THE PRODUCTION OF A PLASTIC FROM SULFATE LIGNIN

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I. INTRODUCTION

Lignin is an important constituent of wood. Apparently the function of lignin is to stiffen and strengthen the cell walls of trees and plants. Sometimes it is referred to as the cementing material in wood. The lignin content of plant stalks averages about 15 to 25 per cent.

Millions of tons of lignin are available each year in the United States. The largest quantity comes from the wood using industries. Most of this supply is wasted or burned as low-grade fuel. The saw mill waste in the lumber industry is estimated at 30,000,000 tons per year of which roughly 25 per cent is lignin. This industry either burns or wastes 2,500,000 tons of lignin each year. The stalks of plants furnish another source of lignin. Those which are produced in large quantities are pea vines, bagasse, wheat and rye straw, flax straw, cotton stalks, corn stalks, soybean straw, rice straw, and numerous grasses and shrubs.

Industry has tried numerous ways of utilizing lignin waste. Most work has been done on sulfite waste liquor (which contains lignin) produced by the sulfite process for manufacturing pulp and paper. Adhesives, insecticides, fertilizer, soaps, vanillin, and dyes are some of the products made from sulfite liquor. The manufacture of these materials utilizes only a very small percentage of the lignin that is available.

The fact that lignin contains a phenolic radical in its structure suggests that it might be useful as a resin in making plastics. However, the phenolic content is so low that it has not been successfully used as a substitute for phenol-formaldehyde resins, but has been used as an extender in plastics containing these resins. A thermosetting lignin used for making wallboard has been obtained by treating lignin first with a zinc salt and then with a reducing agent. One disadvantage of most lignin plastics is their dark color. To be used for decorative materials that will compete with other plastics they must be produced in lighter colors and the ratio of water absorption must be reduced.

The purpose of this investigation was to make a lignin resin and plastic from sulfate lignin by refluxing it with a metallic salt, treating it with hydrogen sulfide, condensing it with a condensing agent, and molding the resinous product.

II. LITERATURE REVIEW

A. Production of Lignin Plastics

Wallboard Produced from Zinc Salt Treated Lignin- A process for making a lignin wallboard has been described by Seiberlich (19, 20). A 50 gram sample of Scholler lignin was refluxed with a 10% solution of zinc oxide or zinc sulfate for 2 hours. The lignin was filtered, washed, placed in an Erlenmeyer flask, and gassed several times with hydrogen sulfide. The hydrogen sulfide treated lignin was heated in a commercial solution of formaldehyde for 30 minutes. The product was molded at 2,000 lbs. per sq. in. at a temperature of 300°F for three minutes. The molded material compared favorably with Masonite and other wood pressed wallboards.

Seiberlich has treated lignin in a similar way with a 10% sodium tetrasulfide solution and then with ethylene chloride. However, the product exhibited properties inferior to those made from the zinc salt treated lignin.

Lignin-Wood Laminated Material- One of the first lignin plastics was of the laminated board type. Boehm (1, 4, 5) has described a process used by the Masonite Company in making lignin plastics.

Wood chips were treated for a matter of seconds at a steam pressure of 1200 lbs. per sq. in. In this short time lignin was first softened by the high temperature steam and then upon sudden release of the chips to atmospheric pressure, they were exploded by the high internal pressure resulting in a mass of fibers still coated with lignin.

In the manufacture of the plastic, this fiber was subjected to a temperature of 175°C. and a pressure of 1500 lbs. per sq. in. and the fibers were again bonded by the lignin. Curing was very rapid. In fact it was only required that the temperature be raised to the curing temperature before chilling was started.

Similarity of this action to that of the thermosetting resins led to further study of this phenomenon. Some fractions of exploded fiber exhibited a very high degree of plasticity which, when molded, produced a product similar in many ways to phenolic laminated materials.

The sheets or panels produced from exploded wood chips can be made in any thickness from 0.1 in. to 1.0 in. It has a specific gravity of 1.45, a modulus of rupture of about 20,000lbs. per sq. in., a tensile strength of 10,000 lbs. per sq. in., a compression strength of about 25,000 lbs. per sq. in. and a 24 hour water absorption of less than 1 per cent. Its dielectric properties are good. It may be drilled, tapped, or turned readily, presenting a lustrous black finish.

Lignin-Phenol Resin- Champer and Christensen (7) have described a method of making a lignin plastic by condensing it with phenol. An excess of phenol, for example 600 grams containing 7.5 grams of sulfuric acid, was heated to approximately 100°C. and approximately 250 grams of lignin was added to the phenol as rapidly as dissolution occurred. This mixture was held at about 100°C. for an hour, and then the reaction vessel was connected to a condenser and vacuum pump. With continuous agitation, the temperature was raised at the rate of about 15°C. per hour until the ultimate temperature of 155°C. was reached. During this treatment a mixture of phenol and water was distilled over, the phenol being recovered.

As the condensation reaction progressed, the viscosity of the mass increased. The reaction was continued until all unreacted phenol was distilled off. At this phase, the initial mass had become a viscous black product. This resin can be dissolved in suitable solvents and used as a varnish for protective coatings or it can be dispersed by a dispersing agent and used as a filler in fiber boards.

The resin can be mixed with suitable inert fibers such as wood flour, asbestos, or ground vegetable fibers and molded. This treatment was carried out at a pressure of 1,000 lbs. per sq. in. and at a temperature of 160-180°C. The polymerization product was a hard lustrous, insoluble, and infusible resin.

Resins from Lignin by Condensing With a Polybasic Carboxylic Acid- A wide range of useful resins may be obtained from lignin by condensing it with various polycarboxylic acids. Wallace (18) has made this type resin successfully by using such acids as succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic. From 10 to 40 parts of polycarboxylic acid is usually sufficient to resinify 100 parts of lignin by weight, when the acid and lignin are heated to between 150°C. and 210°C. The time required varies with the source of the lignin, but generally 4 to 20 hours heating are sufficient. For example, a good resin can be obtained from a mixture of 70 to 75 parts of lignin and 30 to 25 parts of either succinic or phthalic acids heated to between 160°C. and 190°C. for 6 to 8 hours.

Such resins are useful for molding compositions, surface coatings, and bonding agents for abrasive wheels.

Lignin-Phenol-Formaldehyde Resins- Collings, Freeman, and Upright (8) have discovered a process for making a phenol-formaldehyde-lignin resin. Lignin was digested in phenol or a solution of a phenolate such as sodium phenolate, potassium phenolate, barium phenolate, sodium-ortho-cresolate, sodium xylenolate, or ammonium-4-chlorophenolate. The digestion took place between 150°C. and 180°C. The mixture was cooled to between 50°C. and 80°C. and an aldehyde added thereto. Substantially any aldehyde, for example, acetaldehyde, formaldehyde, butyraldehyde, benzaldehyde, salicylaldehyde, or furfuraldehyde, can be used. The reaction mixture was thoroughly agitated and maintained at a temperature of 150°C. for a period of time required to cause condensation but insufficient to cause precipitation of the condensation product from solution. The temperature of the solution was adjusted to between 20°C. and 40°C. and acidified to precipitate the thermo-setting material. This material was then washed and filtered.

A mixture was prepared of 70 parts by weight of the resinous product with 30 parts of commercial rubber dust, 1 part of calcium hydroxide, 2 parts of sodium stearate, and 4 parts of carbon black. This composition was molded at 150°C., and a pressure of 2,000 lbs. per sq. in., the molding cycle being 3 minutes. The molded article was hard and had a glossy, black surface.

A similar phenol-aldehyde-lignin resin has been described by Hochwalt (14). Approximately 25 parts of lignin by weight were dissolved in 25 parts of phenol by heating the mixture on a steam bath. A solution containing 34 parts of 40% formaldehyde and 2 parts of sodium hydroxide was added and the two solutions were thoroughly mixed. Heating was continued until the mass showed evidence of solidifying. It was then cooled and a tough dark brittle solid was formed. This substance was mixed with a filler and passed between the nip of a pair of smooth rolls and heated to a temperature of 230°F. for 60 seconds.

D'Alelio (10) has prepared several different phenol-aldehyde-lignin resins. He dissolved lignin in phenol and added a formaldehyde solution containing sulfuric acid as a catalyst. This mixture was heated for 15 minutes, made alkaline with sodium hydroxide, and heated for an additional 30 minutes. The resin produced was molded at 2,000 lbs. per sq. in. and at a temperature of 175 to 180°C. for 60 seconds.

Another group of phenol-formaldehyde resins have been described by Fiedler (11). For example, 300 parts of lignin by weight were dissolved in 300 parts of phenol at a temperature between 50°C. and 100°C. 450 parts of cold formaldehyde were added and when the temperature reached approximately 65°C. to 75°C., 11.5 parts of sodium hydroxide were added. The reaction was allowed to proceed for approximately 30 minutes at the boiling point. 15.3 parts of aniline were added and the reaction allowed to continue for approximately five minutes longer. The liquid resinous mass was dehydrated under reduced pressure. The hard resin produced was powdered and molded.

Aromatic amines such as pyridine, piperidine, naphthylamine, and quinoline may be used in place of aniline. These substances react with free formaldehyde and possibly with lignin. Whatever its composition may be, the reaction product thus formed appeared to plasticize the main resinous body so that moldable compositions produced therefrom had better flow or plasticity, and the molded articles better surface finish than products free from such reaction products.

Lignin-Formaldehyde Resin- Bailey and Ward (3) claim to have developed a lignin-formaldehyde resin which compares favorably in critical laboratory tests with the best commercial plastics. 15 grams of butanol lignin were dissolved in 200 ml. of water and 15 ml. of 2.5N sodium hydroxide. This solution was made up to 750 ml. with water; 33 ml. of 37% formaldehyde and 6 ml. of 28% ammonium hydroxide were added. At this phase, the electrometric pH was 10.5 to 11.0. This mixture was placed in a stainless steel autoclave and brought to 140°C. (requiring 30 minutes) with continuous stirring through a stuffing box. The temperature was held at 140°C. for 1 hour and then allowed to cool to room temperature (requiring 2 to 3 hours). The pH at this point was approximately 5.3. The solution was made alkaline to a pH of 10.5 to 11.0 with sodium hydroxide (2.5N) and filtered. The yield was 80 to 85% based on original butanol lignin.

