

## Some Viscosity Properties of Lignosulfonates Isolated by Ultrafiltration

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Sulfite pulping of wood chips produces a pulping liquor rich in sulfonated aryl alkyl ether polymers called lignosulfonates. Ultrafiltration of these liquors produces concentrates of these lignosulfonates some of which are present as a salt of the cation used to buffer the cook. Ultrafiltration concentrates of calcium lignosulfonates were found to undergo significant viscosity increases when made alkaline. Gels can be formed from 42% solids from spruce and birch calcium lignosulfonates in a few minutes by making the solution 15% on solids in sodium hydroxide. A molecular weight distribution analysis of spruce calcium lignosulfonates and decationized samples by gel chromatography showed a drop in molecular weight suggesting that the calcium ion holds together portions of the lignosulfonates. Additions of calcium back to an ion exchanged sample showed no gel formation, only the formation of a precipitate.

Spent sulfite liquor (SSL), the by-product of sulfite pulping of trees, has been known for some time to produce gels by treating with chromates (Hyashi and Goring, 1965). The gel has been used to stabilize soil, mine ceilings and walls, and other loose particulate matter. It is a strong gel but leaves chromium in the soil. The gel to be discussed below is much weaker and more water soluble with little binding strength but good green strength. It is made from ultrafiltration (UF) concentrates of calcium base SSL by adding about 15% (on solids) sodium hydroxide as a 50% concentration.

Hydrodynamic volume changes in lignosulfonate (LSs) molecules were first reported by Gardon and Mason (1955). At low concentrations decreases in ionic strength resulted in swelling for the molecules. Gupta and McCarthy (1968) used gel chromatography to show a doubling of hydrodynamic volume while decreasing from 0.1 N NaCl to distilled water. In the work described below the change in hydrodynamic volume occurred as the sodium phenolate ion was formed in the presence of calcium ion. The way calcium was added was shown to be significant in the formation of a complex microgel insensitive to ionic strength.

The molecular weight of lignosulfonates has been reviewed by others including Sarkanen and Ludwig (1971). Difficulties have been reported for most methods including light scattering, ultracentrifugation, viscosity, and diffusion. Values for softwood lignosulfonates has been reported from nominal figures of 5000 to over 100000. The results of several gel chromatography techniques (Lindberg et al., 1965; McNaughton et al., 1967) have not shown differently. Using gel chromatography, the work below suggests that when freshly UF prepared LSs are depleted of divalent cations the molecular weights are much lower than previously reported.

### EXPERIMENTAL SECTION

SSL samples were obtained from Wisconsin mills pulping 100% birch and 100% Canadian spruce. The mill concentrated liquors were diluted to 10% solids and concentrated on commercially available ultrafiltration membranes. The birch LSs (BLS) were concentrated to 45% solids on a Westinghouse module and the spruce (SLS) to 42% solids on a Rev-O-Pak module. Operating pressure on the Rev-O-Pak module with a polysulfone membrane was 300 psi with a 15 gpm feed rate. The overall flux rate for permeate production was 6.6 gal (sq

Table I. Change in Viscosity of Birch CaLSs with Alkali Addition at Different Solids Concentration

Sol-ids, %	Start <sup>a</sup>	Viscosity, CP				
		5 min <sup>b</sup>	15 min	30 min	1 h	24 h
46	280	c	c	c	c	c
40	88	2580	6040	9920	29600	c
35	54	96	121	146	184	190

<sup>a</sup> 5 mL of 50% NaOH added to 50 mL of sample.

<sup>b</sup> Temperature reaches maximum 40 °C when started at room temperature. <sup>c</sup> Viscosity > 100 000 CP.

Table II. Change in Viscosity of Spruce CaLS with Alkali Addition at Different Solids Concentration

Sol-ids, %	Start <sup>a</sup>	Viscosity, CP				
		5 min <sup>b</sup>	15 min	30 min	1 h	24 h
41	80	4820	27900	44600	c	c
40	94	4040	29300	31700	92200	c
35	50	204	382	490	690	5480

<sup>a</sup> 5 mL of 50% NaOH added to 50 mL of sample.

