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A Study of the Nature of Lignosulfonic Acids
Fractionated by Chemical and Physical Methods

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**A STUDY OF THE NATURE OF LIGNOSULFONIC ACIDS
FRACTIONATED BY CHEMICAL AND PHYSICAL METHODS**

A thesis submitted by

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INTRODUCTION

When the lignin in wood is treated with bisulfite solutions it is sulfonated and eventually dissolved. In the production of sulfite pulp based on this reaction, the excess of sulfur dioxide is recovered but the sulfur combined with the lignin is lost. The loss depends chiefly upon the degree of sulfonation of the lignin which, in turn, depends upon the cooking conditions. The lowest sulfur content of lignin necessary (1) to render it soluble in water is about 3.5-4.0 per cent, which corresponds to one sulfonic acid group per lignin building unit (with a molecular weight of 840). The sulfur contents of lignosulfonic acids reported by various investigators from both commercial waste liquors and experimental cooks vary from 5-7 per cent, with some as high as 10-11 per cent (2). The question arises as to how the higher sulfonation of lignin occurs. Does the lignin building unit react with a second molecule of sulfite to give a lignodisulfonic acid or is the lignin degraded into units of a lower molecular weight with only one sulfonic acid group and, if the latter occurs, is the chemical nature changed in a way that can be detected? Mitchell and Yorston (3) expressed the practical need for investigation of this subject when they stated that--"While there is evidence that the consumption of sulfur (in sulfite pulping) is greater than it need be, not enough is known of the reactions in which the excess sulfur takes part to enable any methods of reducing that consumption to be suggested."

The sulfur contents reported in the literature for various lignosulfonic acids do not usually correspond to stoichiometric amounts of combined sulfur. This indicates that, in most lignosulfonic acid solutions, there is a mixture of monosulfonic acids (with a molecular weight of 921) and sulfonic acids in which the S:C ratio is higher than that of the mono acid. A study of the nature of lignosulfonic acids which have a high sulfur content must, therefore, include a fractionation of each sulfite waste liquor studied, as well as a comparison of liquors having a high sulfur content with those which have a low sulfur content.

HISTORICAL REVIEW

Lignosulfonic acids are one of the most important derivatives of lignin from a theoretical as well as practical standpoint and the amount of work done on their isolation and properties has been large. Due to the inherent nature of the material, as in all lignin studies, investigations of their chemical characteristics are difficult. The chemical properties of lignosulfonic acids vary widely with the conditions of sulfonation. To obtain the material from sulfite waste liquor it must be precipitated by some means, such as salting out or the addition of one of many precipitating agents. In either case the products are amorphous, difficult to wash, and contaminated with fermentable and unfermentable sugars. When the product is finally isolated there is no accurate method of determining its homogeneity. Many investigators have not recognized these conditions and have (1) neglected to report the conditions of sulfonation, (2) used many different precipitating agents, and (3) failed to establish the purity of the products obtained. For this reason there is little agreement in the literature and it is difficult to present a clear picture of what is definitely known concerning the nature of lignosulfonic acids. Phillips (4) has published a brief survey of the literature dealing with this phase of lignin chemistry, and Freudenberg, (5), Fuchs (6), and Hawley and Wise (7) have interpreted the pertinent literature dealing with this material. The most recent literature survey and interpretation has been published by Hagglund (8) which, although not complete, presents the important facts known on the subject. The present review has of necessity been

limited to that work dealing with the fractionation of lignosulfonic acids, and the degree of sulfonation of the products obtained.

The Fractionation of Sulfonated Lignin

The means used to isolate the lignosulfonic acids in sulfite waste liquor, from the earliest work of Pederson (9), and Lindsey and Tellens (10) to the most recent investigations of Erdtman (11) and Racky (2), have resulted in some fractionation of the acids. None of the precipitating agents which have been used, with the possible exception of basic lead acetate, will precipitate all of the methoxyl-containing material from sulfite waste liquor. Most investigators have recognized this and have concluded that sulfite waste liquor contains a mixture of different lignosulfonic acids. However, there are workers whose results indicate that lignosulfonic acids are chemically homogeneous.

Klason, whose work extends from the earliest investigations up to the present period, is the principal exponent of the chemical homogeneity of sulfonated lignin. The number of papers published by this worker is very large and although many of the concepts he has proposed are not now generally accepted, his work has stood as the basis with which other investigators have agreed or disagreed; his work and theories have been summarized by Bailey (12). Briefly, Klason believes the lignin building unit consists of nine molecules of coniferyl aldehyde (or a closely related compound) with one molecule of water on each double bond. The sulfonation reaction is believed to occur at the unsaturated group formed by the loss of one molecule

of "aldol" water -- the lignin molecule then splitting into three molecules of lignosulfonic acid each containing three coniferyl aldehyde units. Two of the molecules of lignosulfonic acid may then be quantitatively precipitated by salting out or by formation of an insoluble salt with beta-naphthylamine, and are designated as alpha-lignosulfonic acid. The third lignosulfonic acid molecule from each lignin building unit is precipitated by lead salts and is designated beta-lignosulfonic acid. This theory postulates two lignosulfonic acids which can be separated easily, which are chemically homogeneous and are incapable of further fractionation. In his early work, Klason (13) precipitated alpha-lignosulfonic acid with calcium chloride. In all recent work the alpha-fraction has been precipitated as the salt of beta-naphthylamine. In the course of his investigations Klason has published analyses of lignosulfonic acids in which the sulfur contents varied widely but has always presented an empirical formula (based on coniferyl aldehyde) which accounted for the sulfur content found.

Dorée and Hall (14) isolated and investigated lignosulfonic acids which were obtained from cooks in which the cooking agent was free sulfurous acid (7 per cent sulfur dioxide). The crude waste liquor obtained was dialyzed -- about 40 per cent of the total solids being removed. The remaining sulfonated lignin was practically all precipitated (96 per cent) by beta-naphthylamine and analysis showed the empirical formula to be $C_{26}H_{30}O_{12}S$ (5.7 per cent sulfur). The material was subject to various reactions including nitration but always retained the C_{26} unit and, therefore, was considered to be

uniform. In a later work (15), the waste liquor from a cook using 7 per cent total sulfur dioxide and 0.36 per cent ammonia was investigated. Of the total solids in the liquor, 58 per cent were precipitated by beta-naphthylamine and about 65 per cent were precipitated by basic lead acetate. An additional amount of lead salt was obtained by the addition of alcohol. After dialysis the analysis of these materials indicated the empirical formula $2C_{20}H_{20}O_6 \cdot 2H_2SO_3 \cdot NH_3$.

Freudenberg and Sohns (1) and Freudenberg, Sohns, and Janson (16) have isolated lignosulfonic acids both from very mild cooks and from drastic cooks carried out in the laboratory. Each waste liquor was treated with quinoline acetate and the precipitated lignosulfonic acids regenerated with alkali. The two fractions from each waste liquor were then dialyzed and treated with naphthylamine hydrochloride. Using this procedure, it was found that quinoline precipitated all of the material precipitated by naphthylamine or by basic lead acetate. The authors concluded that there was no beta-fraction (Klason designation) in the lignosulfonic acids prepared by them.

Fractionation by Chemical Methods

Tollens and Lindsey (10) first isolated lignosulfonic acids from sulfite waste liquor by precipitation with strong hydrochloric acid and by basic lead acetate. The material precipitated by lead acetate was regenerated by acidification with sulfuric acid and fractionated by reprecipitation into alcohol. The sulfur contents of the different products, which were of questionable purity, varied from 4.1-7.1 per cent. Seidel (17) isolated the lignosulfonic acids from different waste liquors by the same procedure and found that the products obtained had different chemical compositions.

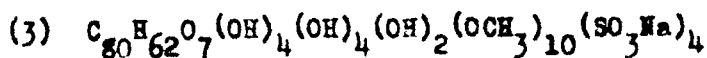
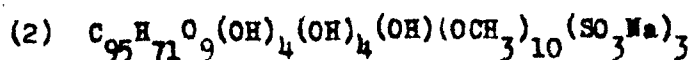
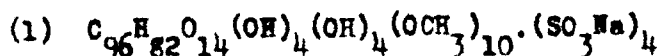
Sodium chloride was used by Melander (18, 19) to precipitate a fraction of the lignosulfonic acids from several waste sulfite liquors. It was found that the material salted out was the sodium salt of lignosulfonic acid and the composition was not the same as that obtained by Klason using calcium chloride. The fraction precipitated by sodium chloride varied also with different liquors. A purified lignosulfonic acid was then separated by fractional precipitation with concentrated hydrochloric acid into seven fractions with sulfur contents varying from 4.0 to 4.8 per cent. From these results it was concluded that sulfite waste liquor contains a number of chemically different lignosulfonic acids. Similar results were obtained with lignosulfonic acids isolated by means of aromatic amines.

Hönig and Spitzer (20) precipitated lignosulfonic acids with 50 per cent sulfuric acid. The precipitate was regenerated with barium carbonate and the sulfuric acid was removed as barium sulfate. Barium salts of varying composition were isolated by fractional precipitation with alcohol. This method was later used by König (21), who found the products to be contaminated.

The homogeneity of Klason's alpha-lignosulfonic acid was investigated by Hågglund (22). Sprucewood was cooked with sulfite liquor containing 4.13 per cent total, and 0.70 per cent combined sulfur dioxide. As the cooking time was increased by one-hour intervals from 15 to 19 hours, the yield of alpha-lignosulfonic acid isolated by the method of Klason increased from 18.9 to 21.2 per cent (calculated on

the basis of the wood). The sulfur contents of the five alpha-lignosulfonic acids increased with cooking time from 5.25 to 5.95 per cent. This indicated that Klason's alpha-lignosulfonic acid was not a uniform compound. In the same work, however, Hagglund was unable to fractionate the alpha-acid obtained from a commercial sulfite waste liquor.

Nippe and Ogait (23) isolated the sodium salt of a sulfonated lignin from waste liquor by salting out with sodium chloride and purified the material by repeated precipitation into ethanol. The product was considered uniform and had the empirical formula $C_{48}H_{45}O_{17}SNa_2(OCH_3)_5$. Later, Nippe (24) carried out a detailed fractionation of the lignosulfonic acids which he precipitated by aromatic amines. The alpha-lignosulfonic acid of Klason was separated into three fractions by successive precipitations with (1) sodium chloride, (2) alpha-naphthylamine (acidified with sulfur dioxide), and (3) benzidine hydrochloride. The products obtained had the formulas:



(The extra OH groups in (2) and (3) were of acidic nature.) The three fractions obtained were considered to be uniform materials because (1) their composition showed a stoichiometric relation, (2) they reacted stoichiometrically to form esters, and (3) fractions with the same formula were obtained from different liquors. However, the

possibility that each fraction was made up of several isomeric compounds was considered very likely.