Bailey and Ward (3) used many different plasticizers and fillers in their molding methods. Some of the plasticizers used were: castor oil, flexalyn, dibutyl phthalate, phenol, butyl phthalyl butyl glycolate, o-and p-toluene sulfonamide, triethyl citrate, and tricresyl phosphate. Various concentrations of plasticizers were employed and effects on water resistance, flexural strength, modulus of elasticity, flow, etc. were noted. Tricresyl phosphate produced effects generally superior to those of other plasticizers. Water resistance was improved 200 to 300 % while the flow point was reduced from 120-140°C. to 80-100°C. when 10% tricresyl phosphate was added.

The fillers used were high-strength cotton cloth, glass thread, and wood flour. The amount of filler ranged from 5 to 50%. Small proportions increased impact strength 200-300% without adversely affecting the moduli of rupture or elasticity. Enormously high impact strengths (200% higher than the phenolic plastics) were obtained by the use of larger quantities of filler, but simultaneous loss of flexural strength and stiffness occurred.

The butasin resin was molded at a pressure of 5,000 lbs. per sq. in. The platens were heated from room temperature to 250°C. (20 minutes), held at 250°C. for 5 minutes, and cooled to 75°C. (20 minutes), and the molded butasin was removed.

<u>A Lignin Plastic from Crude Cellulosic Material Such As Sawdust</u>- Geller (12) has described a method of making a lignin resin from sawdust. 100 grams of sawdust, or other lignocellulosic material, were added to a molten bath of a paraffin hydrocarbon. The mixture was agitated slowly, 2-6 grams of urea were added, followed by 3 milliliters of mixed

acid and 4 parts of 98% acetic acid. The mixture was maintained in a molten state and agitated for 10 to 15 minutes. One to three per cent of pure lignin was added, and mixed thoroughly. The wood was allowed to settle and was separated from the paraffin.

For molding, ½ to 1% of 98% acetic acid and 3 to 4% lignin were added. The mixture was molded at pressures from 2,000 to 5,000 lbs. per sq. in. and at temperatures between 240 and 330°F. This plastic may be incorporated with phenol-formaldehyde resins if desired.

Uses and Future of Lignin Plastics- According to Aries (1,2) and Lewis (15), to date the chief use of lignin plastics has been in laminates, wallboards, and in lignin-extended phenolic resins. Lignin laminates have been useful in the electrical industry. Due to good electrical properties they have been used as switchboards, switch bases, spoolheads, insulating spacers, and insulating supports. They are also being used for ice cube trays, office chair bearings, foundry patterns, and other applications. Lignin has been used as an extender in phenolic resins to lower the cost, but no large amount has been used in this way. Lignin has not proved to be a successful phenol substitute in the preparation of phenol-formaldehyde resins, possibly because of the fact that only one phenolic radical exists per molecular weight of 840.

The use of lignin plastics in any large quantity is not yet a reality. Lewis (15) has estimated that 20 tons a week of lignin plastics and extenders were being marketed in 1945. This is small compared with a weekly production of 8,000 tons of resins and plastics at that same time. Some lignin plastics are brittle and all are dark colored. Before they can be more widely used it will be necessary to develop better plastic properties. To compete in the decorative field, lignin must be converted to a form which will produce colorless strong thermoplastic and thermosetting resins.

B. Chemistry of Lignin

Early scientists thought that wood was a definite chemical substance. A French chemist, Anselme Payen (17), was the first to show that wood was a heterogeneous mixture. He treated wood with nitric acid, alkalies, alcohol, and ether and obtained a substance which he called cellulose. In the process of isolation he had removed a group of substances which he called the "true woody material" (la matiere ligneuse veritable). He considered the cellulose to be surrounded or impregnated with this material.

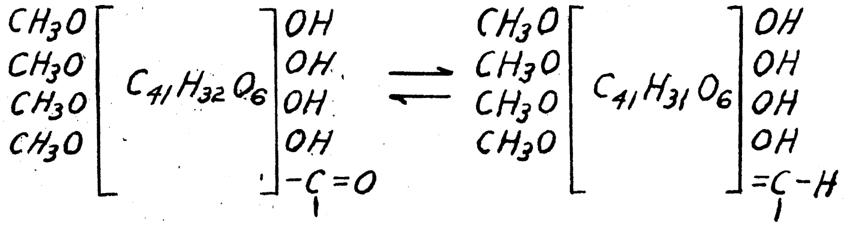
Our present day theory, according to Hasche (13), considers wood to be made chiefly of cellulose, lignin, and pentosans. The function of lignin in the plant is to give strength and rigidity to the cell wall which is mainly cellulose. It is believed that lignin is derived from the pentosans in wood. The analyses of various types of wood are shown in the following table:

Analysis of Woods
(% of oven dry samples)

Type of Wood	Acetic Acid	Pentosans	Cellulose	Lignin
Redwood	1.06	7.80	48.45	34.2
Western Yellow Pine	1.03	6.97	59.71	26.44
Douglas Fir	1.04	6.02	61.47	-----
Hemlock	1.73	9.06	52.85	30.31
Tanbark Oak	5.23	19.56	58.03	24.85
Red Oak	5.08	21.43	53.78	29.79
Shellbark Hickory	2.51	18.82	56.22	23.44

Phillips (17) states that the chemical structure of lignin is complex and not thoroughly understood. "It can not be emphasized too strongly that it is entirely premature to propose any constitutional formula for lignin considering our incomplete knowledge of the chemistry of this substance" (17). The presence of certain constituent groups, however, has definitely been established.

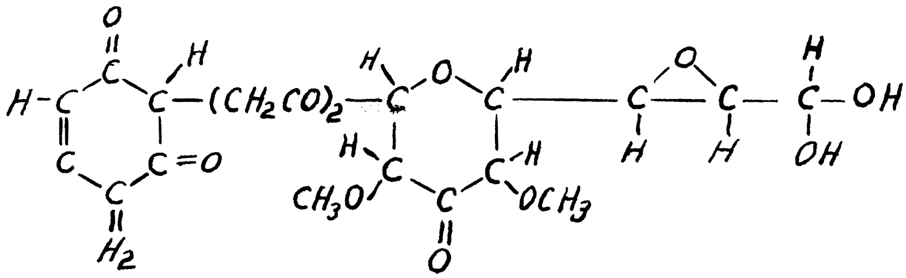
It is known that a number of methoxyl and hydroxyl groups are present in the lignin structure. Other groups consisting of a number of aromatic combinations are also present. Braun's (17) formulation for lignin involves a keto-enolic isomerism which may be represented by:



$$\begin{array}{l}CH_3O\\CH_3O\\CH_3O\\CH_3O\end{array}\left[\;C_{41}H_{32}O_6\;\right]\begin{array}{l}OH\\OH\\OH\\OH\\-\underset{|}{C}=O\end{array}\rightleftharpoons\begin{array}{l}CH_3O\\CH_3O\\CH_3O\\CH_3O\end{array}\left[\;C_{41}H_{31}O_6\;\right]\begin{array}{l}OH\\OH\\OH\\OH\\=\underset{|}{C}-H\end{array}$$

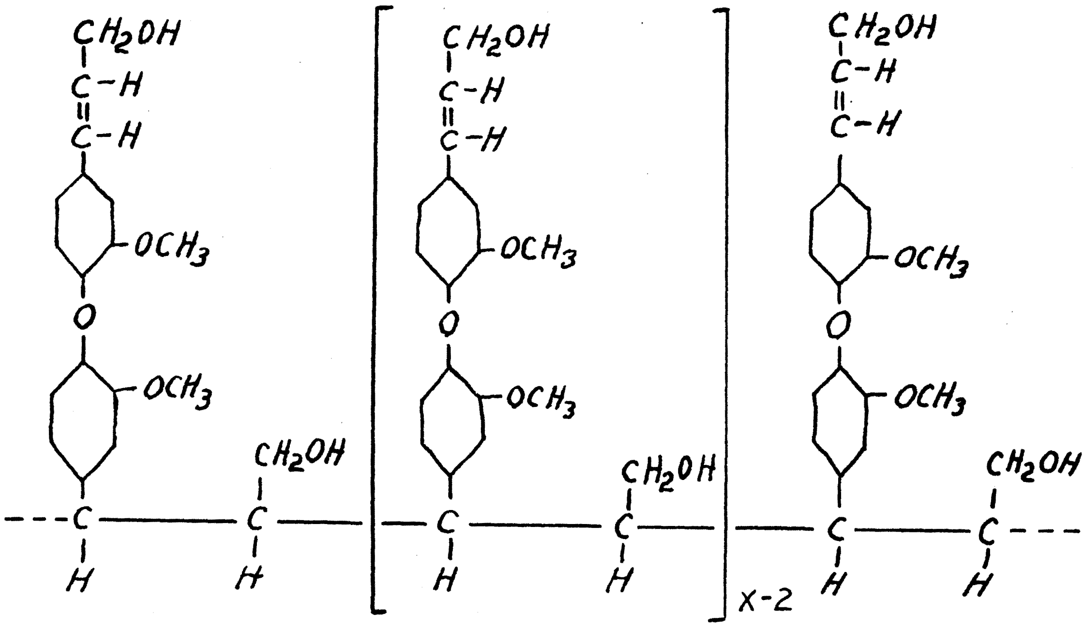
I.

Cross and Bevan (17) were the first to propose a constitutional formula for lignin. Although it is not in harmony with modern concepts, it is presented for historical reasons:



II.