<sup>b</sup> Temperature reaches maximum 40 °C when started at room temperature. <sup>c</sup> Viscosity > 100 000 CP.

ft)<sup>-1</sup> day<sup>-1</sup>. The BLS was concentrated at 300 psi with a feed flow rate of 5 gpm and showed an overall flux of 6.2 gal (sq ft)<sup>-1</sup> day<sup>-1</sup> on a polysulfone membrane on Westinghouse equipment.

The LSs are present in 10% spruce SSL at 50–60 g/L and the reducing sugars 20–25 g/L. The reducing sugars undergo a negative rejection during ultracentrifugation resulting in approximately 90% of the original concentration in the final concentrate. Birch SSL contains 10–20% fewer LSs and 5–10% more reducing sugars.

Viscosity measurements were made on a Brookfield LVF meter. Ultraviolet absorbance, reducing sugars, solids, methoxyl, and calcium were determined by standard laboratory procedures developed for SSL by the Pulp Manufacturers Research League. Ion exchange was carried out with IR-120 Rohm and Haas cation-exchange resin charged with 1 N HCl.

Gel chromatography was done on Sephadex LH-20 alkylated epichlorohydrin cross-linked dextran. Decationized distilled water was used to irrigate the 5 or 10 mL of 10% solids samples.

The diepoxide was Epon 812, a product of Shell Chemical Company, and epichlorohydrin was an Eastman Kodak Company product.

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Table III. Change in Viscosity of CaLS as a Function of Caustic Addition

Caustic, g	H <sub>2</sub> O, <sup>a</sup> g	Start	1 h	24 h
4.58	42.0	48	88	76
3.82	41.3	54	184	190
3.06	40.5	49	248	424
2.67	40.1	26	554	1880
2.29	39.7	26	969	2500
1.91	39.4	27	790	1980

<sup>a</sup> Each sample contained 20.2 g of birch CaLS solids.

Table IV. Change in Viscosity of Birch CaLS as a Function of Temperature

Temp, °C	Start <sup>a</sup>	15 min	1 h
40-44	52	14000	55200
53-57	48	12800	6420
60-63	22	9240	6000

<sup>a</sup> 40% Solids BLS, 5.73 g of NaOH, 75-mL sample.

Table V. Effect of Cross-Linking Agents on Gelling of Lignosulfonates

	Viscosity, CP (26-40%)					
	Time <sup>a</sup>					
84% Conversion	6 min	15 min	30 min	1 h	24 h	
A - (50 ± 2% solids)	100000	c	c	c	Gel	
B - H <sub>2</sub> O (46 ± 2% solids)	38000	94000	100000	c	Gel	
C - Epon 812 <sup>b</sup>	c	c	c	c	Hard gel	
D - Epichlorohydrin	70000	100000	c	c	Gel	
E - Propylene oxide	23800	42400	52400	73300		

<sup>a</sup> Time after addition of 5 mL of 50% caustic (to 40 mL of concentrate, 48-52% solids). <sup>b</sup> 5% by volume. <sup>c</sup> Viscosity > 100 000 CP.

## RESULTS

Table I shows the viscosity change for birch lignosulfonates (BLS) after alkali addition at different solids concentrations. The ultrafiltration was carried out to 42% solids and the liquor adjusted by evaporation or dilution to obtain the different solids concentrations. A gel mass was formed quickly which goes above 100 000 cp within 5 min when a 42% solids sample was used. Table II shows a similar viscosity change for spruce LSs (SLS). The ultraviolet extinction coefficient for the LSs was 9 L g<sup>-1</sup> cm<sup>-1</sup> compared with 4.5 L g<sup>-1</sup> cm<sup>-1</sup> for the original liquor.

The amount of caustic applied affected the rate of gel formation. Table III shows the effect of different amounts of alkali on the rate of viscosity development. Apparently about 2.3 g of caustic per 20.2 g of BLS was optimum. Raising the temperature was found to have a significant effect on slowing the rate of gel formation. Table IV shows the magnitude of the rate loss as the temperature was raised from 40 °C to the low 60s.

The gelation could be enhanced by the addition of diepoxides and epichlorohydrin. Tables V and VI show the enhanced gel formation by Epon 812, a diepoxide, and epichlorohydrin. Propylene oxide, being monofunctional, had no effect, actually interfering with the viscosity development. Table VI shows the slower rate of gel formation for a sample which was not concentrated as much by ultrafiltration.