A systematic separation of lignosulfonic acids was attempted by Tomlinson and Hibbert (25) on two materials obtained from laboratory cooks with sprucewood. The first cook was very mild (21 hours at 100° C., with 5 per cent total sulfur dioxide) and the second more nearly approached commercial conditions (12 hours at 125° C., with 6 per cent total sulfur dioxide). The sulfonated lignin derivatives from the latter cook were separated into three fractions: (1) that easily salted out with calcium chloride, (2) that salted out with difficulty by calcium chloride and (3) that precipitated by basic lead acetate. The liquor from the mild cook was fractionated by successive precipitation with quinoline, beta-naphthylamine and, finally, basic lead acetate. The fractions from both cooks were regenerated, dialysed, precipitated into organic solvents, and analysed for sulfur and methoxyl contents. Upon dialysis, about 40 per cent of the lignosulfonic acids were lost. The results showed that the sulfur content increased as ease of precipitation decreased, whereas the methoxyl contents (calculated on the basis of the unsulfonated lignin) remained practically the same. By repeated methylation with dimethyl sulfate, the methoxyl content (calculated on the lignin) was increased to 30.0-31.6 per cent. The results were as follows:

Cook Conditions	Mild			More Drastic		
	21 hours at 100°C. 5% total SO ₂ - K base			12 hours at 125°C. 6% total SO ₂ - Ca base		
Fraction pre- cipitated by:	Quino- line	Naphthyl- amine	Lead Acetate	CaCl ₂	CaCl ₂	Lead Acetate
Sulfur, %	5.4	6.6	5.6	9.4	9.6	10.4
K or Ca, %	3.7	5.0	5.8	3.5	3.8	5.0
Methoxyl, %	12.8	12.0	9.2	11.2	11.35	10.45
Methoxyl on basis of lignin, %	15.5	15.3	11.5	15.4	15.8	15.2
Distribution, %				70	10	14

The efficiencies of several reagents used for precipitating lignosulfonic acids were also investigated and found to increase in the following order: sodium chloride, calcium chloride, quinoline, iso-amylamine, beta-naphthylamine, and basic lead acetate.

The same method of fractionation (using quinoline, beta-naphthylamine, and basic lead acetate) was applied to commercial western hemlock sulfite waste liquor by Friedman and Rusk (26). The results obtained were very similar to those of Tomlinson and Hibbert. It should be pointed out that these investigators only reported the distribution of the material isolated and do not account for all of the material having a high methoxyl content in the waste liquor.

The ability of fluoro-silicic acid to precipitate lignosulfonic acids has recently been used by Rasky (2) to fractionate this material. A concentrated solution of spruce sulfite waste liquor was treated with at least 27 per cent fluoro-silicic acid. The portion precipitated, in keeping with the terminology of Klason, was designated

the alpha-fraction and that remaining in solution the beta-fraction. The soluble beta-fraction was extracted with butanol and precipitated as the sodium salt with sodium bicarbonate. In the first work using this method (presumably on commercial liquors), about 70 per cent of the total lignin material was precipitated as the alpha-acid. The beta-fraction, after precipitation, was separated into six parts based on solubility in methanol, ethanol, and butanol. The analysis of these fractions showed that the sulfur contents varied from 8.6 to 12.2 per cent and the methoxyl content from 6.6 to 10.2 per cent, with no correlation between solubility and sulfur and methoxyl contents.

Erdtman (11) carried out some work to find a more suitable means of precipitating lignosulfonic acids. 4,4'-Bis-(dimethylamino) diphenylmethane was found to satisfy the requirements of his ideal precipitating agent. Although no analytical data were included, the fractionation of commercial waste liquor by organic bases was investigated. It was found that those fractions which were easily precipitated had a greater molecular size, higher methoxyl content, lower reducing power, and lower sulfur content than those fractions not easily precipitated. The author considered the alpha and beta designation of Klason to be merely a question of molecular size.

The most successful commercial means of isolating and partially purifying lignosulfonic acids is that proposed by Howard, in which a large fraction of the lignin material in sulfite waste liquor is precipitated by calcium hydroxide. Crude liquor is treated with lime to

a pH of 10-11, at which point calcium sulfite is precipitated and separated. Additional lime is then added until a pH above 12 is reached, which causes the precipitation of about 50-60 per cent of the total organic material as the basic calcium salt of lignosulfonic acid. The precipitate is flocculent and easily filtered. The mother liquor contains carbohydrate material and also lignosulfonic acids which may be precipitated by a short pressure cook. Certain properties of lignosulfonic acid salts isolated in this manner have been investigated (27). The crude precipitate was relatively pure and analysis (based on a pure product) showed the ratio of sulfur to organic material to be about 32/600 and the ratio of sulfur to lime to be 1/1.5. After acidification with carbon dioxide the ratio S/CaO was 1/(0.5-1) and upon acidification with sulfur dioxide the ratio S/CaO increased to 1/0.5. The ash-free acid was obtained by acidification with strong mineral acids. The conclusion was reached that there are three acidic groups of unequal strength in the lignosulfonic acid molecule. Apparently the weakest acidic group governed the solubility of these lignosulfonic acids because they were dissolved if the pH was lowered to 10. The precipitated basic calcium lignosulfonate was also dispersed by salts of weak bases and strong acids and by certain alkali metal salts. When given an alkaline pressure cook, the lignosulfonic acid salts became acid insoluble and were then desulfonated and, finally, the lignin complex began to disintegrate.

Fractionation by Physical Methods

Samec and Rebek (28) obtained a "purified" fraction of lignosulfonic acids by prolonged dialysis followed by electrodialysis. The loosely bound sulfur dioxide was completely removed and the ash content of the final product was greatly reduced by dialysis. Some colored material was lost by passage through the membrane. Upon electrodialysis of this material, a free lignosulfonic acid was obtained in the anode compartment with a sulfur content of 8.85 per cent, whereas the material in the middle compartment had a sulfur content of 5.3 per cent. In a later work Samec and Ribaric (29) investigated the two fractions of lignosulfonic acid obtained by electrodialysis. The material retained in the middle compartment of the cell was designated "colloidal residue" and that passing the membrane to the anode compartment "primary anode dialysate." The anode fraction was then electrodialyzed into two fractions -- the "anode colloid" and the "secondary anode dialysate." The products were considered to be uniform and were analyzed for ash, sulfur, methoxyl contents, and total acidity. The results were as follows:

	Colloid Residue	Primary Anode Dialysate	Anode Colloid
Ash, %	0.12	0.25	0.21
Sulfur, %	5.81	8.85	6.08
Methoxyl, %	14.15	5.15	6.80
Equivalent of base per 100 g.	0.18	0.82	--

Fractional ultrafiltration was used by Friese and coworkers (30) for the separation and purification of lignosulfonic acids.

Commercial sulfite waste liquor was neutralized with calcium carbonate, evaporated to dryness and extracted successively with methanol and 80 per cent methanol. The undissolved material was subject to fractional ultrafiltration, using a collodion membrane and four Cella-Filters varying in pore size from 20-3000 millimicrons. Analysis and characterization showed the methanol-soluble fraction to be mostly sugars. The fraction soluble in 80 per cent methanol was found to be a mixture of lignin and carbohydrate material which were considered to be chemically united. The insoluble material was found to be a mixture of lignosulfonic acids which could be separated by ultrafiltration but all the fractions so obtained had approximately the same chemical composition.

Factors Affecting the Degree of Sulfonation

Although there is no published theory for the mechanism of the sulfonation reaction which will explain all of the known experimental facts, investigations have shown how sulfonation proceeds during the course of sulfite cooking and some of the factors affecting the degree and rate of sulfonation. The most important studies on this subject have been made by Hagglund (31). He found that, during the course of a sulfite cook the sulfonation reaction took place to a S/C ratio of 1/40 at 110-120° C. As cooking was continued the sulfur content of the lignin increased only slowly until the latter part of the cook, when the S/C ratio changed quite rapidly to 1/20 -- this final reaction being considered a sulfonation of the lignosulfonic acids in solution. Further investigations showed that, within the range

0.6-1.5 per cent of lime in the cooking liquor, the degree of sulfonation as well as pulp yield and quality increased with the concentration of combined sulfur dioxide. Increasing the concentration of free sulfur dioxide was found to have little effect upon the degree of sulfonation but greatly increased the rate at which sulfonation and solution of the lignin took place. The form and distribution of nonrecoverable sulfur were also determined. Twenty per cent of the sulfur was converted to sulfates, presumably by the air present in the wood; 20 to 30 per cent was in the waste liquor as loosely combined sulfur dioxide. The remainder of the sulfur (50-60 per cent) was chemically combined with the lignin.

Mitchell and Yorston (3) have reported that the degree of sulfonation increased with increasing concentration of combined sulfur dioxide but differ from Hägglund in that the pulp yield and quality were found to decrease under these conditions.

Bergman (32) made a study of the effect of cooking acid composition upon pulp yield, pulp quality, and sulfur consumption. It was found that doubling the amount of base used caused a 50 per cent increase in the firmly bound sulfur.

The permutoidal property of lignosulfonic acids was used by Mottet (33) as the basis of a quick method for determining the degree of sulfonation of lignin not dissolved during cooking. Using this technique, the work of Hägglund and of Bergman on the effect of combined sulfur dioxide was confirmed. By the same method it was shown that the

effectiveness of the base used increased in the order sodium, calcium, and ammonium. Maximum sulfonation occurred when about 20 per cent of the total sulfur dioxide was combined. Additional experiments showed that sulfonation increased linearly with temperature in the range 60-90° C. and with time up to 100 hours.

The lowest sulfur content which has been reported for lignosulfonic acids from sulfite waste liquor is 3.8-4.0 per cent. Freudenberg (1) cooked extracted wood with liquor having a total of 4 per cent sulfur dioxide and 1 per cent lime for 4-5 hours at 120-125° C. A sulfonated lignin was precipitated from the waste liquor with quinoline in a yield of 8-10 per cent, which after electrodialysis had a sulfur content of 4 per cent. This corresponded to one sulfur atom for every four methoxyl groups originally present in the lignin. Methylation studies indicated that the lignin molecule had not been altered in any other way by this cook.

By successively cooking laboratory waste liquor with fresh cooking liquor Freudenberg (16) increased the sulfur content of lignosulfonic acids from 3.0 to 5.4 per cent in the case of one liquor and from 4.0 to 5.6 per cent in another. He concluded (1) that there is no stoichiometric reaction between bisulfite and lignin.

Klason (34) studied the degree of sulfonation necessary for solution of lignosulfonic acid and also the maximum degree of sulfonation attainable. A material with the formula $3C_{10}H_{10}O_3 \cdot H_2SO_3 \cdot C_{10}H_9N - H_2O$ (4.3 per cent sulfur) was considered to be sulfonated to the minimum

degree necessary for solution. The empirical formula $C_{10}H_{10}O_3 \cdot H_2SO_3$. $C_{10}H_9N - H_2O$ (12.8 per cent sulfur calculated on the lignosulfonic acid) corresponded to the analysis of a product which had been sulfonated to the maximum degree.

The analysis of lignosulfonic acids reported by Racky (2) on material soluble in fluorosilicic acid but separated by methanol, ethanol, and butanol showed some fractions to have sulfur contents as high as 12.2 per cent.