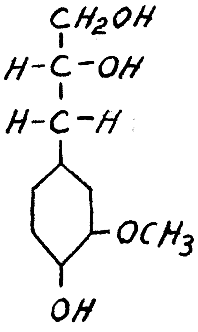
Kurschner (17) considered that lignin is a polymer of glucoside coniferin which yields coniferyl alcohol on hydrolysis. He pointed out that coniferin and spruce lignin show an analogous behavior in several chemical reactions. Kurschner advanced the following structural formula for lignin:



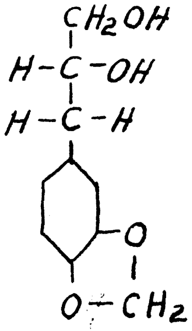
III.

The fact that lignin does not act like a true unsaturated compounds discredits Kurschner's concept. In this formula the benzene nuclei are connected through oxygen in ether-like linkages. A compound with this type of structure ought to yield fairly simple derivatives of benzene when heated with hydriodic of hydrochloric acid. No such compounds have been obtained from spruce lignin.

Freudenberg (17) considered lignin as a linear condensation product of building units (IV and V), number V being the end group of the lignin complex.

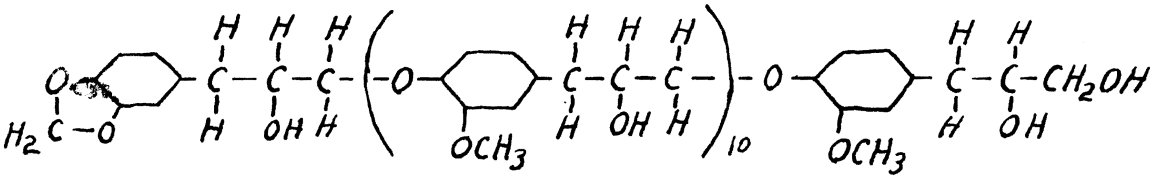


IV.



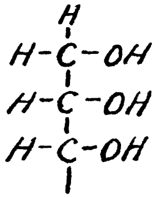
V.

The condensation product of these groups were represented by formula (VI). This was designated as "primary lignin by Freudenberg. The polymerization of "primary lignin" produces "secondary lignin".

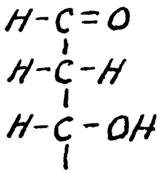


VI.

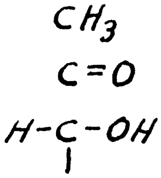
The above structure of lignin was subsequently modified by Freudenberg. He considered that the three-carbon side chain may be either (VII), (VIII), or (IX) and that these are attached to aromatic nuclei (X), (XI), and (XII).



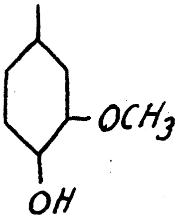
VII.

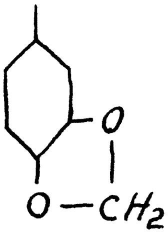


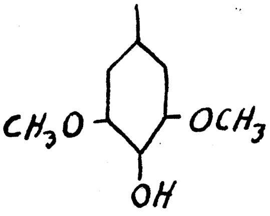
VIII.



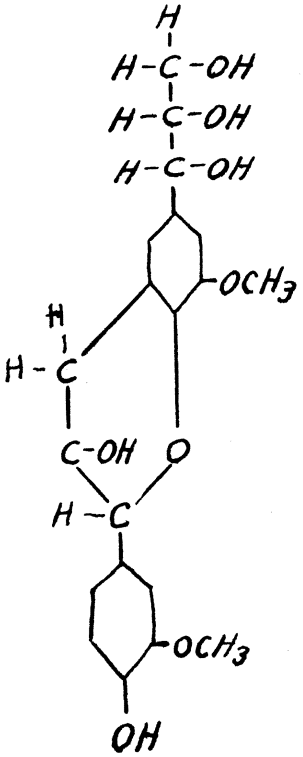
IX.

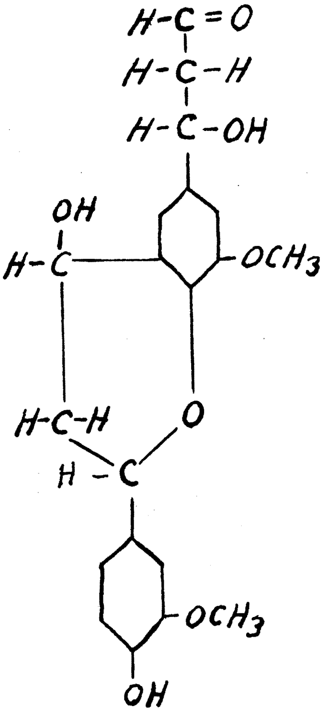

X.

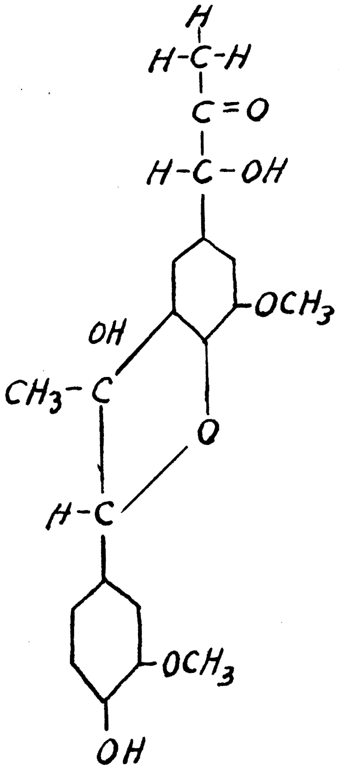

XI.


XII.

Through etherification and subsequent condensation of the above units, lignin is probably the resulting product. These products are represented by formulas (XIII), (XIV), and (XV).


XIII.


XIV.


XV.

In the above formulas, only aromatic nucleus (X) was used. Similarly, aromatic nuclei (XI) and (XII) may undergo etherification and condensation forming analogous products. The condensation products (XIII), (XIV), and (XV) may undergo further condensation with other building units and form complex products of high molecular weight.

C. Theory of Metallic Salt Treatment and Subsequent Reduction of Lignin

Lewis (16) says that lignin in itself is a poor material for plastics. This may be due to the presence of various types of hydroxyl groups which make it relatively hydrophilic. In the condensation of lignin with formaldehyde and other compounds, the phenolic hydroxyl groups in the lignin may be covered, but there still remain alcoholic hydroxyl groups which will affect the water resistance of plastics made from it. Covering these hydroxyl groups by acylation should make the lignin less hydrophilic.

Brauns, Lewis, and Brookbank (6) have prepared lignin ethers and esters from Meadol, a water soluble lignin. A solution of lead acetate is reacted with Meadol and lead Meadol precipitates. The salt thus formed appears to be a mixture of lead lignin containing one lead atom for two hydroxyl groups per building unit (assuming a molecular weight of 860) and one containing three lead atoms for each two building units. Lignin esters have also been made using divalent tin and copper, and monovalent nickel.

R. Combes (9) treated lignin membranes with either a lead or zinc salt in a color reaction of lignin which he discovered. Cuts were made in the chosen organic plant, and subjected to the action of javelle water for about 15 minutes to eliminate cellular material. After being washed repeatedly with ordinary water and then distilled water, the preparations were placed in a closed glass container under aqueous lead sub-acetate. The time of submersion varied with the thickness of the cut, 12-14 hours for the best preparations. They were then washed with distilled water. After this treatment it was certain that the cellular membranes were impregnated with a lead composition as proven by treatment with an acetic acid solution of potassium iodide resulting in a yellow precipitate of lead iodide.

The preparations thus obtained were immediately placed in a covered glass container, containing a solution of hydrogen sulfide, and there appeared a black precipitate of lead sulfide, whereof part remained in the membranes while part was eliminated by washing with distilled water. The cuts have to be maintained in the hydrogen sulfide solution for 10-15 minutes.

If to these preparations a drop of concentrated sulfuric acid were added, there immediately appeared on all lignified portions a magnificent red coloration analogous to that produced by means of phloroglucinol and hydrochloric acid. The color remained for a length of time depending upon the lignification. It disappeared little by little, the walls of the cell being last. The reaction was only produced by lignified membranes.

In place of lead sub-acetate, saturated solutions of neutral lead acetate and lead nitrate may be used.

The reaction takes place in three steps:

1. The prolonged action of a concentrated solution of lead salts on the specimen (12 hours at room temperature or half-an-hour on a water bath).
2. Treatment with hydrogen sulfide.
3. Treatment with sulfuric acid.

If step 1 is omitted, there are no results except those probably due to hydrolysis. It is absolutely necessary to carry out steps in the order shown. Results show that treatment with lead salts results in the formation of an insoluble compound and not a simple impregnation. This compound is relatively stable.

The lead salts have been replaced with zinc sulfate. On using the same procedure, a red coloration was obtained absolutely identical with that obtained when lead was used.

Cupric sulfate and salts of mercury and barium gave no results. Furthermore the formation of an insoluble sulfate is not necessary. Zinc hydrate (Zinc hydroxide) can be used.

An acceptable procedure follows: The specimen is treated with javelle water for periods of not longer than one hour, carefully washed, and then placed in a large glass flask. One gram of zinc oxide suspended in 30 grams of water is then added and the mixture heated on a water bath for about 30 minutes. The specimens are removed, washed and placed in a saturated solution of hydrogen sulfide. After five minutes the specimens are quickly washed, placed on a slide cover which has been moistened with a drop of concentrated sulfuric acid. A red color in all the lignified portion is immediately formed.

III. EXPERIMENTAL

A. Purpose of Study

The purpose of this investigation was to make a lignin resin and plastic from sulfate lignin by refluxing it with a metallic salt, treating it with hydrogen sulfide, condensing it with a condensing agent, and molding the resinous product.