The importance of calcium is shown in Table VII. A cation exchange sample in the acid form showed a loss of viscosity with the addition of caustic. The BLS sample

Table VI. Effect of Cross-Linking Agents on Gelling of Lignosulfonates

	Viscosity, CP (26-40+C)			
	Time <sup>a</sup>			
78% Conversion	6 min	15 min	30 min	1 h
A - (50 ± 2% solids)	18800	35400	*	
B - H <sub>2</sub> O (46 ± 2% solids)	6400	10000	14400	15000
C - Epon 812 <sup>b</sup>	8600		18500	*
D - Epichlorohydrin	10000	22400	70800	*
E - Propylene oxide	2000	4680	7480	12500

<sup>a</sup> Time after addition of 5 mL of 50% caustic (to 40 mL of concentrate, 48-52% solids). <sup>b</sup> 5% by volume.

Table VII. Change in Viscosity of Decationized BLS

Sample	Solids, %	Ca, %	Caustic added to 50 mL, g	Viscosity, CP			
				Start	5 min	30 min	1 h
CaLS	45.9	3.4	3.8	280	a	a	a
LS	46	0.13	2.3	2540	180	628	770

<sup>a</sup> Over 100 000 CP.

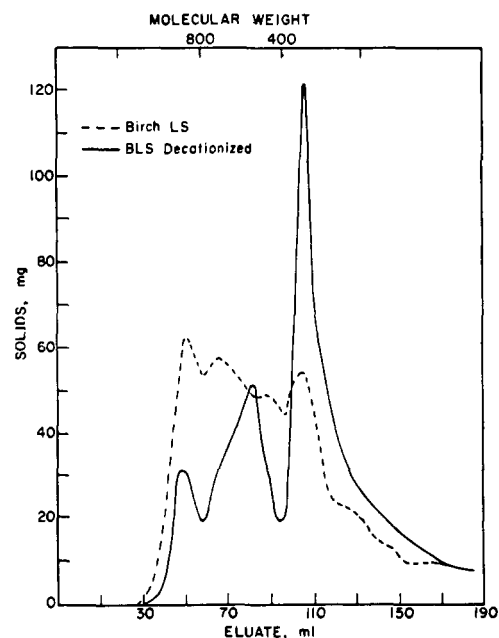


Figure 1. Gel chromatography of birch LS before and after decationizing Sephadex LH-20 gel column dimensions 2.5 cm × 100 cm, 25 mL/1 h solvent flow rate, sample size 10 mL of 10% solids BLS.

contained 3.4% calcium (on solids) and the SLS 3.2%. The exchange with IR-120 in the acid form gave values of 0.13% (on solids) for the BLS and 0.04% (on solids) for the SLS. The remaining calcium was very difficult to remove. Adding back the calcium did not result in a mixture that would form a gel. When calcium was mixed with the decationized LS and alkali added, a precipitate formed. Apparently the calcium in the lignosulfonates obtained during pulping occupies different sites than those when the calcium is removed and added back to the lignosulfonates as calcium chloride. A chelating agent, ethylenediamine tetraacetic acid, was found to interfere with the viscosity development, further emphasizing the importance of calcium in hydrodynamic volume changes.

The removal of calcium affected the molecular weight of the LS as determined by gel chromatography and ultracentrifugation. Figures 1 and 2 show the effect of

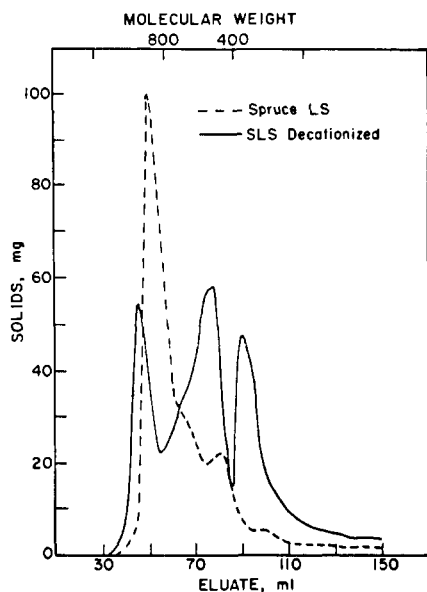


Figure 2. Gel chromatography of spruce LS before and after decationizing. Conditions similar to those described in Figure 1.