The degrees of sulfonation reported by these investigators represent the two extremes which are to be found in the literature. The sulfur contents of these lignosulfonic acids discussed under the section Fractionation are representative of the products obtained by most investigators.

Summary

Lignosulfonic acids have been isolated, fractionated, and partially purified (1) by salting out with sodium chloride or calcium chloride, (2) by precipitation with mineral acids, lead acetate, and certain organic bases, and (3) by dialysis, electrodialysis, and ultrafiltration. Most investigators have found that their products were nonhomogeneous and did not contain stoichiometric amounts of sulfur. Those lignosulfonic acids which were considered homogeneous were usually isolated from very mild cooks in which only a portion of the lignin was dissolved and had been purified by dialysis in membranes whose pore size was not reported. It has been shown that lignosulfonic acids can be subjected to a separation based solely on molecular size by fractional electrodialysis or fractional ultrafiltration. Most investigations indicate that the ease of precipitation decreases as the molecular size of sulfonated lignin becomes smaller, and that simultaneously the sulfur content and reducing capacity increase. The change, if any, in the methoxyl content (calculated on the basis of the unsulfonated lignin) has not been definitely established. A direct comparison of the analysis of lignosulfonic acids fractionated by different investigators is unsatisfactory and unjustified, because, with one exception, the lignosulfonic acids were prepared or fractionated by different methods.

The nature of lignosulfonic acids from the same waste liquor which has been fractionated by chemical and physical means has not been reported in the literature, nor has the percentage of the lignosulfonic

acids in the various fractions obtained from a sulfite waste liquor been accurately determined.

The degree of sulfonation found by various investigators varied widely. Some workers have been unable to obtain a lignosulfonic acid with a sulfur content of over 6-7 per cent by repeated sulfonation, whereas others have reported products containing over 12 per cent sulfur. If pure lignosulfonic acids can be isolated which contain 10-12 per cent sulfur, the means of obtaining this degree of sulfonation are still not definitely known.

STATEMENT OF PROBLEM

The objective of this investigation was to devise a scheme of fractionation and purification of lignosulfonic acids based on chemical and physical methods which, when applied to two sulfite waste liquors prepared by widely different cooking conditions, would contribute fundamental information on the question of the extent of the degree of sulfonation of lignin. In addition it was considered necessary to obtain data which would permit a comparison of the distribution and sulfur contents of lignosulfonic acids from different waste liquors which had been fractionated by the same procedure.

EXPERIMENTAL

The experimental work carried out in this study consisted of four main phases: (1) the investigation of membranes for dialysis, (2) the preparation of two sulfite waste liquors by laboratory cooks, (3) the fractionation, purification, and isolation of lignosulfonic acids from each waste liquor and (4) the characterization of the products isolated.

Laboratory Methods

1. Analysis of Cooking Liquor

The strength of the sulfite cooking liquor used in the preparation of lignosulfonic acids was determined by the following procedure:

A 10 ml. sample of cooking liquor was diluted to 100 ml. in a volumetric flask. Ten ml. of the diluted solution were added to 25 ml. of standard iodine solution and the excess iodine back-titrated with standard thiosulfate solution. The equivalent weight of iodine reacting with the cooking liquor was expressed as percentage total sulfur dioxide.

Ten ml. of diluted liquor were titrated with standard sodium hydroxide to the phenolphthalein end point and the equivalents of base used calculated as percentage of free sulfur dioxide.

The percentage of combined sulfur dioxide was obtained by subtracting the percentage of free from the percentage of total sulfur dioxide.

2. Ash Determination

The ash contents of the sprucewood, the pulps, and the solid lignosulfonic acid fractions were determined by the Institute Method No. 4.

3. Lignin Determination

Institute Method No. 13 was followed for the determination of the lignin contents of the wood and the pulps.

4. Concentration of Lignosulfonic Acid Solutions

During the course of the investigation it was frequently necessary to concentrate solutions of lignosulfonic acids.

These solutions were always concentrated by vacuum distillation, a good aspirator being used to maintain the vacuum. Heat was supplied through a water bath, care being taken that the temperature of the solution being concentrated did not exceed 35° C. A slow stream of nitrogen was continually passed through the distillation system to sweep out oxygen and thereby minimize oxidation of the lignosulfonic acids.

5. Analysis of Solutions of Lignosulfonic Acid Salts

Solutions containing lignosulfonic acids were analyzed by the following procedure, which was designed so the total grams of methoxyl in the solution could be calculated:

An aliquot portion (usually 10 ml.) of the total solution was taken and its specific gravity determined by weighing the sample in a

tared weighing bottle. The sample was then dried in a 60° C. vacuum oven, the residue ground and again dried. The weight of the residue was determined and its moisture content obtained by drying a small portion to constant weight in an Abderhalden drying apparatus over phosphorus pentoxide at 100° C. The percentage of total solids was then calculated. The methoxyl content of the residue was determined using the oven-dry sample from the moisture determination. The ash content of the partly dried residue was obtained and expressed on the basis of the oven-dry material. The total grams of methoxyl in the original solution were then calculated.

6. Methoxyl Determination

The methoxyl contents of all fractions and solid products obtained were determined by Institute Method No. 18.

7. Precipitation of Lignosulfonic Acid Salts

The following procedure was used for the precipitation of lignosulfonic acids from their solution by organic agents unless otherwise stated:

Centrifuge cups with a capacity of about 250 ml. were filled with 200-225 ml. of the precipitating agent being used. Five to ten ml. of lignosulfonic acid solution were added dropwise to the centrifuge cup with vigorous stirring by a mechanically driven stirrer. The suspension was centrifuged 2-3 minutes at 2000 r.p.m. and the supernatant liquid decanted off. The precipitate was immediately suspended in ether

and removed from the centrifuge cup. This procedure was repeated until all material had been precipitated. The combined precipitates were then washed 2-3 times with ether and finally three times with petroleum ether. Each washing consisted of suspension of the precipitate, stirring, centrifuging, and removal of the wash liquor by decantation. The washed precipitate was then dried in a vacuum desiccator containing paraffin, concentrated sulfuric acid, and solid sodium hydroxide.

The reagents used in the precipitation of lignosulfonic acids and their salts were:

C.P. absolute methanol
C.P. glacial acetic acid
Dioxane -- refluxed over sodium
Ethyl ether -- refluxed over sodium
Commercial petroleum ether (boiling point 30-60° C.)

8. Sulfur Determination

The following procedure was used for the determination of sulfur:

A 100-150 mg. sample was heated with 2 ml. of fuming nitric acid for 6 to 8 hours at 250° C. in a sealed Carius combustion tube. After cooling, the contents of the tube were transferred to a beaker and evaporated to dryness after the addition of a pinch of pure sodium chloride. The nitric acid was removed by twice dissolving the residue in 10 per cent hydrochloric acid and evaporating to dryness. The dry residue was then taken up in about 25 ml. of 10 per cent hydrochloric acid and heated on a water bath. An excess of hot barium chloride

solution in dilute hydrochloric acid was added. The precipitate which formed was digested 2-3 hours and filtered on a tared Berlin crucible. The precipitate was washed, ignited, and weighed as barium sulfate.

Investigation of Dialysis Membranes

The possibility of preparing a series of membranes of graduated pore size for fractional dialysis was investigated. To carry out a fractional dialysis it is necessary to have a satisfactory method of determining the relative pore size of the membranes and to be able to prepare or obtain membranes of suitable porosity.

Method of Determining Relative Pore Size

The relative pore size of membranes was measured by determining which of a series of dyestuffs (in 0.025 per cent solution) of known diffusion constants would pass through and which were retained by each membrane studied. The dyestuffs which were available, their Schultz number, and the diffusion constants ($(\text{sq.cm./sec.}) \times 10^5$) by Freundlich (35) are tabulated in Table I.

TABLE I

DYESTUFFS FOR DETERMINATION OF PORE SIZE

Dyestuff	Schults No. (36) 7th Ed.	Diffusion Constant		Dialysis Rate
		Water	5% Gelatin	
Mosin-J	881	-----	0.023	Rapid
Alkali blue	813	-----	-----	-----
Patent blue	826	-----	-----	-----
Night blue	823	-----	-----	None
Gentian violet	785	0.398	-----	Medium
Chrysoidine	249	0.488	0.079	Rapid
Auramine	752	-----	0.132	Rapid
Methylene blue	---	-----	0.040	Rapid
Purpurine 4B	448	-----	-----	None
Congo red	360	0.126	small	Slow

Investigation of Commercial Viscose Membranes

Eight viscose membranes of varying dimensions--used commercially for sausage skins were obtained from the Visking Corporation. These were numbered from I to VIII according to increasing wall thickness and tested with the dyestuffs Congo red, Purpurine 4B, Gentian violet, and Auramine. The dyestuffs Congo red and Purpurine 4B were retained by all eight membranes, whereas the other three dyes diffused through all of the membranes. By this method the eight viscose membranes all had the same pore size.

The method described by McBain (37) for increasing the pore size of viscose membranes by treating with 60-65 per cent zinc chloride solutions for 15 to 20 minutes was applied to Membrane I. This procedure did not increase the pores of the membrane sufficiently to permit diffusion of Congo red, although the swelling time was increased stepwise to 45 minutes when the membrane began to disintegrate.

Investigation of Collodion Membranes

The preparation of collodion membranes of controlled pore size has been investigated by various workers interested in preparing films for ultrafiltration (38). The pore size of these membranes has been controlled by two methods--the first based on swelling of the membrane in alcohol and the second on the formation of membranes from solutions in which dissolving power of the nitrocellulose solvent is varied. In the latter method collodion is dissolved in a mixture of two organic solvents, one of which is a good solvent for nitrocellulose and the other a poor solvent. As the proportion of good solvent in the mixture

is increased, the pore size of the membrane formed from the solution decreased since a denser film is attained before the nitrocellulose sets to a gel structure.

Three collodion membranes with the desired variation in pore size were formed from four, three, and two per cent collodion solutions. The three and two per cent solutions were prepared by diluting commercial four per cent collodion to the desired concentration with a 7:1 mixture of ether and absolute methanol. It was found that the pore size of these membranes changed radically if the film was allowed to dry.

The collodion membranes were very fragile and difficult to support. Because large volumes of solution were to be dialyzed, the possibility of forming collodion membranes on wire cups and porous extraction thimbles was investigated as a means to simplify the problem of support, and to minimize the danger of tearing the membranes. Satisfactory membranes were formed on both fibrous extraction cups and small cups made of 75-mesh wire. However, it was difficult to form membranes which did not have small pin holes on cups with a capacity of 800-1000 ml.

The study of collodion membranes indicated that films of controlled pore size can be prepared but that these membranes are suitable only for dialysis of small volumes of solutions in an apparatus designed so that no part of the membrane is allowed to become dry. Collodion membranes therefore were considered unsuitable for the requirements of this work.