B. Plan of Investigation

1. Salt Treatment: Sulfate lignin was refluxed at the boiling point with the following salts:

Zinc Sulfate
Cupric Sulfate
Lead Acetate
Stannous Chloride

2. Hydrogen Sulfide Treatment: A water suspension of the salt treated lignin was gassed with hydrogen sulfide.

3. Preliminary Molding: To determine which of the salt treated lignins have the best molded product and absorbed the least amount of water, preliminary molding runs were made.

4. Condensing: The salt treated lignin which gave the best product in preliminary molding runs was chosen. This

salt treated lignin at the end of the hydrogen sulfide treatment (without being molded) was condensed in the presence of sodium hydroxide with the following condensing agents:

Furfural
Formaldehyde

5. Molding: The condensed lignin was mixed with wood flour and molded.

6. Testing: The following tests were made on molded samples:

Per Cent Water Absorption
Comparative Impact Test

C. Materials

Lignin: The lignin used in this investigation was sulfate lignin obtained as a by-product in the sulfate or Kraft process for making paper pulp. It was manufactured in the Charleston, South Carolina plant on the West Virginia Pulp and Paper Company under the trade name of "Indulin", lignin from pine wood. The lignin used was from lot # 2-823.

Hydrogen Sulfide: Hydrogen sulfide was generated by pouring 10 per cent sulfuric acid over iron sulfide.

Catalyst for Condensing Reaction: Reagent grade sodium hydroxide was used.

<u>Salts for Refluxing with Lignin</u>: The following salts were used; $ZnSO_4.7H_2O$, $Pb(CH_3COO)_2.2H_2O$, $CuSO_4.5H_2O$, $SnCl_2.2H_2O$. All salts were reagent grade.

<u>Formaldehyde</u>: 37 per cent U.S.P. formaldehyde was used as a condensing agent.

<u>Furfural</u>: Technical grade furfural was obtained from the Quaker Oats Company, Cedar Rapids, Iowa.

<u>Phenol</u>: Technical grade phenol was used.

<u>Para-nitro-aniline</u>: Reagent grade p-nitro-aniline with a melting point of 146-147°C. was used to determine the temperature of the mold.

<u>Wood Flour</u>: 45 mesh wood flour, which was almost entirely white pine, was obtained from the Becker, Moore and Company, North Tonawanda, New York.

D. <u>Apparatus</u>

A sketch of the equipment used in refluxing, gassing, and condensing the lignin is shown in Fig. 1.

<u>Distilling Flask and Condenser</u>: A three neck, round bottomed, pyrex glass, ½ liter distilling flask was used in refluxing lignin with metallic salts, gassing with hydrogen sulfide, and in refluxing the lignin with a condensing agent. The condenser was of the Liebig type.

<u>Compression Mold</u>: The mold used was constructed by

Fred. S. Carver, Engineer, Manufacturer of Hydraulic Equipment, New York. It was 2¼ inches in diameter. A picture of the mold is shown in Fig. 2.

Hydraulic Press: The hydraulic press used in the molding process was manufactured by Fred S. Carver, Engineer, Manufacturer of Hydraulic Equipment, New York. The press had a 1¼ inch ram, with the maximum total pressure on the ram being 20,000 pounds. A picture of the press is shown in Fig. 3.

Heating Element for Mold: A 500 watt heating element was made from nichrome wire having a resistance of 1.66 ohms per foot.

Electrical Resistors: Three 20 ohm fixed resistors and one 19.6 ohm variable resistor were used to control the current and therefore the temperature of the heating element of the mold.

Air Stirrer: A circular piece of galvanized steel was cut and bent to form blades so that an air stream would cause it to rotate. This was attached to a glass stirring rod which was used to agitate solutions and mixtures used in this investigation.

Impact Testing Machine: The impact testing machine used was manufactured by the International Equipment Company, Boston, Mass. The serial number was No. A5017.

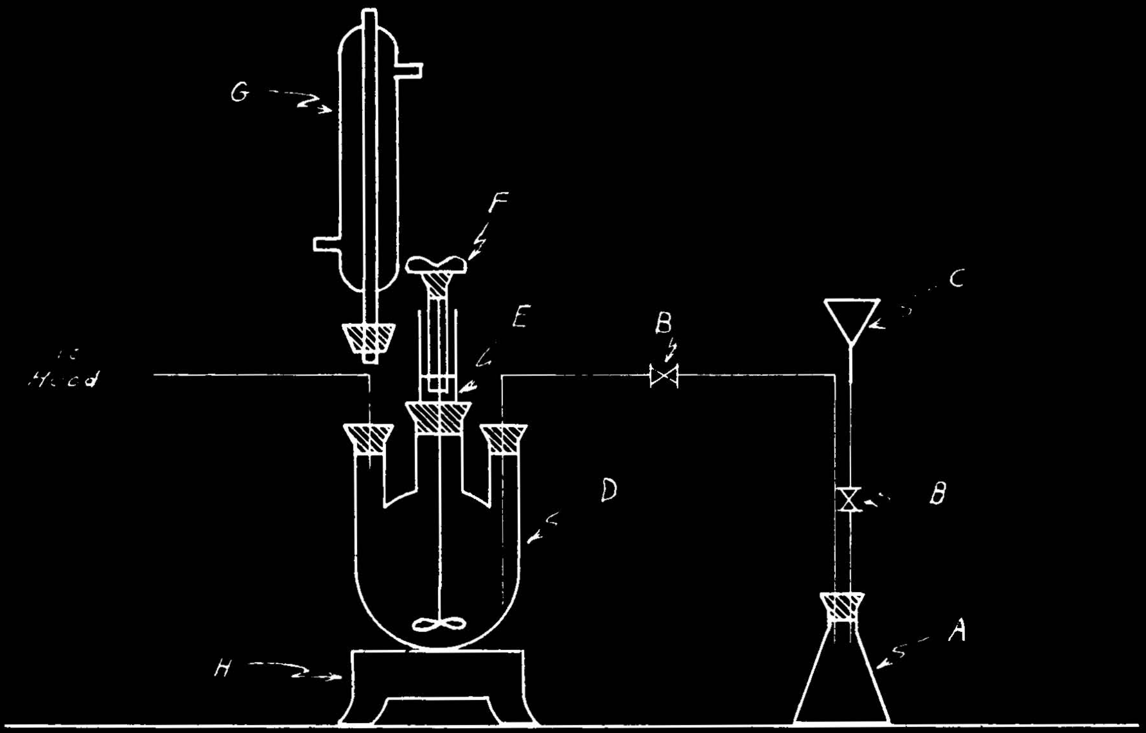


Fig. 1

Legend

A- 500 cc. Erlenmeyer Flask
B- Pinch Cock
C- Funnel
D- 2 liter Woulfe Flask
E- Mercury Vapor Seal
F- Air Stirrer
G- Condenser
H- Hot Plate

CHEMICAL ENGINEERING DEPARTMENT
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

REFLUXING AND GASSING
APPARATUS

Scale No Scale
Drawn by W.L.P.
Checked by R.A.F.