Table VIII. Recovery of LS Fractions from Gel Chromatography Before and After Decationizing by Ion Exchange

Sample	Fraction from Sephadex gel column			
	High mol wt 800 and up solids, % <sup>a</sup>	Middle mol wt 400 to 800 solids, %	Low mol wt 400 and less solids, %	Loss on column, %
Spruce CaLS	43.6	31.0	4.5	3.4
Spruce LSA	23.1	49.0	24.5	11.0
Birch CaLS	9.0	25.4	39.7	17.3
Birch LSA	20.0	35.4	27.4	16.0

<sup>a</sup> Solids in fraction as percent of solids applied to column.

calcium on the distribution of molecular weights as shown by Sephadex LH 20. The elution of solids changes dramatically as summarized in Table VIII. While 43.6% SLS elutes in the fraction corresponding to 800 daltons and above, following decationization the amount decreases by almost one-half. The birch CaLSs showed 90% of the molecules to be less than 800 daltons. Ion exchange caused an increase in molecular weight distribution perhaps because of the ineffectiveness of the ion-exchange resin in removing all of the cations. Ion exchanged samples of spruce and birch LSs showed approximately the same molecular weight distribution, suggesting that the higher molecular weights reported for softwood LS might be because of some of these microgel effects caused by divalent cations.

The molecular weights were derived from data obtained for the elution of *p*-phenyl phenol oligomers. Figure 3 shows the elution pattern for these oligomers and their molecular weights using dimethyl sulfoxide as the solvent.

To ascribe such low molecular weights to most of the LSs does not seem reasonable. It may be that there is absorption taking place although it would be expected that the fractions would elute after the internal volume of the gel if there were adsorption. Furthermore, experiments at much lower sample concentrations showed similar

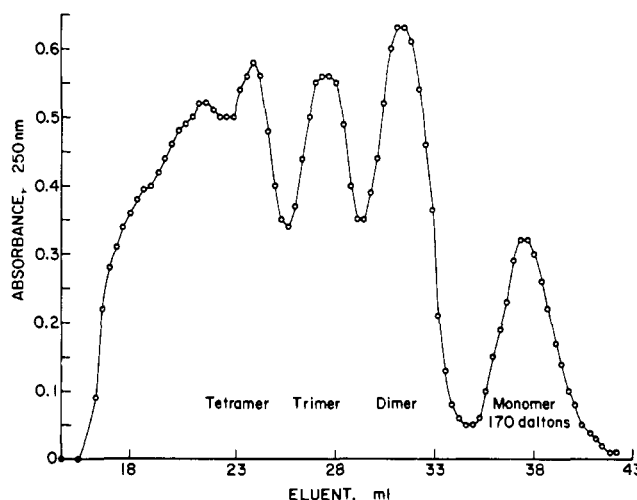


Figure 3. Elution of *p*-phenyl phenol oligomers from Sephadex gel LH-20 using dimethyl sulfoxide as solvent. Column dimensions were 1 × 60 cm, solvent flow rate 0.15 mL/min.

changes in molecular weight distribution.

Data from the ultracentrifuge showed that calcium removal reduced the sedimentation coefficient. A sample of the middle peak in Figure 2 for the SLS decationized material showed a sedimentation coefficient less than one-tenth (0.21) that of the high molecular weight peak (2.3).

## DISCUSSION

Lignosulfonates have a gel-like structure in that they have three-dimensional binding and with oxidation and chromate ions form a gel of SSL. Apparently under alkaline conditions the calcium ion will hold together a matrix of LS micelles to form this gel. Unlike pectin the gel cannot be formed by the addition of calcium ion; the calcium has to be in matrix as obtained during pulping. The calcium ions which cannot be removed by ion exchange are of interest since they could be holding more of the LSs together. Other cations are tightly bound also. Iron is said to be difficult to remove from LS and is responsible for residual color of the molecule (Meshitenka and Nakano, 1973). The iron would also help hold LS micelles together.