Experimental Cooks

Two laboratory sulfite cooks were carried out. The cooking conditions were established to give, in the first case, the minimum degree of sulfonation required to dissolve a representative fraction of the lignin in the wood (Cook I) and, in the second case, to be representative of commercial conditions for producing rayon pulps (Cook II). The waste liquor from the second cook was black, turbid, and had a 'burnt' odor. For this reason the waste liquor from Cook II was set aside and a third cook (Cook III) carried out in which the conditions were modified. Although the liquor from Cook III was also black, turbid, and smelled burned, it was used as the starting material for the isolation of lignosulfonic acids.

Preparation of Wood

Sound black sprucewood was used as the source of all products isolated in this investigation. Unscreened sawdust cut from a green log was extracted with 95 per cent ethanol and then with a 2:1 alcohol-benzene mixture, and stored in air-tight bottles until ready for use. As needed, the extracted sawdust was washed twice with 85 per cent ethanol, twice with water, and air dried. Care was taken that the moisture content of the final extracted sawdust did not fall below 10-15 per cent.

Preparation of Cooking Liquor

To prepare cooking liquor, sulfur dioxide was passed into softened water until the solution was saturated. Sufficient C.P. lime

to give approximately a one per cent solution was then added and additional sulfur dioxide passed in until the lime was completely dissolved. The strength of the cooking liquor was then determined according to the method on Page 21 and adjusted to the desired concentration of free and combined sulfur dioxide. A clear colorless cooking liquor was obtained by this procedure.

Cooking Conditions

The cooking conditions for the three cooks are shown in Table II.

TABLE II
COOKING CONDITIONS

	Cook I	Cook II	Cook III	Toler- ance
CaO, %	1.0	1.0	1.0	0.05
Combined SO ₂ , %	1.14	1.14	1.14	0.05
Total SO ₂ , %	4.5	5.5	5.5	0.05
Maximum temperature, ° C.	125	140	140	2.0
Time to maximum, hr.	3	4	4	0.25
Time at maximum, hr.	5	6	5.5	0.25
Liquor ratio (not in- cluding wood moisture)	8:1	8:1	8:1	----

Cooking Equipment

Cook I

Cook I was carried out in a stainless steel autoclave which had a capacity of about 5400 ml. and was equipped with a calibrated diaphragm-type pressure gage, a safety valve, and a 1/4-inch stainless steel relief line. The autoclave was heated by immersion in a wax bath.

Cooks II and III

Cooks II and III were carried out in a horizontal rotary, stainless steel digester which had a capacity of 24-25 liters. The digester, which rotated at $1/3$ r.p.m., was equipped with a $3/8$ -inch stainless steel relief line, a diaphragm-type pressure gage, and a safety valve which had been set for 200 pounds gage pressure. Heat was applied directly to the digester by six gas jets. To avoid local overheating and the resulting dangerously high gas pressure, the gas jets were never ignited unless the digester was rotating.

Cooking Procedure

Cook I

The autoclave was charged with the equivalent of 400 grams oven-dry sawdust and 3200 ml. of cooking liquor added. The digester was then immersed in the wax bath which had been heated to $130-135^{\circ}$ C. and the temperature of the bath was controlled to give the desired cooking schedule. No relief was employed during the cook. When the cooking schedule was completed, the autoclave was cooled in cold water to temperature of $80-90^{\circ}$ C. and opened.

To obtain the desired amount of lignin it was considered necessary to cook about 1500 grams of sawdust. For this reason, Cook I was repeated four times--the pulps and the waste liquors from the four cooks being combined and thoroughly mixed before further treatment.

Cooks II and III

The horizontal rotary digester was charged with 1600 grams (oven-dry) of sawdust and 12,800 ml. of cooking liquor added. The digester was then capped, rotation started, and the gas flames ignited and adjusted to give the correct temperature schedule. The digester was not relieved during cooking--the pressure being a dependent variable. When the specified time at maximum temperature had elapsed, the gas was turned off, rotation stopped, and the digester relieved to zero pressure while hot--the relief gases being passed through a trap to collect any cooking liquor which was mechanically carried along.

The procedure followed for Cook III differed from the above in that, upon completion of the cook, the gas was turned off and the digester was rotated overnight before opening.

Waste Liquor Recovery and Pulp Washing

The waste liquor and pulp from each cook were washed from the digester and filtered as soon as possible after the digester was opened on a large Büchner funnel equipped with a 200-mesh stainless steel wire screen. The pulp was washed by suspending it in softened water acidified with sulfur dioxide, allowing the mixture to stand overnight and then filtering. This process was repeated until the wash liquor was practically colorless. The waste liquor plus washings from each cook was bottled, labeled, and stored for later treatment. The thoroughly washed pulp was pressed in a small cider press, weighed, and its moisture content determined, from which the yield of pulp was calculated. The pulp was then stored in glass bottles.

Pulp Analysis

A representative sample of pulp from each cook was air dried and analyzed for ash and lignin content by the methods on Page 22.

Fractionation and Purification of Lignosulfenic Acid Salts

The general scheme for the fractionation and purification of the lignosulfenic acids and their salts in the waste liquors from Cooks I and III is outlined in Figure I. As a guide to the following description of the experimental work, a detailed diagram (Figure II) of the successive steps taken in the isolation of the final fractions of lignosulfenic acids is also included. By this scheme a large number of fractions were obtained from each waste sulfite liquor. To aid in distinguishing each fraction the following system of designation was set up:

All fractions from Cook I were designated -- "I". All fractions from Cook III were designated -- "III". The fraction of material precipitated by lime in each case was labeled "A" and that not precipitated by "B". When a fraction was obtained from A or B it was designated by an arabic numeral. This system may be clarified by an example. The Product III-A₁ was isolated from the waste liquor of Cook III by a fractionation of the material which was precipitated by lime. Inorganic precipitates which separated were designated successively by arabic numerals.

The various fractions were also assigned abbreviated names which were indicative of their source. For example the material from Cook III which was precipitated by excess lime and after regeneration

FIGURE I

THE ISOLATION AND
FRACTIONATION OF LIGNOSULFONIC ACIDS
FROM SULFITE WASTE LIQUORS

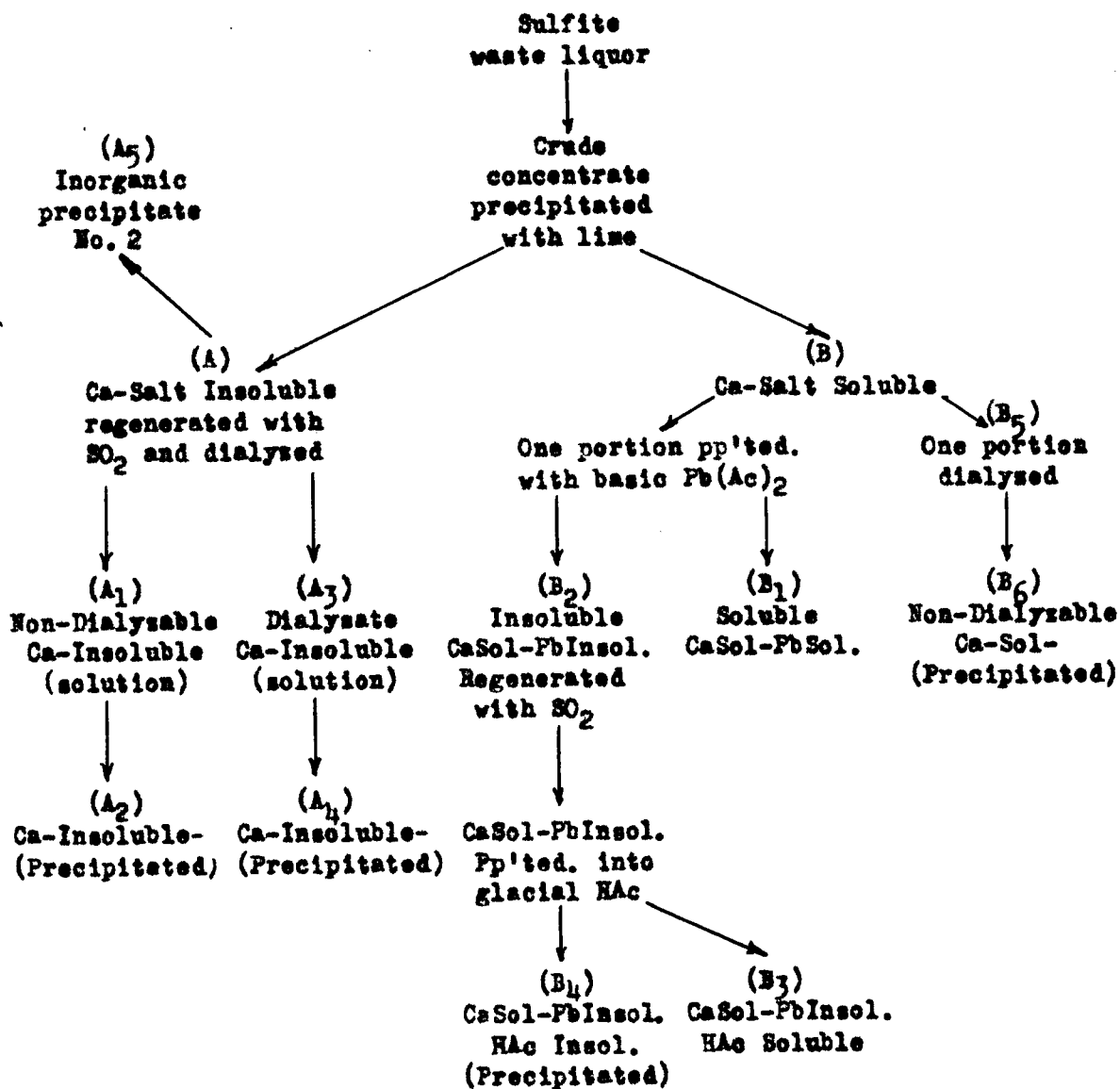
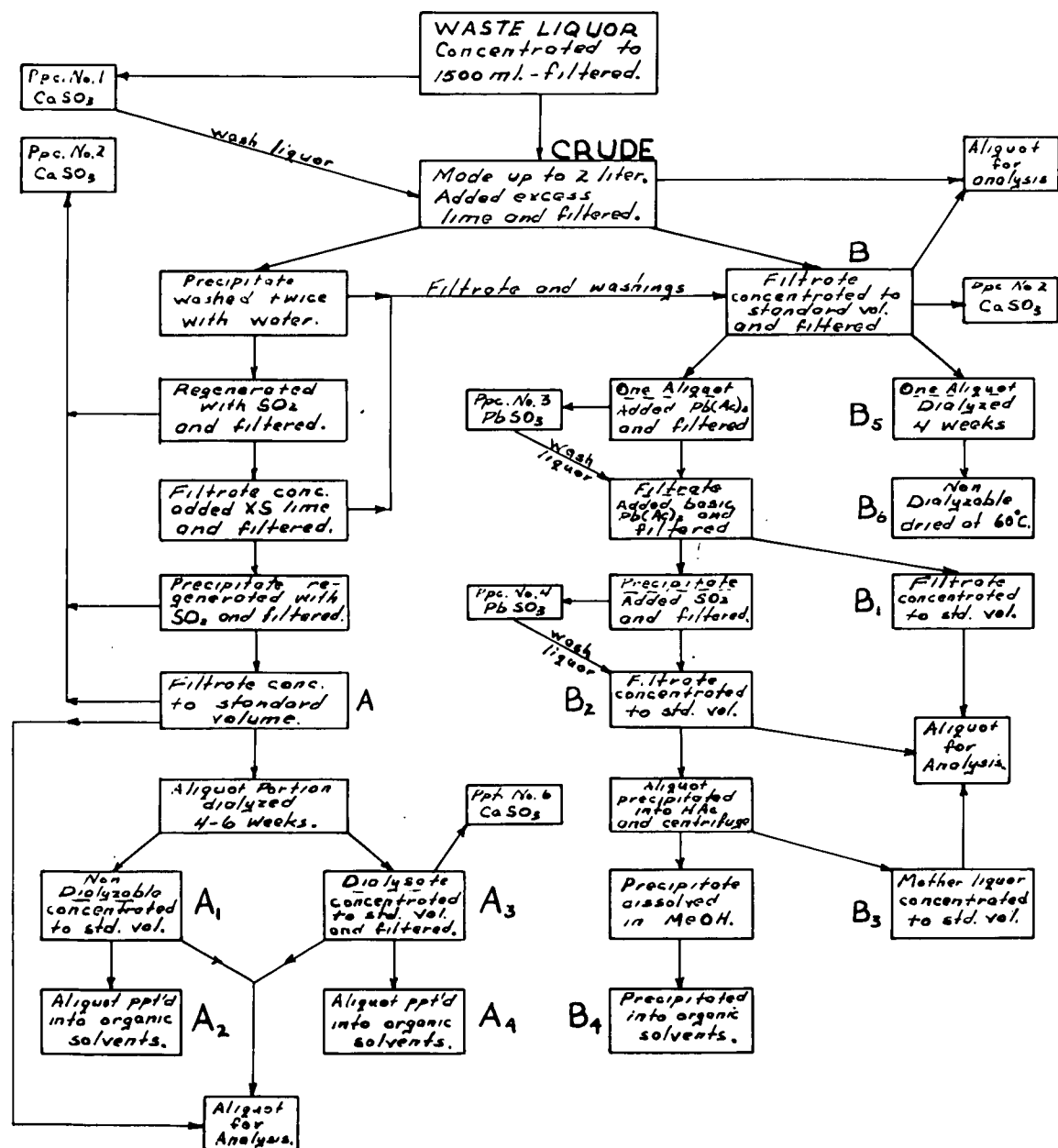