Drawing No. 1
Date 5/21/47

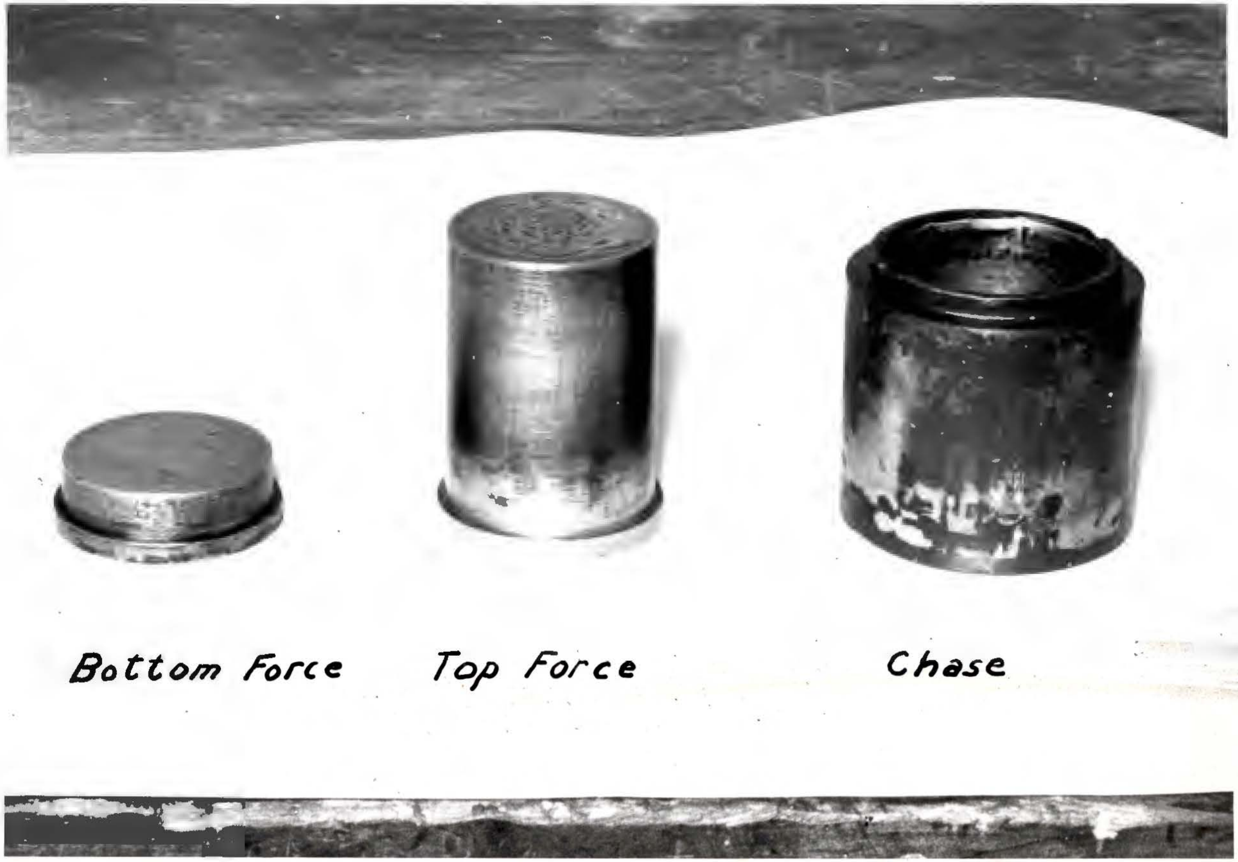


Fig. 2

Mold Components

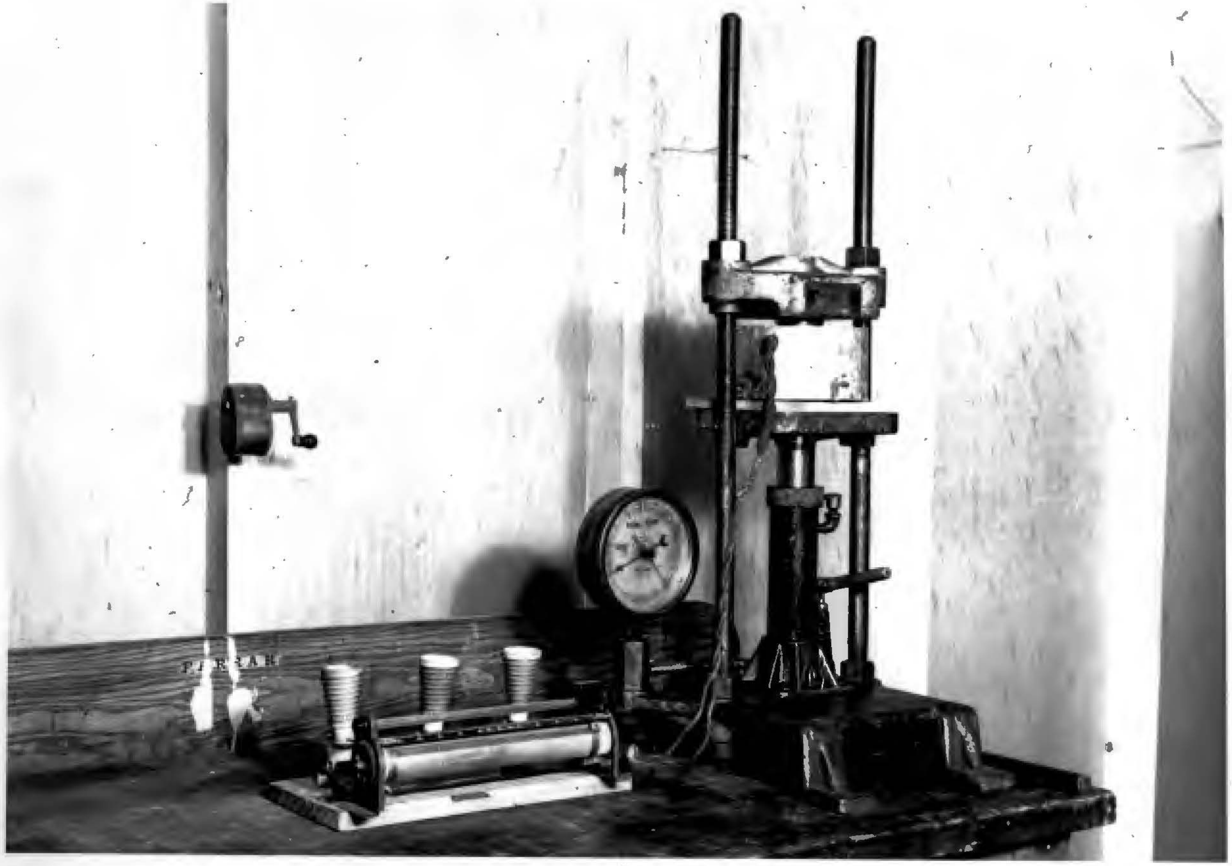


Fig. 3

Carver Laboratory Press

E. Method of Procedure

Refluxing with Salts: A lignin sample weighing 60 gms. was placed in a 2 liter Woulfe flask and 500 cc. of a 10% salt solution were added. The mixture was agitated to keep the lignin from settling. An electric heating element was used to bring the mixture to the boiling point. This required approximately 15 to 20 minutes. The mixture was refluxed at the boiling point, with continuous agitation, for 2 hours. The mixture was filtered on a Buchner funnel and the precipitate washed with 2 liters of distilled water.

Hydrogen Sulfide Treatment: The salt treated lignin was placed in a Woulfe flask and 500 cc. of distilled water were added. The mixture was agitated continuously and hydrogen sulfide gas was passed into it for a period of 15 minutes. Hydrogen sulfide was generated by pouring 100-125 cc. of 10% sulfuric acid, which had been heated to approximately 70°C., over 30 gms. of iron sulfide. The lignin was separated from the mixture by filtering it on a Buchner funnel. The lignin was washed with 2 liters of distilled water and dried in an air drier at room temperature for 24 hours. The hydrogen sulfide treatment was carried out under a hood.

Preliminary Molding: The treated lignin was mixed with wood flour, the percentage of wood flour being either 25 or 50%. Both the wood flour and the lignin were preheated in a 110°C. oven for a period of time varying from 1 to 12 minutes to drive off excess moisture; therefore preventing the molded piece from blowing out on the surface. The mold was brought to a temperature of 150°C., plus or minus approximately 10°C. The correct temperature was reached when a crystal of p-nitro-aniline melted when placed on the top of the mold. The melting point of p-nitro-aniline is 146-147°C. The mold was lubricated with stearic acid and the sample was molded at a temperature of 150°C. for 3 minutes under a pressure of 2,000 psig. The salt which gave the best preliminary molded product was chosen and lignin treated with this salt was used in all subsequent runs. The best product was chosen by simple inspection tests such as appearance, water absorption, and scratching the surface with the fingernails.

Condensing: Salt treated lignin was condensed with from ½ to 2 mols of formaldehyde, furfural, and mixtures of formaldehyde and furfural. A 50 gm. sample of salt treated lignin was dissolved in a sodium hydroxide solution. Usually 200 cc. of 5% sodium hydroxide were used and this was diluted with from 100 to 800 cc. of distilled water. To this solution the condensing agent was added with constant agitation. The solution was heated with an electric heating element. From 15 to 20 minutes were required to reach the boiling point. The solution was refluxed with continuous agitation for 2 hours. If the resinous product had not precipitated at the end of the condensing period the solution was made acid with 5% sulfuric acid, causing the lignin to precipitate. The product was filtered on a Buchner funnel and washed with distilled water. It was then dried for 24 hours in an air drier at room temperature.

Molding: This procedure was similar to that stated under preliminary molding. In some runs from 5 to 10% phenol was used as a plasticizer.

Testing: All the molded discs used for testing had approximately the same size and shape. The diameter was 2¼ inches. The thickness of a single disc varied as much as 0.08 inch. This was due to the fact that the mold used was worn and there were large tolerances between mating parts of the mold. The average thickness of the discs was approximately 0.22 inches. The weight of the discs varied from 19 to 20 gms., the average weight being approximately 19.5 gms.

Water absorption tests were made on the basis of the weight of water absorbed in a 2 hour period. The molded disc was weighed accurately on an analytical balance. A 250 cc. beaker was filled with distilled water and the disc was completely submerged in the water. At the end of two hours the disc was taken out and the surface water was wiped off with a dry cloth. The disc was weighed again on an analytical balance and from the weight gained the per cent water absorbed was calculated.

The relative impact strength was determined on an impact testing machine manufactured by the International Equipment Company. The disc was laid flat on the steel bottom of the testing machine. On the top surface of the disc a small steel cylinder was placed (the end of the cylinder in contact with the disc was rounded or shaped like a hemisphere). On top of the steel cylinder was a weight which could be raised to any desired height. The weight was raised to a height of 2 or 3 cms. and suddenly dropped onto the steel cylinder. The distance the weight was raised was increased in increments of 2 cms. until the disc was cracked or broken when the weight fell. This distance of fall was recorded and called the relative impact strength of the sample being tested.

F. Data and Results

The experimental data include the molding of the treated lignin and the tests made on the molded discs.

Lignin Treated with Various Metallic Salts: The following five runs, included in Table I, shows the effect of molding lignin which has been treated with a metallic salt and hydrogen sulfide. The four different salts used were zinc sulfate, lead acetate, cupric sulfate, and stannous chloride. Runs 1A and 1B show the effect of varying the length of time that lignin is refluxed with a salt.

In numbering the mold runs, the number before the hyphen indicates the treated lignin that was used and the number after the hyphen indicates the number of the mold run made on that specificly treated lignin.

The samples for which no water absorption characteristics or relative impact strengths are given were imperfect samples or of such poor quality that testing was of little or no value.

All molded samples when placed in water for two hours became so soft and distorted that the per cent of water absorbed could not be determined. Molded discs which had been treated with either $Pb(CH_3COO)_2$ or $CuSO_4$ disintegrated immediately when placed in water. Samples which were treated with either $ZnSO_4$ or $SnCl_2$ were distorted only slightly after being immersed in water for two hours, and of these two salts the $SnCl_2$ treated sample was the better.

