of lignin in small increments with stirring to 20 parts by volume of methyl alcohol at 25°C.

2. Lignin cannot be kept in methyl alcohol suspension above 43°C due to coagulation of the lignin.

3. Forty two per cent of the weight of sulfate lignin added can be dissolved in methyl alcohol when using the following conditions:

   a. Add in small increments with mechanical stirring one part by weight of lignin to 20 parts by volume of methyl alcohol with the temperature of the alcohol at 65°C.

   b. Sulfate lignin has a methyl alcohol soluble fraction. Under these conditions an average of 42.1 per cent of the lignin dissolved in the methyl alcohol.

4. The chlorination of suspended lignin is an exothermic reaction that proceeds through color changes from dark brown to a final orange color.

5. For chlorinations of suspended lignin at 25°C the following conditions hold:

a. At a chlorine rate of flow of 0.85 gm. Cl_2/min., 87 per cent of the total chlorine was utilized, and for a chlorine flow of 1.084 gm. Cl_2/min., 77 per cent of the chlorine was utilized.

b. By increasing the rate of chlorine flow from 0.85 to 1.084 gm. Cl_2/min., a 26.4 per cent increase, the chlorine consumption was increased from 0.74 to 0.833 gm. Cl_2/min.

c. The chlorine percentage of the lignin product of the reaction varied between 25.0 and 25.3 per cent.

6. Chlorination of lignin dissolved in methyl alcohol results in an exothermic reaction, and a color change of the reactants from dark brown to bright red. The reaction will produce two chlorinated compounds: The first which will be precipitated by the chlorination, and the second which will remain dissolved in the methyl alcohol solution. The second can be precipitated by adding equal volumes of 1:10 hydrochloric or sulfuric acid, or by adding an equal volume of ice water at 0°C to the solution.

7. For chlorination of dissolved lignin at 25°C without the addition of heat the following conditions hold:

a. For a chlorine rate of 0.472 gm. Cl_2/min. 96.7

per cent of the chlorine was utilized, and for a chlorination rate of 1.084 gm. Cl_2/min. 84.6 per cent of the chlorine was utilized in the reaction.

b. By increasing the rate of chlorine flow from 0.472 gm. Cl_2/min. to 1.084 gm. Cl_2/min., a 129.5 per cent increase, the chlorine consumption was increased from 0.454 to 0.935 gm. Cl_2/min.

c. The percentage of combined chlorine of the two lignin products from the reaction were:

(1). Lignin precipitated during the reaction: 20.9 and 27.7 per cent .

(2). Lignin precipitated from the resulting solution by the action of ice water: 25.2 and 28.0 per cent.

8. For chlorinations of dissolved lignin at 65°C the following conditions hold:

a. A chlorine rate of 0.472 gm. Cl_2/min. utilized 99.3 per cent of the total chlorine, and a chlorine rate of 1.084 gm. Cl_2/min. utilized 70.6 per cent of the total chlorine. For a chlorine rate of 1.084 gm. Cl_2/min., using $FeCl_3$ as a catalyst, the utilization of chlorine was 89.0 per cent.

b. By increasing the rate of chlorine flow from 0.472 to 1.084 gm. Cl_2/min., a 129.5 per cent increase, the chlorine consumption was increased from 0.47 to 0.768 gm. Cl_2/min.

c. Utilization of $FeCl_3$ as a catalyst increased the rate of chlorination for rates of 1.084 gm. Cl_2/min. from 0.768 to 0.967 gm. Cl_2/min.

9. By increasing the reaction starting temperature from 25 to 65°C for chlorination rates of 1.084 gm. Cl_2/min. the chlorine consumption was decreased from 0.935 to 0.768 gm Cl_2/min.

10. Adhesive properties are exibited by the chlorinated lignin products when bonded with sawdust at temperatures from 100 to 115°C and pressures from 1000 to 5000 lb/in^2. Based on the results of the impact tests on the molded samples the chlorinated lignin which was precipitated by ice water was the more effective bonding agent for sawdust.

VI SUMMARY

The study of lignin with the aim of correlating data, which may lead to a greater utilization of this wood waste product, has been the subject of investigations since 1838. Previous investigations by Othmer, Harris, Sherrard and others have indicated that chlorinated lignin had potential value as a plastic.

The purpose of this investigation was to study the chlorination reaction of lignin obtained from the black liquors of the sulfate process of paper manufacture. Results of preliminary experimental work indicated that the optimum method of chlorinating lignin was by suspending or dissolving the lignin in methyl alcohol.

The sulfate lignin was chlorinated in two liter wolff flask which was equipped with a motor driven stirrer, and the chlorine flow was measured by a calibrated U-tube differential gage. The flask was charged with the alcohol-lignin mixture and chlorinated from one to seven hours. The rates of chlorine flow for the tests were 0.472, 0.85 and 1.084 gm. Cl_2/min at temperatures of 25 and 65°C. The reactant gases were passed through a condenser to return the vaporized alcohol to the reaction flask and then into a 3 normal sodium hydroxide solution to react the excess chlorine gas. Samples of the reaction gas, which were analyzed for chlorine, were collected in a 1.5 normal sodium hydroxide solution at 10 minutes intervals. With this information the progress of the reaction could be plotted and the rate of chlorination measured.

The chlorination of a suspension of lignin in methyl alcohol in a ratio of 1 to 20 was possible at 25°C. The critical temperature above which the lignin would not stay in solution was 43°C. The reaction was exothermic and produced an orange colored product containing 25 per cent chlorine. Increasing the rate of chlorine flow from 0.85 to 1.084 gm. Cl_2/min. increased the chlorine consumption from 0.74 to 0.833 gm. Cl_2/min.

The chlorination of lignin dissolved in methyl alcohol produced two chlorinated products. One was precipitated as a orange red powder from solution during the chlorination reaction, and had a chlorine percentage as high as 29 per cent. The other lignin remained dissolved in the alcohol solution. When precipitated from solution by ice water this chloro-lignin was a light yellow powder with a chlorine percentage as high as 28.0 per cent. Increasing the rate of chlorine flow from 0.472 to 1.084 gm . Cl_2/min. during tests at 25°C resulted in increasing the rate of chlorination from 0.454 to 0.935 gm. Cl_2/min. Adding ferric chloride, as a catalyst, increased the chlorine consumption from 0.768 to 0.967 gm. Cl_2/min. Raising the reaction temperature from 25 to 65°C decreased the chlorine consumption from 0.935 to 0.768 gm. Cl_2/min.

The chlorinated product showed definite bonding value when mixed with sawdust and pressed at a temperature of 112°C and pressures from 1000 to 5000 lb/in^2. The percentage lignin in the samples was varied from 5 to 60 per cent. The lignin-sawdust samples were light yellow in color and firmly bonded and water resistant.

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