FIGURE II
DETAILED SCHEME OF FRACTIONATION
OF LIGNOSULFONIC ACIDS



was retained by a dialysis membrane was designated III-CaInsol (Non. Dial.), recognizing that the calcium salts of all products obtained were soluble but that some were precipitated by an excess of calcium ions at an elevated pH.

Since the method of fractionation was the same for both waste liquors until the final products were precipitated they are discussed together to that point. The precipitation of each final product is discussed separately.

Concentration of Waste Liquors

The waste liquor plus all wash liquors from each cook was concentrated to about 1500 ml. by vacuum distillation. A precipitate of fine fibers, calcium sulfite, and calcium sulfate which separated from time to time was filtered off, washed, and set aside as Precipitate 1.

After a solution was concentrated and filtered, it was made up to 2000 ml. in a volumetric flask and two 10 ml. samples were taken for analysis according to the procedure on Page 22. The remaining solution was designated "crude concentrate" and was ready for precipitation with lime. The crude concentrate from both liquors was thick, syrupy, and smelled slightly of sulfur dioxide. That concentrate from the mild cook (Cook I) was dark brown in color and that from the more drastic cook (Cook III) was almost black.

Precipitation with Lime

The crude concentrate from each waste sulfite liquor was treated with a slurry of lime with vigorous stirring. In both cases a heavy

precipitate formed and eventually the whole mass became very viscous. Lime was added until test showed that the precipitation was complete, at which time the viscosity had dropped somewhat. The precipitate was filtered and washed three times by suspending it in water, allowing the mixture to stand for 20-24 hours and filtering. The filtrate and washings were acidified with sulfur dioxide, labeled CaSol, and set aside for later treatment.

The washed precipitate in each case was suspended in water and sulfur dioxide was passed into the suspension. At a pH of about two the lignosulfonic acids were completely dissolved and a precipitate of calcium sulfite had formed which was filtered off, thoroughly washed, and set aside as Precipitate 2. The brown filtrate and washings were concentrated to about 1000-1500 ml. by vacuum distillation and the precipitation with lime, filtration, and washings repeated. The filtrate and washings were combined with the fraction CaSol. The washed precipitate was regenerated with sulfur dioxide as before. The calcium sulfite which formed was filtered and combined with Precipitate 2. The clear filtrate was concentrated and designated CaInsol.

The amount of precipitating agent and results of the lime precipitation are shown in Table III.

TABLE III
CONDITIONS AND RESULTS OF LIME PRECIPITATION

	Cook I	Cook III
Initial volume of solution, ml.	1980	1980
Lime, g.		
First precipitation	240	500
Second precipitation	200	250
Color of precipitate	Canary yellow	Dark brown
Color of solution CaSol-B	Honey-colored	Brown
Color of Solution CaInsol-A	Green brown	Black

The precipitate which formed when lime was added to the crude concentrate from Cook III was full of lumps which were very gummy and difficult to wash. This did not occur in the case of the crude concentrate of Cook I.

Lignosulfonic Acid Calcium Salts Precipitated by Lime (A-Series)

The fraction CaInsol was concentrated to about 800 ml. by vacuum distillation and the precipitate which formed was filtered off, washed, and combined with Precipitate 2. The Solution I-A obtained in this way was made up to 1000 ml. and III-A to 2000 ml. in volumetric flasks and two 10 ml. samples taken from each for determination of the total methoxyl content by the method on Page 23.

These solutions, 930 ml. of I-A and 1000 ml. of III-A were dialyzed using Visking Membrane I, Page 27. This membrane was chosen because it was the thinnest of those available and, therefore, would have the highest rate of dialysis. Distilled water saturated with sulfur dioxide was passed through the dialysis membranes at the rate

of about two liters in 24 hours and the resulting dialysate collected and concentrated by the usual method. The distilled water used for dialysis was saturated with sulfur dioxide to minimize oxidation by the air and to retain, if possible, the loosely bound sulfur dioxide associated with the sulfonated lignin. Since the solutions being dialyzed were diluted by osmotic effect, they had to be concentrated daily.

There was a possibility that the dialysis of the fraction III-A would not be complete in time to precipitate and analyze the product. For this reason about 25 ml. of this fraction were dialyzed in a Visking Membrane I which was tied at both ends to maintain a definite concentration of the solution being dialyzed and the distilled water used for dialysis was changed more frequently to increase the rate of dialysis. While the distribution of the lignosulfonic acids in the fraction III-A was determined from the large-scale dialysis experiment, the small-scale experiment was used for the isolation of products for a complete analysis.

After six weeks of dialysis of fraction I-A the dialysis was considered to be complete, because no colored material was passing through the membrane. Practically no colored material dialyzed from III-A (small experiment) after four weeks of continuous dialysis. Traces of colored material were diffusing from the solution III-A (large experiment) after four weeks but dialysis was discontinued at this time. After the dialyses were finished, the membranes were tested for leaks and change in pore size by immersion in a 0.025 per cent solution of Congo red. In all cases the membranes retained the dye molecules.

When the dialyses were completed, the dialysed materials were concentrated and designated CaInsol-A₁ (Non-Dial.) and the dialysate after concentration was called CaInsol-A₃ (Dialysate).

(a) Fractions CaInsol I-A₁ and III-A₁

The dialysed calcium-insoluble fraction from Cook I was made up to 250 ml. and that from Cook III to 1000 ml. and a 10 ml. sample taken from each for analysis. At this point these fractions were practically pure and ready for precipitation. I-A₁ was dark brown in color and III-A₁ was almost black.

Precipitation of CaInsol I-A₁

The solution I-A₁ (240 ml.) was concentrated to a thick syrup under reduced pressure, dissolved in absolute methanol, and the solution made up to 110 ml. with absolute methanol. This solution was miscible with ethanol, but immiscible with anhydrous dioxane, glacial acetic acid, and anhydrous ether. For the isolation of the lignosulfonic acid salts 50 ml. of the solution were precipitated into glacial acetic acid by the technique described on Page 23. After careful drying, the product had a methoxyl content of 13.6 per cent. It was dissolved in about 50 ml. of absolute methanol and reprecipitated into glacial acetic acid as before. After the second precipitation, the product had a methoxyl content of 14.8 per cent and was insoluble in methanol and water, so that it could not be dissolved for further purification. For this reason, 25 ml. of the original methanol solution was precipitated into anhydrous dioxane

using the same procedure. The product so obtained had a methoxyl content of 14.7 per cent. Because this was the same methoxyl content as that of the product precipitated twice into glacial acetic acid, the material designated I-A₂ was considered pure and ready for complete analysis.

Precipitation of Calnsol III-A₁

The dialyzed solution III-A₁ from the small scale experiment was concentrated to about 15 ml. and the miscibility with various organic agents determined. When tested, the solution was slightly miscible with methanol and ethanol but the sulfonated lignin was completely precipitated in anhydrous dioxane and glacial acetic acid. The solution was diluted to about 40 ml. with distilled water and precipitated into dioxane by the procedure given on Page 23. The methoxyl content of the oven-dried product was 11.9 per cent. The precipitate was redissolved in 30 ml. of distilled water and reprecipitated into dioxane. The dioxane mother liquor of the first precipitation was clear and colorless but that from the second purification contained a colloidal suspension which could not be centrifuged at 3000 r.p.m. The methoxyl content of the fraction after the second precipitation was 11.1 per cent. The brown powdery product was labeled III-A₂ and set aside for analysis.

(b) Fractions Calnsol I-A₃ and III-A₃

The fractions I-A₃ and III-A₃ each gave a precipitate upon concentration. This was filtered off, washed, and set aside as Precipitate 6. The solutions were then made up to 500 and 1000 ml., respectively, and a 10 ml. sample taken from each for determination of

the methoxyl content. The solution from Cook I was dark brown (almost black) in color and that from Cook III was intensely black.

Precipitation of CaInsol I-A₃

The aqueous solution of I-A₃ formed a precipitate when added to methanol, ethanol, anhydrous dioxane, and glacial acetic acid. For the isolation of the lignosulfonic acid salts contained in this solution, 125 ml. were added in a fine stream to 1000 ml. of absolute methanol in a large beaker with vigorous stirring. The white precipitate which formed was filtered on a Buchner funnel, washed once with methanol and three times with ether in a centrifuge cup, and dried over concentrated sulfuric acid in vacuo. The dry product was dissolved in 75 ml. of distilled water and precipitation, washing, and drying repeated as before. About one half of this product was dissolved in 35 ml. of water and precipitated into glacial acetic acid by the technique described on Page 23. The dry product was then precipitated again into glacial acetic acid and twice more into methanol. The product then had methoxyl content of 10.7 per cent. After two additional precipitations into methanol, followed by precipitation into dioxane and final washing with petroleum ether, the methoxyl content was 9.8 per cent. The fraction was then considered pure and was labeled I-A₄.