Table 1

The Effect of Treating Lignin with Metallic Salts
Showing
Refluxing, Molding and Testing

Mold Run No.	Salt Used in Refluxing the Lignin	Time of Reflux (hr.)	Wgt. of Salt Treated Lignin (gms.)	Wgt. of Wood Flour (gms.)	Time of Preheating Lignin and Wood Flour at 110°C. (min.)	Relative Impact Strength (gms.)	Water Absorption 2 hr. Test	Flow in Mold	General Appearance of Molded Disc
1A-1	$ZnSO_4 \cdot 7H_2O$	2	25.0	2.5	0	-	-	poor	blown out on surface
1A-2	$ZnSO_4 \cdot 7H_2O$	2	12.5	12.5	0	22	-	poor	blown out on surface
1A-3	$ZnSO_4 \cdot 7H_2O$	2	10.0	10.0	0	-	-	poor	blown out on surface
1A-4	$ZnSO_4 \cdot$ [illegible]H_2O	2	9.5	9.5	30	-	-	poor	very soft and easily scratched with fingernail
1A-5	$ZnSO_4 \cdot 7H_2O$	2	10.0	10.0	10	-	-	poor	very soft and easily scratched with fingernail
1A-6	$ZnSO_4 \cdot 7H_2O$	2	10.0	10.0	5	12	-	poor	hard and smooth
1A-7	$ZnSO_4 \cdot 7H_2O$	2	10.0	10.0	1	21	good	poor	hard and smooth
1B-1	$ZnSO_4 \cdot 7H_2O$	6	10.0	10.0	1	22	good	poor	hard and smooth
2-1	$Pb(CH_3COO)_2 \cdot 3H_2O$	2	10.0	10.0	1	10	disintegrated	poor	could be scratched with fingernail
3-1	$CuSO_4 \cdot 5H_2O$	2	10.0	10.0	1	12	disintegrated	poor	could be scratched with fingernail
4-1	$SnCl_2 \cdot 2H_2O$	2	10.0	10.0	1	21	good	poor	hard and smooth

Note: In all runs, 60 gms. of lignin were refluxed with 500 cc. of 10% salt solution and subsequently treated with H_2S for 15 minutes.

All samples were molded at a temperature of 150°C. and at a pressure of 2,000 psig for 5 minutes.

Runs Number 5, 6, 7, and 8: Table 2 shows the various ways in which lignin was treated in runs 5, 6, 7, and 8. In run 5, lignin was molded without being treated at all. In run 6, lignin was treated with stannous chloride only. Lignin was treated with hydrogen sulfide only in run 7. In run 8 lignin was treated with stannous chloride followed by treatment with hydrogen sulfide.

The results of molding samples of runs 5, 6, 7, and 8 are shown in Table 3.

Table 4 shows evidence of a reaction between lignin and stannous chloride which was obtained in run 6. The per cent moisture in the original lignin and the stannous chloride treated lignin was determined and from this the dry weights given were calculated. The per cent ash in the untreated and stannous chloride treated lignin was determined and results are tabulated in Table 4.

Table 2

Lignin Treated with $SnCl_2$ only; H_2S only, $SnCl_2$ and H_2S, and Lignin Not Treated at All

Run No.	Wgt. of Lignin (gms.)	Salt used in Refluxing Lignin	Amount of Salt Solution (cc.)	Concentration of Salt Solution %	Time of Reflux (hr.)	Time of H_2S Treatment (min.)
5	60	none	none	none	0	0
6	60	$SnCl_2.2H_2O$	500	10% $SnCl_2$	2	0
7	60	none	none	none	0	15
8	60	$SnCl_2.2H_2O$	500	10% $SnCl_2$	2	15

Table 3

Molding and Testing of Runs 5, 6, 7, and 8

Molding						Testing			
Mold Run No.	Wgt. of Treated Lignin (gms.)	Wgt. of Wood Flour (gms.)	Time of Preheating Lignin at 110°C. (min.)	Time of Preheating Wood Flour at 110°C. (min.)	Time of Molding (min.)	Relative Impact Strength (cms.)	Water Absorption 2 hr. Test %	Flow in Mold	Appearance of Molded Disc
5-1	15	5	2	6	3	-	-	poor	stuck to mold
5-2	15	5	2	2	3	-	-	poor	blown out
5-3	15	5	0	8	5	-	-	poor	blown out
5-4	15	5	1	8	5	-	-	poor	blown out
5-5	15	5	2	8	5	20	7.3	poor	hard and smooth
6-1	15	5	2	8	5	10	5.9	poor	hard and smooth
7-1	15	5	3	8	5	14	10.9	poor	hard and smooth
8-1	15	5	2	8	5	10	1.8	poor	hard and smooth

Note: All of the discs were molded at a temperature of 150°C. and a pressure of 2,000 psig.

Table 4

Evidence of Reaction Between Lignin and Stannous Chloride

in Run 6

Wgt. of Treated and Untreated Lignin

(dry basis)

Wgt. of original lignin	57.852 gms.
Wgt. of $SnCl_2$ treated lignin	73.000 gms.
Gain in wgt.	15.148 gms.
Gain in wgt.	26.0%

Per Cent Ash Determination On Treated and Untreated Lignin

Ash in original lignin	0.26%
Ash in $SnCl_2$ treated lignin	11.2%

$SnCl_2$ Treated Lignin Condensed With Formaldehyde: Runs 9, 10A, 10B, 10C, and 11 show the effect of condensing $SnCl_2$ treated lignin with 41 gms. (½ mol), 82 gms. (1 mol), and 164 gms. (2 mols) of 37 per cent formaldehyde. Table 5 shows the conditions under which the lignin was condensed. In Table 6 the molding conditions and the results of testing are tabulated.

At the end of the condensing period in run 9 no resin had precipitated; so the solution was made acid with 5% H_2SO_4. In run 10A the resin precipitated from the solution, but at the end of the condensing period the solution was made acid to be sure that all the lignin had precipitated. So much solid was precipitated in the 300 cc. of solution that it became very viscous and hard to stir. In run 10B at the beginning of the condensing period 300 cc. of water were added to the 300 cc. of NaOH solution so that the solution would not become viscous and hard to stir when the resin precipitated. No acid was added at the end of the condensing period. In run 10C it was discovered that only 200 cc. of 5% NaOH were necessary to dissolve the lignin when 300 cc. of water were added. This run was stopped immediately after the resin precipitated. However the mixture was almost colloidal in nature and was impossible to filter. The mixture was dried without filtering. In run 11, condensing again was carried out for 2 hours.

Table 5

$SnCl_2$ Treated Lignin Condensed with Formaldehyde

Run No.	Wgt. of $SnCl_2$ Treated Lignin (gms.)	Amount of 5% NaOH Solution (cc.)	Amount of Water Added (cc.)	Wgt. of 37% HCHO (gms.)	Time of Reflux (min.)	Amount of 5% $HgSO_4$ Added (cc.)
9	50	300	0	41	120	Until acid to litmus
10A	50	300	0	82	120	50
10B	50	300	300	82	120	0
10C	50	200	300	82	70	0
11	50	200	300	164	120	0

Note: In all runs in table 5, $SnCl_2$ treated lignin was prepared by refluxing 60 gms. of lignin with 500 cc. of 10% $SnCl_2$ for 2 hours followed by treatment with H_2S for 15 min.

Table 6

Molding and Testing SnCl$_2$ Treated Lignin

Condensed with Formaldehyde

Molding							Testing			
Mold Run No.	Wgt. of SnCl$_2$ Treated Lignin (gms.)	Wgt. of Wood Flour (gms.)	Wgt. of Phenol (gms.)	Time of Preheating Lignin at 110°C. (min.)	Time of Preheating Wood Flour at 110°C. (min.)	Time of Molding (min.)	Relative Impact Strength (cms.)	Water Absorption 2 hr. Test %	Flow in Mold	Appearance of Molded Disc
9-1	10	8	2	1	1	3	22	-	very poor	phenol was on the surface
9-2	14	5	1	1	1	3	20	-	very poor	phenol was on the surface
9-3	15	5	0	1	1	3	15	disintegrated	very poor	surface was scratched with fingernail
10A-1	15	5	0	1	1	3	17	15.1	very poor	surface was scratched with fingernail
10B-1	18	0	2	1	0	3	-	-	very poor	phenol on surface, easily broken
10B-2	15	5	0	1	1	3	22	disintegrated	very poor	surface was scratched with fingernail
10C-1	15	5	0	1	1	3	18	disintegrated	very poor	surface was scratched with fingernail
11-1	15	5	0	1	1	3	15	disintegrated	very poor	surface was scratched with fingernail

Note: All the discs were molded at a temperature of 150°C. and a pressure of 2,000 psig.

$SnCl_2$ Treated Lignin Condensed With a Mixture of Formaldehyde and Furfural: Runs 12, 13, and 14 show the effect of condensing $SnCl_2$ treated lignin with a mixture of 41 gms. (½ mol) of 37% formaldehyde and 48 gms. (½ mol), 96 gms. (1 mol), and 144 gms. (1½ mol) of furfural. Table 7 shows the conditions under which the lignin was condensed. Table 8 shows the conditions under which mold runs were made and shows the results of testing the molded discs.

At the end of the condensing period in run 12, no resin had precipitated; so the solution was made acid with 5% H_2SO_4. In runs 13 and 14 the resin precipitated during the condensing period and no acid was added. The condensation product of run 14 was gummy and had to be air dried for 10 days before it could be molded.

Table 7

$SnCl_2$ Treated Lignin Condensed with a Mixture of Formaldehyde and Furfural

Run No.	Wgt. of $SnCl_2$ Treated Lignin (gms.)	Amount of 5% NaOH Solution (cc.)	Amount of Water Added (cc.)	Wgt. of 37% HCHO (gms.)	Wgt. of Furfural (gms.)	Time of Refluxing (hr.)	Amount of 5% H_2SO_4 (cc.)
12	50	200	400	41	48	2	75
13	50	200	400	41	96	2	0
14	50	200	400	41	144	2	0

Note: In all runs in table 7, $SnCl_2$ treated lignin was prepared by refluxing 60 gms. of lignin with 500 cc. of 10% $SnCl_2$ for 2 hours followed by treatment with H_2S for 15 minutes.