Lignosulfonic Acid Calcium Salts Not Precipitated by Lime (B-Series)

The two solutions (CaSol I-B and III-B), which included the filtrate and washings from the lime precipitations and which had been acidified with sulfur dioxide, were concentrated to about 800 ml. The

precipitate of calcium sulfite which formed was filtered off and added to Precipitate 2 in each case. The filtrates were made up to 1000 ml. in a volumetric flask (in the following pages this is referred to as a 'standard' solution), and two 10 ml. samples taken from each for analysis.

(a) Dialysis of CaSol Fractions

An aliquot of 10 ml. of the standard solution of I-B and a similar sample from III-B were used for dialysis in Visking I membranes. The two portions were dialyzed for four weeks in running tap water. At the end of this time the dialysis was considered complete and the dialyzed solutions were concentrated to about 10 ml. by vacuum distillation, and dried in a vacuum oven at 60° C. The dried residues were ground to a very fine powder, and their oven-dry weight determined, as well as their methoxyl contents. The product obtained from fraction I-B (designated I-B_G) had a methoxyl content of 10.4 per cent. That isolated from III-B (designated III-B_G) had a methoxyl content of 9.5 per cent.

(b) Precipitation of CaSol I-B and III-B with Lead

Each of the two solutions (CaSol I-B and III-B) was treated in the following way. Nine hundred and thirty ml. of the standard solution were placed in a vacuum to remove all dissolved sulfur dioxide, the precipitate which formed being filtered off and included with Precipitate 2. The clear filtrate was treated with 150 grams of neutral lead acetate in solution to precipitate all sulfite and sulfate ions. The precipitate formed was filtered on a Büchner funnel, washed and set aside as Precipitate 3. The filtrate, which was very black in both

cases, was treated with increasing amounts of a slurry of basic lead acetate until a test showed that the precipitation was complete. The precipitate was then filtered and washed by suspending it in distilled water and filtering. The wash liquors were combined with the honey-colored mother liquor and the whole designated CaSol-PbSol-B₁. The washed filter cake was suspended in distilled water and acidified with sulfur dioxide to a pH of 2-3, whereby the lignosulfonic acids were dissolved and a precipitate of lead sulfite was formed. The latter was removed, washed, and labeled Precipitate 4. The filtrate and washings which contained those lignosulfonic acids precipitated by lead and which had been regenerated by sulfur dioxide was called CaSol-PbInsol-B₂. Eight hundred grams of basic lead acetate were required for the complete precipitation of the lignosulfonic acid salts as a pale yellow lead salt from the solution CaSol I-B, and 1200 grams were required to isolate the lignosulfonic acid salts from CaSol III-B as a light brown precipitate.

(c) Fractions CaSol-PbSol-B₁

The methoxyl contents in the fractions CaSol-PbSol I-B₁ and III-B₁ were determined by analysis of a 10 ml. aliquot sample of each solution--the former having been made up to a standard volume of 1000 ml. and the latter to 2000 ml.

(d) Fractions CaSol-PbInsol-B₂

The dark brown solution I-B₂ and the black solution III-B₂ were concentrated to about 200 ml. under reduced pressure and each made up to 250 ml. in volumetric flasks. A 10 ml. sample was taken from each flask to be analyzed according to the method on Page 22.

(e) Isolation of CaSol-PbInsol I-B₂

One hundred and forty ml. of the standard solution I-B₂ were concentrated in vacuo to about 50 ml. This solution was completely miscible with absolute methanol but on addition to glacial acetic acid or dioxane a gummy precipitate was formed. The concentrated solution was therefore added dropwise to about 2000 ml. of glacial acetic acid in a large beaker. The highly colored acetic acid was decanted from the sludgy precipitate which had formed and was concentrated by vacuum distillation to about 50 ml. This solution was neither miscible with ether nor did it become solid, indicating that it contained a considerable amount of water. Attempts to remove the water by distillation with anhydrous dioxane were not successful. The solution was then reprecipitated into glacial acetic acid in centrifuge cups as described on page 23 with the exception that the precipitate was not finally washed with petroleum ether. The acetic acid mother liquor, after concentration under reduced pressure, was designated CaSol-PbInsol-HAcSol-B₃ and an aliquot portion was taken for analysis. The sludge from the first precipitation into glacial acetic acid and the precipitate obtained from the concentrated glacial acetic acid solution were dissolved in a small amount of absolute methanol and precipitated into anhydrous dioxane in centrifuge cups as before. The material was redissolved in methanol and the precipitation into dioxane repeated. The dry product obtained had a methoxyl content of 11.6 per cent. The material was redissolved in methanol and reprecipitated a second time into glacial acetic acid and two additional times into dioxane. The methoxyl content was then 12.6 per cent. After solution

in methanol and another precipitation into dioxane, followed by three washings with petroleum ether, the methoxyl content was 12.5 per cent. This product which had been precipitated three times into glacial acetic acid and five times into anhydrous dioxane was considered purified and was designated CaSol-PbInsol I-B₄.

(f) Isolation of CaSol-PbInsol III-B₂

A portion (50 ml.) of the standard solution of III-B₂ was evaporated nearly to dryness by vacuum distillation, care being taken that the temperature of the heating bath did not exceed 35° C. The thick syrup obtained was dissolved in absolute methanol and the miscibility of the solution with various organic solvents determined. A gummy precipitate formed in glacial acetic acid and anhydrous dioxane, whereas no precipitate was formed upon addition to absolute methanol.

The remainder of the methanol solution was then precipitated into glacial acetic acid in centrifuge cups, the final washing with petroleum ether being omitted. The precipitate was dissolved in methanol, and the precipitation into glacial acid repeated. The mother liquor from the two precipitations into glacial acetic acid was brown in color and after concentration was labeled CaSol-PbInsol-HAcSol III-B₃. The material isolated from the second precipitation into glacial acetic acid was dissolved in absolute methanol and precipitated into anhydrous dioxane by the usual procedure. The product had a methoxyl content of 12.7 per cent. After a second precipitation, the methoxyl content was 12.6 per cent. The lignosulfonic acids in this fraction were considered pure and were labeled CaSol-PbInsol III-B₄.

Characterization of Precipitated Products

Seven purified solid products were isolated by fractionation of the lignosulfonic acid salts in the waste sulfite liquors from Cook I and Cook III. These products were CaInsol I-A₂ and III-A₂, CaSol-PbInsol I-B₄ and III-B₄, CaSol I-B₆, and III-B₆, and CaInsol I-A₄. Each of these fractions was characterized by determination of its ash content, sulfur content, color, and solubility in various organic and inorganic solvents. The sulfur and ash determinations were carried out according to the procedures given on Pages 24 and 22 respectively.

The methoxyl content of Precipitates I-2 and III-2, were determined by the method given on Page 23.

PRESENTATION OF DATA

FIGURE I

THE ISOLATION AND
FRACTIONATION OF LIGNOSULFONIC ACIDS
FROM SULFITE WASTE LIQUORS

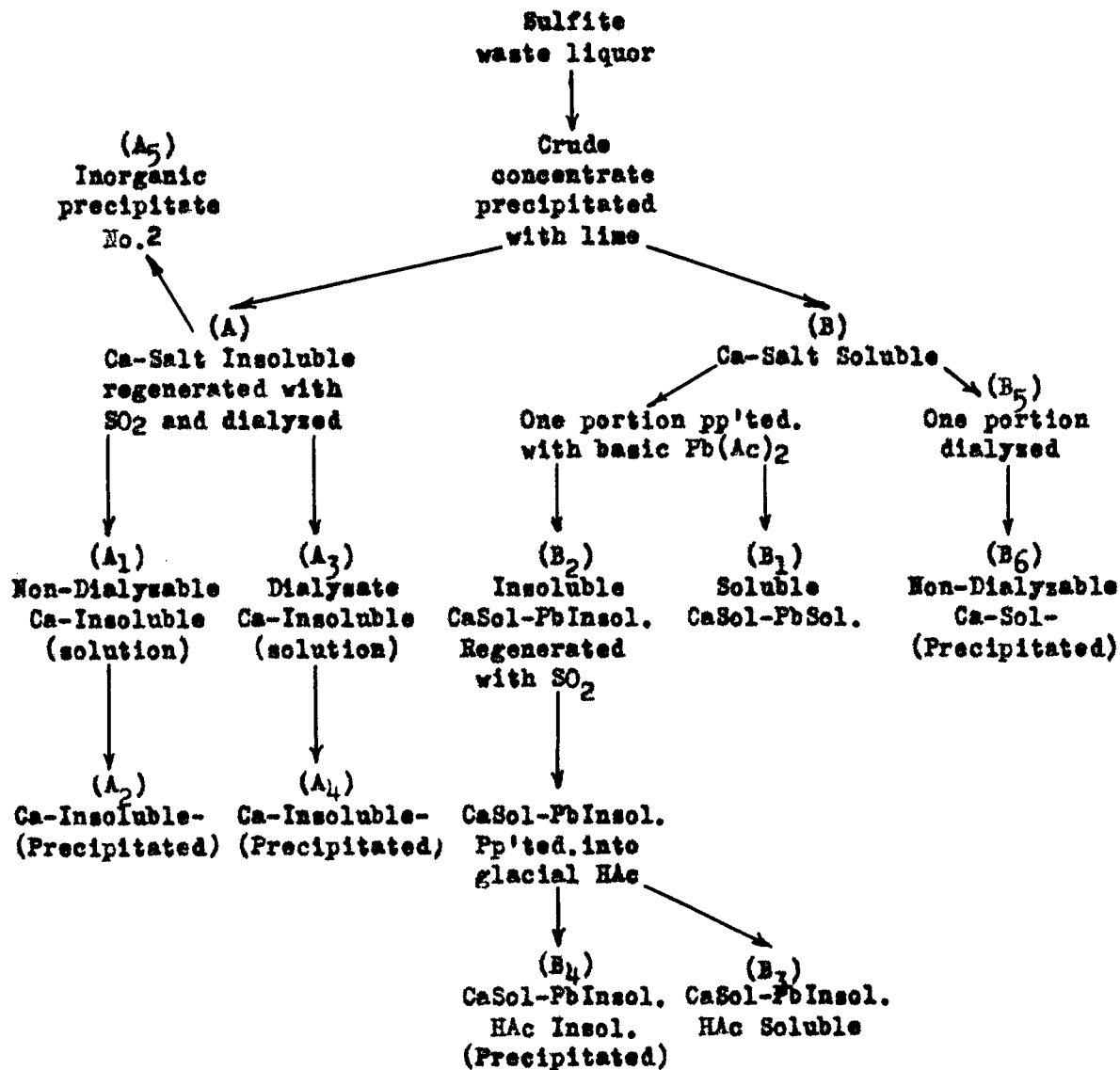


TABLE IV
EXPERIMENTAL DATA FROM SULFITE COOKS

	Cook I	Cook III
Wood		
Oven-dry, g.	1600	1600
Lignin, %	26.9	26.9
Lignin, g.	403	403
Pulp		
Form	like sawdust	mushy
Color	like wood	chalky
Yield, %	64.2	48.2
Lignin, %	13.7	0.6
Lignin, g.	141	5
Ash, %	1.7	12.5
Waste liquor		
Color	honey-colored	black
Appearance	clear	turbid
Lignin dissolved, g. (by difference)	262	398

TABLE V

ANALYSIS OF LIGNOSULFONIC ACID SOLUTIONS

In all cases except III-B₃, the sample used for analysis was 10 ml.; it was 25 ml. for III-B₃.

No.	Solution	Total Volume ml.	Density	Solids by Weight %	CH ₃ O %	Ash %	Total CH ₃ O g.	Volume Worked Up ml.
Cook I								
Crude:	Crude Concentrate	2000	1.146	31.9	5.9	18.3	43.15	1980
A	CaInsol	1000	1.136	29.5	7.1	15.7	23.77	930
A ₅	Inorganic ppt. No. 2	605 g.	---	---	0.5	---	3.03	---
A ₁	CaInsol (Non-Dial)	250	1.061	16.5	13.6	2.6	5.96	---
A ₃	CaInsol (Dialysate)	500	1.187	38.4	5.6	10.4	12.75	---
B	CaSol	1000	1.128	25.5	4.5	19.5	12.92	930
B ₁	CaSol-PbSol	1000	1.486	47.3	0.25	66.8	1.76	---
B ₂	CaSol-PbInsol	250	1.157	33.4	8.6	1.0	8.30	140
B ₃	CaSol-PbInsol-HAcSol	100	0.994	23.2	---	0.24	---	---
B ₅	CaSol (Dialyzed)	1000	1.128	1.75	10.4	17.5	0.021	---
Cook III								
Crude:	Crude Concentrate	2000	1.197	41.0	7.5	4.7	73.50	1980
A	CaInsol	2000	1.130	26.9	6.5	20.8	39.50	1000
A ₅	Inorganic ppt. No. 2	715 g.	---	---	0.35	---	2.50	---
A ₁	CaInsol (Non-Dialyzable)	1000	1.037	9.9	11.0	7.1	11.28	---
A ₃	CaInsol (Dialysate)	1000	1.085	17.1	4.7	21.8	8.72	---
B	CaSol	1000	1.186	34.6	6.5	28.5	26.70	930
B ₁	CaSol-PbSol	2000	1.331	36.3	1.4	66.8	13.52	---
B ₂	CaSol-PbInsol	250	1.229	42.6	8.0	1.0	10.47	50
B ₃	CaSol-PbInsol-HAcSol	100	0.903	9.8	---	0.22	---	---
B ₅	CaSol (Dialyzed)	1000	1.186	2.5	9.1	19.5	0.027	---

TABLE VI

THE LIGNOSULFONIC ACID IN EACH SOLUTION

No.	Product	Methoxyl, g.		Factor ^Δ		Monobasic L-S Acid ^θ		Per Cent of Total, g.	
		I	III	I	III	I	III	First Fraction I	Second Fraction III
Crude	Crude Concentrate	43.15	73.50	1.00	1.00	320	544	---	---
A	CaInsol	23.77	39.50	1.01	1.01	178	296	55.6	54.4
A ₅	Inorganic ppt. No. 2	3.03	2.50	1.00	1.00	22	18	6.9	3.3
A ₁	CaInsol (Non-Dial.)	5.96	11.28	1.086	2.00	48	168	---	---
A ₃	CaInsol (Dialysate)	12.75	8.72	1.086	2.00	102	131	---	---
								14.7	30.9
								31.8 ^π	24.1
B	CaSol	12.92	26.70	1.01	1.01	97	200	30.3	38.8
B ₁	CaSol; PbSol	1.76	13.52	1.086	1.086	14	109	---	---
B ₂	CaSol; PbInsol	8.30	10.47	1.086	1.086	67	85	---	---
B ₃	CaSol; PbInsol-HAc Sol	---	---	---	---	---	---	---	---
	Unaccounted for	---	---	---	---	---	---	7.2	3.5
								28.2	9.4
B ₅	CaSol (Dialyzed)	0.021	0.027	100.00	100.00	15	22	4.7	4.0
								---	---

* From Table V

Δ Factor - Correction applied when all of a fraction was not worked up.

θ Grams monobasic lignosulfonic acid - grams methoxyl x factor x (1/13.5) x 100.

π An undetermined amount of this fraction was misplaced.

TABLE VII

ANALYSIS OF ISOLATED PRODUCTS

(Calculated on Basis of Oven-Dry Material)

No.	Product	Experimental			Sulfur		Sulfur on		Calculated	
		Ash %	I	III	Methoxyl %	I	Ash Free I-S Acid, %	III	Methoxyl on SO ₃ and ash Free Lignin, %	I
A ₂	CaInsol (Non-Dial.)	1.65	6.2	14.7	11.1	4.86	5.36	4.88	5.49	16.8
A ₄	CaInsol (Dialysate)	14.2	---	9.8	---	8.4	---	8.77	---	13.1
E ₄	CaSol; PbInsol	2.7 ^g	2.3 ^g	12.8	12.5	5.93	9.11	6.04	9.26	15.4
B ₆	CaSol (Dialysed)	17.5	19.5	10.4	9.5	7.47	10.00	7.88	10.61	13.6
										13.1

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$$A \quad \frac{\% \text{CH}_3\text{O (as determined)} \times 100}{100 - \% \text{S}(\text{SO}_3/\text{S}) - \text{Ash} \times \text{Ignition Factor}}$$

* Ignition factor - (Ca/CaSO₄)

^g Total ash was accounted for as iron oxide
 Ignition factor - (2Fe/Fe₂O₃)

TABLE VIII

PHYSICAL PROPERTIES OF
ISOLATED LIGNOSULFONIC ACIDS

No.	Product	Form of Powder	Color	Anhy- drous MeOH	Anhy- drous EtOH	Anhy- drous Diox.	Glacial Acetic Acid	Ether	Water
I-A ₂	CaInsol (Non. Dial.)	Fine	Pale brown	S	I	I	I	I	S
I-A ₄	CaInsol (Dialysate)	Fine	Pale yellow	I	I	I	I	I	S
I-B ₄	CaSol-PbInsol	Fine	Gray	S	I	I	I	I	S
I-B ₆	CaSol (Dialyzed)	Coarse	Light brown	-	-	-	-	-	S
III-A ₂	CaInsol (Non. Dial.)	Fine	Brown	Slight	I	I	I	I	S
III-B ₄	CaSol-PbInsol	Fine	Dark brown	S	S	I	I	I	S
III-B ₆	CaSol (Dialyzed)	Coarse	Dark brown	-	-	-	-	-	S

DISCUSSION

Experimental Cooks

The conditions of the experimental cooks as stated previously were established to give in the first case, a very mild cook and, in the second, a relatively more drastic cook which approximated commercial cooking conditions for the production of dissolving pulps. The results of the experimental cooks tabulated in Table IV indicated such pulps were produced. Cook I resulted in a pulp yield of 64.2 per cent and removed over half of the lignin in the wood, so that a representative fraction of the total wood lignin was obtained in the waste liquor. Cook III produced an ash-free pulp yield of 42-43 per cent $[48.2 \times (100-12.5)/100]$ and practically all of the lignin in the wood was dissolved.

Method of Fractionation and Purification

The scheme of fractionation applied to the waste liquors of Cook I and Cook III (Figure I) consisted of two main steps. The first step was precipitation with calcium hydroxide, and resulted in a fraction whose calcium salt was insoluble (A Series) and one whose calcium salt was soluble (B Series). This precipitating agent was used for the following reasons: (1) the use of lime did not introduce any additional complicating ions into the solutions, (2) the work of Howard (27) indicated that lime precipitated those lignosulfonic acids containing a very weakly acidic group which is capable of salt formation only at a relatively high pH and (3) the insoluble calcium salts of lignosulfonic acid are more easily handled than those salts precipitated by most other agents.

The second phase of the fractionation was a further separation of each of the two fractions (A and B). The material precipitated by lime (A) after regeneration with sulfur dioxide was separated into two fractions (A_1 and A_3) by dialysis. This step was carried out because the nondialyzable fraction (A_1) corresponded to that part of the total sulfonated lignin which several investigators have obtained as a final product, whereas those lignosulfonic acids passing the dialysis membrane (A_3) represented material which has usually been discarded.

The fraction of lignosulfonic acid salts which was not precipitated by lime (B) was divided into two portions. The first portion was dialysed to give a fraction (B_5) which corresponded to the dialysed material (A_1) which had been precipitated by lime. The second portion was precipitated with basic lead acetate in an effort to isolate a solid material (B_4) which was representative of the total calcium-soluble fraction (B).

The criterion of purity of the solid products obtained was that the methoxyl content did not change upon solution and reprecipitation of the material. All products analysed satisfied this requirement with exception of I- B_6 and III- B_6 which, however, had been dialysed for four weeks in running water. This period of dialysis was about twice as long as that employed by most other investigators.

In this scheme of isolation the sulfonic acids were not subjected to high temperatures, excessive oxidation, or the action of strong acids and bases. For this reason it is believed that the products obtained were not changed in any way during their isolation.

Distribution of Lignosulfonic Acids

There is no accurate method for determining the amount of lignosulfonic acids in a solution containing organic or inorganic impurities. The method used in this work was actually an accurate determination of the grams of methoxyl and the amount of lignosulfonic acids was calculated from that value, assuming a methoxyl content of 13.5 per cent for the sulfonated lignin. This assumption is admittedly incorrect, because it has been shown that the lignosulfonic acids in sulfite waste liquor do not all occur as the monosulfonic acid having a methoxyl content of 13.5 per cent and because it is known that all of the methoxyl groups in wood are not associated with lignin. However, if the defects of this indirect method are recognised, it constitutes the best means available for determining the amount of lignin material in a solution and, therefore, for determining the distribution of lignosulfonic acids upon fractionation.

The percentage distribution of lignosulfonic acids from Cook I and Cook III upon fractionation has been calculated from the data in Table V and tabulated in Table VI. With one exception (second fractionation of Cook I) the total methoxyl content was accounted for after each fractionation within the limits of experimental error.