Table 8

Molding and Testing $SnCl_2$ Treated Lignin Condensed with a Mixture of Formaldehyde and Furfural

Molding						Testing			
Mold Run No.	Wgt. of $SnCl_2$ Treated Lignin (gms.)	Wgt. of Wood Flour (gms.)	Time of Preheating Lignin at 110°C. (min.)	Time of Preheating Wood Flour at 110°C. (min.)	Time of Molding (min.)	Relative Impact Strength (cms.)	Water Absorption 2 hr. Test %	Flow in Mold	Appearance of Molded Disc
12-1	15	5	9	9	6	27	62.8	poor	hard and smooth
13-1	15	5	2	6	5	29	37.6	poor	hard and smooth
14-1	15	5	2	8	5	17	2.44	poor	hard and smooth

Note: All the discs were molded at a temperature of 150°C. and a pressure of 2,000 psig.

Salt Treated Lignin Treated With Furfural: Runs 15, 16, 17, 18, 19, and 20 show the effect of condensing salt treated lignin with furfural. Table 9 shows the conditions under which the lignin was condensed. Table 10 shows the conditions under which mold runs were made and shows the results of testing the molded discs.

In run 15, 48 gms. (½ mol) of furfural were used and the precipitate was a fine brown precipitate. In runs in which 96 gms. (1 mol) of furfural were used, the addition of acid caused a thick black syrup to be formed which hardened rapidly on exposure to air. In run 20, 192 gms. (2 mols) of furfural were used and the product precipitated by the acid was a thick black syrup which after four weeks had not hardened enough to be molded. The resin was not precipitated in any of these runs until after the acid was added.

In run 17 the concentration of NaOH was much weaker than that used in runs 16, 18, and 19. (In all these runs 96 gms. (1 mol) of furfural was used.) The results of these runs are shown in Table 10.

Runs 18 and 19 were condensed under the same conditions but $SnCl_2$ treated lignin was used in run 18 and $ZnSO_4$ treated lignin was used in run 19. The results of these runs are shown in Table 10.

Table 9

Salt Treated Lignin Condensed with Furfural

Run No.	Wgt. of $SnCl_2$ Treated Lignin (gms.)	Wgt. of $ZnSO_4$ Treated Lignin (gms.)	Amount of 5% NaOH Solution (cc.)	Amount of Water Added (cc.)	Wgt. of Furfural (gms.)	Time of Refluxing (hr.)	Amount of 5% H_2SO_4 (cc.)
15	50	0	200	400	48	2	175
16	50	0	200	400	96	2	200
17	50	0	150	850	96	2	105
18	50	0	200	400	96	2	143
19	0	50	200	400	96	2	125
20	50	0	200	400	192	7	200

Note: In all runs in table 9, the salt treated lignin was prepared by refluxing 60 gms. of lignin with 500 cc. of 10% salt solution for 2 hours followed by treatment with H_2S for 15 minutes.

Table 10

Molding and Testing Salt Treated Lignin Condensed with Furfural

Molding						Testing			
Mold Run No.	Wgt. of Salt Treated Lignin (gms.)	Wgt. of Wood Flour (gms.)	Time of Preheating Lignin at 110°C. (min.)	Time of Preheating Wood Flour at 110°C. (min.)	Time of Molding (min.)	Relative Impact Strength (cm.)	Water Absorption 2 hr. Test %	Flow in Mold	Appearance of Molded Disc
15-1	15	5	1	1	3	-	-	good	blown out
15-2	15	5	2	2	3	-	-	good	blown out
15-3	15	5	3	3	3	22	15.5	good	hard and smooth
16-1	15	5	2	2	3	-	-	good	blown out
16-2	15	5	4	4	3	-	-	good	blown out
16-3	15	5	6	6	3	-	-	good	blown out
16-4	15	5	9	9	3	15	6.2	good	blown out
17-1	15	5	3	8	5	20	21.3	good	hard and smooth
18-1	15	5	3	8	5	-	-	good	blown out
18-2	15	5	12	12	5	15	21.3	good	hard and smooth
18-3	12.5	4.1	0	8	until cool	-	6.0	good	hard and smooth
19-1	15	5	0	8	until cool	15	1.6	good	hard and smooth

Note: All discs were molded at a temperature of 150°C. and a pressure of 2,000 psig.

<u>Compilation of Testing Results</u>: In Table 11 the testing results of the best molded disc in each run are tabulated.

<u>Flow in the Mold</u>: Flow in the mold is illustrated in Fig. 4. Sample A was condensed with formaldehyde and exhibited little or no flow in the mold. The dark spots of resin did not flow and cover the white wood flour. Good flow was exhibited by sample B which was condensed with furfural. The resin flowed and covered the wood flour giving the molded piece a uniform black color.

Table 11

Compilation of Testing Results

Mold Run No.	Flow in the Mold	Per Cent Water Absorption 2 hr. test	Relative Impact Strength (cms.)
1A-7	poor	*	21
1B-1	poor	*	22
2-1	poor	disintegrated	10
3-1	poor	disintegrated	12
4-1	poor	*	21
5-5	poor	7.3	20
6-1	poor	5.9	10
7-1	poor	10.9	14
8-1	poor	1.8	10
9-3	very poor	disintegrated	15
10A-1	very poor	15.1	17
10B-2	very poor	disintegrated	22
10C-1	very poor	disintegrated	18
11-1	very poor	disintegrated	15
12-1	poor	62.8	27
13-1	poor	37.6	29
14-1	poor	2.4	17
15-3	good	15.5	22
16-4	good	6.2	15
17-1	good	21.3	20
18-3	good	6.0	15
19-1	good	1.8	15
20	Not Molded		

* Although these samples did not disintegrate, they were so distorted and soft at the end of the 2 hour water absorption test that the per cent water absorbed could not be determined.

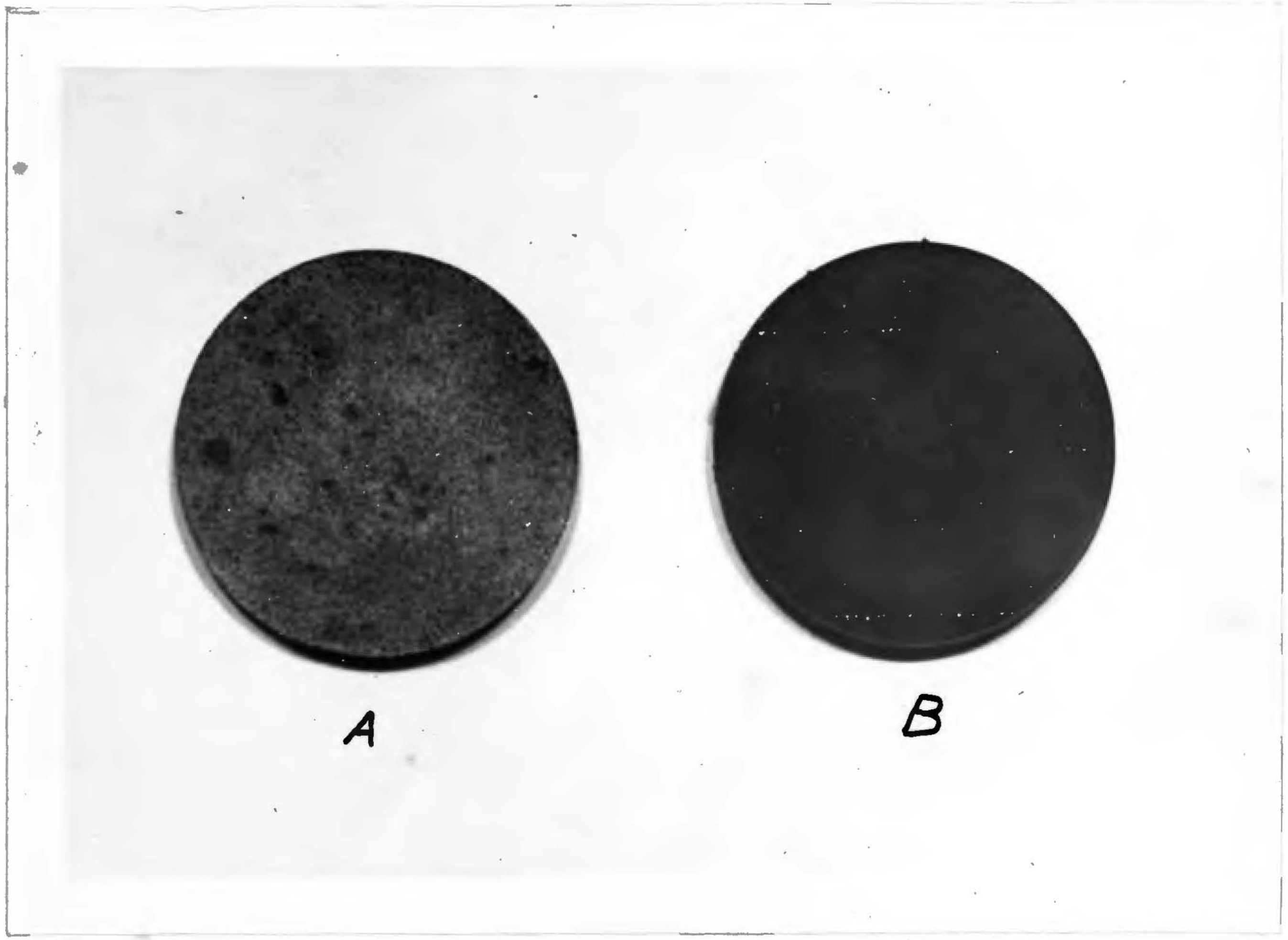


Fig. 4

Comparison of Flow in the Mold

IV. DISCUSSION

Lignin Treated With Various Metallic Salts: Lead acetate treated lignin and cupric sulfate treated lignin were molded with little or no success. Discs molded from these salt treated lignins were easily broken and their surfaces could be scratched with the finger nail. When placed in water they fell apart or disintegrated immediately.

Stannous chloride treated lignin and zinc sulfate treated lignin were molded with some success. Increasing the time that lignin was refluxed with zinc sulfate did not improve the molding characteristics any. The relative impact strengths of stannous chloride and zinc sulfate treated lignin were approximately the same. However stannous chloride treated lignin was better in the water absorption test than zinc sulfate treated lignin. Hereafter stannous chloride treated lignin will be referred to as stannous lignin.

The Value of Treating Lignin With $SnCl_2$ Only, H_2S Only, and $SnCl_2$ and H_2S: Lignin which was treated with $SnCl_2$ followed by treatment with H_2S had better water absorption characteristics than lignin treated with $SnCl_2$ only, lignin treated with H_2S only, or lignin not treated at all. However the relative impact strength of lignin which was not treated at all was the best.

Stannous Lignin Condensed With Formaldehyde: Molded discs made from stannous lignin condensed with formaldehyde had very poor flow in the mold. The wood flour was not covered and could be rubbed or scratched off of the surface of the molded disc with the finger nails. The water absorption characteristics were very bad. There was only one run in which formaldehyde was used that did not disintegrate when placed in water. No explanation is offered as to why one disc did not disintegrate while all others did. The relative impact strengths of these samples were as good as the average of other samples.

Stannous Lignin Condensed With a Mixture of Formaldehyde and Furfural: The amount of formaldehyde used remained constant at ½ mol while ½, 1, and 1½ mols of furfural were used. The per cent of water absorbed decreased as the amount of furfural was increased. The largest amount of furfural that could be used was 1½ mols. When this amount was used the product was gummy and had to be dried for 10 days before it could be molded. The highest relative impact strength of any sample in this investigation was obtained when 1 mol of furfural was used. However the relative impact strength dropped off when 1½ mols of furfural were used.

Salt Treated Lignin Condensed With Furfural: Stannous chloride lignin was condensed with ½ mol, 1 mol, and 2 mols of furfural. The best water absorption was obtained when 1 mol of furfural was used. However the relative impact strength was best when only ½ mol was used. When two mols of furfural were used the product was a thick syrup which after four weeks had not dried enough to be molded. In one run (run 17) a very dilute solution of NaOH was used in the condensing period. However the results were not as good as when higher concentrations of NaOH were added. Higher concentrations of NaOH probably made a better catalyst for the reaction.

A run was made using zinc sulfate treated lignin instead of stannous lignin. Stannous chloride treated lignin gave the best results when no condensing agent was used; however, zinc sulfate treated lignin gave the best results when furfural was used as a condensing agent.

__The Use of Phenol as a Plasticizer:__ Phenol was used as a plasticizer but had to be discarded due to bleeding. During molding the phenol melted and was forced to the surface of the molded disc. When the disc cooled crystals of phenol were left on the surface. Since phenol can cause skin irritation it would not be practicable to have crystals of it on the surface of a plastic.

__The Use of Wood Flour as a Filler:__ When 50% wood flour was used in the preliminary molding of the four different salt treated lignins the water absorption was so great that the per cent of water absorbed could not be determined. Stannous chloride treated lignin molded with only 25% wood flour absorbed only a small amount of water. However the relative impact strength was lowered. In general in most runs made it was noticed that as the water absorption characteristics improved the relative impact strength grew worse.

Recommendations

Increasing the Temperature of the Condensation Reaction Mixture: In this investigation the condensation reaction was carried out at 100°C. In future tests it is suggested that the condensation reaction be carried out in an autoclave so that the temperature may be increased.

Concentration of the Sodium Hydroxide Solution: The highest concentration of NaOH used in the condensing period in this investigation was 5%. In the future it would be desirable to study the effect of using higher concentrations of NaOH.

Amount of Raw Materials Used: In the future it would be desirable to use lignin samples larger than 60 gms. for refluxing and condensing. It is desirable to have a large amount of product so that numerous samples can be molded and used for testing.

Condensing Agents: In future tests condensing agents other than formaldehyde and furfural may be used. For example, polycarboxylic acids are good condensing agents.

Fillers for Molding: The only filler used in molding in this investigation was wood flour. It would be desirable in future tests to use fillers such as glass fiber, cotton cloth, and asbestos.

Chemistry of the Salt Reaction: It would be desirable in future tests to study the chemistry of the reaction between lignin and a metallic salt such as zinc sulfate or stannous chloride.

Testing the Product: It is suggested that in the future sufficient quantity of the product be sent to a laboratory equipped to do accurate molding and testing of plastics.

Percentage Moisture in the Molding Compound: In future tests it would be desirable to determine accurately the highest per cent of moisture that could be left in the molding compound and still not cause the molded piece to blow out. The molding compound should be dried to this moisture content at room temperature. Drying in a 100°C. oven may cause premature setting up of the plastic; and therefore decrease flow in the mold and other plastic properties of the molding compound.

Limitations

Temperature of Condensation Reaction: With the equipment that was used, the condensation reaction had to be carried out at atmospheric pressure. Therefore the temperature of the condensation reaction mixture could not be raised above 100°C.

The Number of Molded Discs Available for Testing: The yield from the condensation reaction was approximately 50 or 60 gms. Only three or four molded discs could be made from this amount of product and used for testing.

Testing the Molded Discs: A 2½ inch diameter disc approximately ¼ inch thick was the size and shape of the piece that could be molded in the mold that was available. Making tensile strength tests and other tests according to ASTM standards that should be made on plastics require molded pieces of special size and shapes.

Plasticizer: It was originally planned to use dibutyl phthalate as a plasticizer. However none was available at the time this investigation was made.

Molding Temperature and Pressure: The molding temperature was limitated to 150°C. and 2,000 psig. The small quantity of product that was available for molding and testing made this limitation necessary.

V. CONCLUSIONS

1. A moldable plastic material was prepared from lignin by treatment with stannous chloride, hydrogen sulfide, and a condensing agent.

2. Water absorption characteristics and impact strength were not appreciably improved by condensing stannous chloride treated lignin with a condensing agent, but flow in the mold was improved by condensing with furfural.

3. The best water absorption value, 1.8%, a relative impact value of 10 cm., and poor flow in the mold were obtained by treating lignin with stannous chloride and hydrogen sulfide, without a condensing agent.

4. The best water absorption value, 1.8%, best flow in the mold, and a relative impact value of 15 cm. were obtained by treating lignin with zinc sulfate, hydrogen sulfide, and furfural.

5. The best relative impact value, 29 cms., a water absorption value of 37.6%, and poor flow in the mold were obtained by treating lignin with stannous chloride, hydrogen sulfide, and a mixture of formaldehyde and furfural.

6. Lead acetate and cupric sulfate treated lignin were very poor molding compounds.

7. Zinc sulfate and stannous chloride treated lignin were molded with some success, and of the two, stannous chloride was the better.

8. The maximum amount of filler that could be used and still obtain good covering was 25% wood flour.

9. Phenol could not be used as a plasticizer due to bleeding.

10. Molded discs blew out unless accorded special treatment.

11. The molded disc could be kept from blowing out and buckling on the surface by: (1) preheating the lignin and wood flour in a 110°C. oven, or (2) leaving the sample in the mold, while under pressure, until the mold cooled to room temperature.

12. Stannous chloride treated lignin which was subsequently treated with hydrogen sulfide and molded had better water absorption characteristics than lignin treated with salt only, lignin treated with hydrogen sulfide only, and lignin not treated at all.

13. Molded samples made from stannous chloride treated lignin condensed with formaldehyde and mixtures of formaldehyde and furfural had poor molding characteristics.

14. Molded samples made from stannous chloride treated lignin which was condensed with furfural had good flow characteristics.

15. Salt treated lignin which was condensed in the presence of approximately 2 per cent sodium hydroxide produced better molded samples than lignin condensed in the

presence of 0.75 per cent sodium hydroxide.

16. Increasing the length of time that lignin was refluxed with zinc sulfate from 2 hours to 6 hours did not appreciably change the molding characteristics of the lignin.

V. SUMMARY

Lignin was refluxed with four different metallic salts. In each case, the salt treatment was followed by treatment with hydrogen sulfide. The $SnCl_2$ treated lignin possessed the best molding characteristics.

To determine the value of the salt treatment and the hydrogen sulfide treatment lignin was treated with $SnCl_2$ only and molded, lignin was treated with hydrogen sulfide only and molded, and lignin was treated with $SnCl_2$ followed by hydrogen sulfide and molded. Lignin that was not treated in any way was also molded. Lignin treated with $SnCl_2$ followed by treatment with hydrogen sulfide had the best water absorption characteristics of any run made in this investigation. Lignin not treated at all had the highest relative impact strength.

Stannous lignin was condensed with ½ mol, 1 mol, and 2 mols of formaldehyde in the presence of NaOH. All molded samples made from formaldehyde condensed lignin had very poor flow in the mold and very poor water absorption characteristics.

Stannous lignin was condensed with a mixture of formaldehyde and furfural. The amount of formaldehyde remained fixed at ½ mol whereas ½ mol, 1 mol, and 1½ mols of furfural were used. A molded sample that had been condensed with a mixture of ½ mol of formaldehyde and 1 mol of furfural had the highest relative impact strength of any sample in this investigation.

Stannous lignin was treated with ½ mol, 1 mol, and 2 mols of furfural. Better flow in the mold was obtained when furfural was used than was obtained in any of the other tests. It was found that 1 mol of furfural was the best quantity to use. A run was made using zinc sulfate treated lignin instead of stannous lignin. The zinc sulfate treated lignin when condensed with furfural had a lower per cent of water absorption than the stannous lignin when condensed with furfural. This low water absorption value was equaled only by stannous lignin which was not treated with a condensing agent.

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