The most interesting result indicated in Table VI was that the same percentage of the total lignosulfonic acids was precipitated by lime from the waste liquors of both cooks--the percentages being 55.6 and 54.4, in spite of the widely different cooking conditions. The

distribution of molecular size in the two fractions precipitated (I-A and III-A) was entirely different, because only about 25 per cent of fraction I-A were retained upon dialysis, whereas about 55 per cent of the lignosulfonic acids in III-A were retained by the dialysis membrane. This indicated that the ease of precipitation of over one half of the lignosulfonic acids from the two waste liquors was not merely a question of molecular size as suggested by some investigators (2, 8). The presence of a characteristic group capable of reacting with calcium ions to form an insoluble salt appeared to be likely and agreed well with the work of Howard (27), in which a very weakly acidic group was found to react with calcium with formation of an insoluble basic calcium salt. The precipitation by excess lime of over one half of the total lignosulfonic acids from two different waste liquors is similar to the much criticized work of Klason (38), who has reported that two thirds of the total lignosulfonic acids in any waste sulfite liquor are precipitated by calcium chloride or beta-naphthylamine. However, although Klason considered the precipitated "alpha" lignosulfonic acid to be a chemically homogeneous compound, the results of this work indicate that the easily precipitated materials from two waste liquors differ in their distribution of molecular size and in their average sulfur contents (Table VII).

Of the material from both waste liquors not precipitated by lime (I-B and III-B), only 12-14 per cent (4.0 and 4.7 per cent of the total material) were retained by the membranes used for dialysis. This established that, in the two waste liquors investigated, there were fewer large molecules in the fraction not precipitated by lime than in that part which was precipitated.

Treatment of the fraction of Cook I which was not precipitated by lime (I-B) with basic lead acetate did not precipitate all of the methoxyl-containing material in the solution. It was impossible to state, however, that the unprecipitated material (I-B₁) containing 0.75 per cent methoxyl (on the ash-free basis) represented unprecipitated lignin derivatives because it is known that some of the carbohydrate material in sprucewood contains methoxyl groups. About 20 per cent of the total methoxyl content of the waste liquor from Cook III was not precipitated by basic lead acetate. This amount of methoxyl could not come entirely from the nonligneous material in the wood. Hence, it must be concluded that, although basic lead acetate may precipitate the total lignosulfonic acids from some waste liquors, it will not necessarily do so in all cases, undoubtedly because of a deep-seated degradation of part of the lignin.

In many studies on lignosulfonic acids the part easily precipitated has been isolated, purified, and analysed. The method of isolation and purification usually consisted of precipitation, regeneration, and dialysis through membranes of unstated pore size. It should be pointed out that, if such a procedure had been followed with the membranes that were used in this work, the final fractions would have represented, at most, about 20 per cent (14.7 + 4.7) in the case of Cook I and 35 per cent (30.9 + 4.0) in the case of Cook III of the total lignosulfonic acids present in the waste liquor.

Sulfur Content

The sulfur, methoxyl, and ash contents of the products which were isolated have been tabulated in Table VII together with the sulfur

contents calculated on the basis of the ash-free product and the methoxyl contents expressed as percentages of sulfur and ash-free lignin.

It can be seen from Table VII that the methoxyl contents calculated on the sulfur and ash-free basis varied from 13.1 to 16.8 per cent. It should be mentioned that the products I-A₂, I-B₄, and III-B₄ were precipitated into glacial acetic acid from their methanol solution. The higher methoxyl content (16.8, 15.4, and 16.5 per cent, respectively,) of these three fractions may be due to a partial methylation by methanol in the presence of glacial acetic acid. Precipitation into glacial acetic acid may also account for the low ash content of these products.

The sulfur contents of the products isolated from each waste liquor (calculated on the ash-free basis) increased in the order CaInsol-A₂, CaSol-PbInsol-B₄, CaSol-B₆ (Dialyzed), and in the case of Cook I, CaInsol-A₄. Highly sulfonated lignosulfonic acids were obtained from both cooks. The maximum sulfur content of a fraction isolated from waste liquor I was 8.77 per cent, and from waste liquor III, 10.61 per cent. The CaInsol-A₂ fraction of Cook I had the relatively low sulfur content of 4.88 per cent, which is of the order of magnitude of the minimum value other investigators have considered necessary for solution of sulfonated lignin.

Although the same method of fractionation was applied to the two crude waste sulfite liquors, the sulfur contents of those fractions isolated from Cook III were always higher than those of the corresponding fractions obtained from Cook I. This indicated that no one fraction of

lignosulfonic acids isolated by the scheme of fractionation which was used could be considered chemically homogeneous.

This investigation was conducted primarily to contribute to the knowledge of the extent of the degree of sulfonation of lignin, by determining whether the lignin building unit reacts with a second molecule of bisulfite to give a lignodisulfonic acid, or whether the lignin building unit is degraded into units of a molecular weight less than 840 with one sulfonic acid group on each smaller fragment. Before discussing the experimental data and its relation to this question, a brief review of the generally accepted concept of lignin structure is given to differentiate between the molecular weight of the lignin and the weight of the lignin building unit. According to this concept, the lignin molecule is made up of a number of lignin building units of a unit weight of about 840. The building unit in turn is made up of five building stones whose basic structure consists of a benzene ring with a three-carbon side chain. The building stone is frequently referred to as the C_6-O_3 unit. The size of a lignin molecule depends upon the number of building units in the molecule in much the same way that the length of cellulose chains depends upon the number of glucose anhydride units in the chain. In chemical reactions, the effective molecular weight of the lignin molecule is that of the lignin building unit--namely, 840. This picture may be shown in the following way.

- lignin building stone
- lignin building unit (M.W. 840)
- . linkage between building units
- ' one sulfonic acid group

Lignin molecule (----.----.----)_x

When lignin is sulfonated, the monosubstituted sulfonic acid containing 3.5 per cent sulfur would be represented by:

Lignomonosulfonic acid (----i.----i.----i)_x

On the basis of this concept, when lignin is sulfonated to a sulfur content above 3.5 per cent, the higher sulfur content may be explained by one or two assumptions. They are:

(1) By the formation of lignopolysulfonic acids which would appear as follows:

Lignodisulfonic acid (----i. -i-i-.----i)_x 6.4% sulfur

Lignotrisulfonic acid (----i. -i-i-i-.----i)_x 8.9% sulfur

(2) By the formation of sulfonic acids from fragments of the lignin building unit:

i	-i	---i	----i
(about 12.9% sulfur)	(about 7.7% sulfur)	(about 5.5% sulfur)	(about 4.25% sulfur)

When examined critically, the data presented in Table VII contributed much enlightenment regarding the question of which of these possibilities occur. The lignosulfonic acids in the fraction Calnsol (Dialysate) I-A₄ had an average sulfur content of 5.77 per cent, which corresponded approximately to that of a trisulfonic acid as shown in (1) or to a mixture of the monosulfonic acids shown under (2). The molecules of this fraction were small enough to pass through the membrane

used for dialysis. The products CaSol (Dialyzed) I-B₆ and III-B₆--- representing 4.0 and 4.7 per cent of the total lignosulfonic acids, respectively--were retained by the membranes used for dialysis in spite of the sulfur contents of 7.88 and 10.61 per cent. If the high sulfur contents of these products were the result of a degradation of the lignin building unit (2), the molecules would of necessity have been as small or smaller than those molecules in fraction I-A₄ and, therefore, small enough to pass the membranes upon dialysis. Because these fractions did not pass the membranes upon dialysis, it must be concluded that the high sulfur contents were due to the presence of lignodisulfonic and possibly trisulfonic acids on the basis of the lignin building unit of 840.

Two assumptions were made in arriving at the conclusion that lignopolysulfonic acids are present in sulfite waste liquor. The first was that each molecule and/or lignin building unit contained at least one sulfonic acid group--an assumption considered valid since, in the sulfite process, lignin is rendered water soluble only by sulfonation and all fractions of the isolated lignosulfonic acid were water soluble (Table VIII). The second assumption was that the colloidal properties which governed behavior upon dialysis were the same for all products.

The fact that lignopolysulfonic acids exist in sulfite waste liquor is quite significant. At the present time there is only one theory which explains the sulfonation of the lignin building unit by one sulfonic acid group. In this theory which was proposed by Brauns (41), the carbonyl group of the lignin building unit is the reactive group in the sulfonation reaction. This theory, however, does not explain the formation of highly

sulfonated lignosulfonic acids, because there is only one carbonyl group present in the lignin building unit.

Most other theories for the mechanism of the sulfonation reaction involve an increase or decrease in the number of hydroxyl groups capable of methylation in the lignosulfonic acid compared with that in the original lignin building unit. These theories have been invalidated by the work of Freudenberg (1), Hagglund (8), and of King, Hibbert, and Brauns (42), who have shown that the number of hydroxyl groups capable of methylation in the lignin building unit remains constant upon sulfonation. It should be especially pointed out that these methylation studies were made on lignosulfonic acids having a low sulfur content, which were easily precipitated, and had been dialyzed in membranes of unstated pore size. The change, if any, in the number of hydroxyl groups which can be methylated in lignosulfonic acids having higher degrees of sulfonation has not been determined. Speculation as to the manner by which a second and third sulfonic acid group reacts with the lignin building unit is not justified, unless the experiments of Freudenberg (43) on the sulfonation of Erdtman's acid are applicable to the sulfonation of lignin. When Erdtman's acid is sulfonated, the reaction takes place by the opening of a heterogeneous oxygen ring with the simultaneous formation of a new phenolic hydroxyl group.

The existence of lignosulfonic acids with relatively low molecular weight but high sulfur contents was shown by comparison of the low sulfur content of fraction CaInsol (Non Dial.) I-A₂, which would not pass the dialysis membrane, with the much higher sulfur content of the fraction CaInsol (Dialysate) I-A₄ which was made up of molecules small

enough to pass through the pores of the membranes used for dialysis. It is impossible, on the basis of these data, to state definitely that these low-molecular weight, high-sulfur content acids were monosulfonic acids of molecular weight less than 921.

CONCLUSIONS

1. Lime precipitated about 55 per cent of the lignosulfonic acid salts from two widely different sulfite waste liquors. The results indicated that the precipitation was not merely the result of the molecular size of the lignosulfonic acid salts but rather of the presence of some characteristic group capable of reacting with calcium ions at a high pH to form an insoluble salt.

2. Basic lead acetate, a reagent used extensively in the isolation of lignosulfonic acids and their salts, will not precipitate the total sulfonated lignin from all sulfite waste liquors.

3. Lignosulfonic acids or their salts isolated by dialysis through membranes of the pore size used in this work may correspond to a small and unrepresentative fraction of the total lignosulfonic acids in a sulfite waste liquor. Therefore, in any investigation, conclusions based solely upon the characterization of lignosulfonic acids isolated in this way are not necessarily applicable to the total material present in sulfite waste liquor.

4. When the same scheme of fractionation was applied to two different sulfite waste liquors, all the fractions obtained from the liquor of the more drastic cook had a higher sulfur content than the comparable fractions from the milder cook. It was concluded that the scheme of fractionation used could not be considered as a means of isolating chemically homogeneous lignosulfonic acids.

5. The fact was established by indirect proof that ligno-polysulfonic acids exist in sulfite waste liquor. A complete theory for the mechanism of the sulfonation reaction must, therefore, account for the formation of polysubstituted lignosulfonic acids.

6. The existence in sulfite waste liquor of lignosulfonic acids of relatively low molecular weight and high sulfur content was established -- but it was not shown that they were lignomonosulfonic acids.

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