Utilization of this phenomenon could take on many forms. Lime addition has long been known as a means of rendering the LSs of whole liquor less soluble. Here it appears that a caustic addition to CaLS makes a mixture which has better green strength which could mean, for example, a more suitable application in foundry core binding. Wind erosion of soil can be controlled by SSL. A less water-soluble gel would possibly be more effective.

## CONCLUSIONS

1. Gel formation (hydrodynamic volume expansion) is a property of concentrated CaLSs when the pH is increased to 10–11.
2. Such gels might be easier to use in some binding situations since they show better "green" strength than other SSL preparations.
3. The calcium ion was shown to play an important role in holding together LS micelles resulting in a new explanation for conventionally accepted molecular weight values.

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Other papers presented at the 172nd National Meeting of the American Chemical Society in the Symposium on General Wood Chemistry but not printed in this issue are: "Characteristics of Tree Rings as Predictors of Climate", by Harold C. Fritts; "Reactions of Hardwood and Softwood Alkali Lignins with Oxygen", by S. Y. Lin and S. I. Falkehag; "Oxidative Degradation of Wood. Characterization of an Air-Oxidized Lignin", by M. M. Merriman and D. L. Brink; "Biodegradation of Synthetic Lignins", by E. Schultz, W. J. Connors, T. K. Kirk, and J. G. Zeikus; "Condensed Tannins from the Barks of Red Alder and Douglas Fir", by Murray L. Laver, Joseph J. Karchesy, and Patricia M. Loveland; "Chemical Analysis of Seedcoat Terpenoids as a Method for Seed Certification", Eugene Zavarin, Karel Snajberk, and Peter Senter.

## Fate of Diamidafos (Phenyl *N,N*-Dimethylphosphordiamidate) in Tobacco, Cured Tobacco, and in Smoke

Richard W. Meikle

Tobacco was treated with diamidafos-<sup>14</sup>C in transplant water at the rate of 0.33 lb/acre. The following radioactive substances—diamidafos, phenyl  $\beta$ -D-glucopyranoside, an unidentified glycoside of phenol, and nonextractable material, the latter three expressed as phenol—were found in mature fresh leaves at concentrations of 2.61, 0.72, 0.15, and 0.07 ppm, respectively. In cured leaves, the concentrations were 1.29, 0.67, 0.08, and 0 ppm, respectively, when adjusted to an equivalent fresh leaf-weight basis. Smoking effectively destroyed diamidafos and the phenol glycosides in the cigarette tobacco. The major breakdown product in the mainstream smoke was phenol which was already present in much larger quantities as a result of thermal degradation of tobacco.

Of the three groups of nematodes which cause problems in tobacco, root-knot (*Meloidogyne* spp.), lesion (*Pratylenchus* spp.), and stunt (*Tylenchorynchus claytoni*), the root-knot group is believed to be by far the most important in flue-cured tobacco and is responsible for about 80% of all losses caused by these organisms (Todd and Nusbaum, 1968). The use of chemical soil treatment plays a vital role in control of nematode disease of tobacco. Diamidafos (proposed common name), phenyl *N,N*-dimethylphosphordiamidate has been shown to give excellent root-knot nematode control when applied in water solution (Youngson, 1959). The efficacy of this compound when used to control root-knot nematodes in a variety of crops has been reported (Youngson and Goring, 1963; Turner, 1963; Coleby et al., 1965; Thomason and Baines, 1969) and in tobacco (Todd and Nusbaum, 1968, 1970, 1971). The metabolism of this compound has been studied in cucumbers (*Cucumis sativus*) (Meikle, 1968) and in soil (Meikle and Christie, 1969).

This investigation was designed to determine the fate of diamidafos, applied in transplant water, in green and cured tobacco leaves, and in the smoke resulting from smoking cigarettes made from this cured tobacco. Such information is a prerequisite to the establishment of recommendations for safe and effective use of pesticides and for development of meaningful analytical methods for determination of residues.

### MATERIALS AND METHODS

**Chemicals.** The preparation of phenyl-<sup>14</sup>C *N,N*-dimethylphosphordiamidate (diamidafos-<sup>14</sup>C) has been described by Meikle (1968). The specific activity of the compound used in this work was 0.060 mCi/mmol and the radiochemical purity was 100% as determined by thin-layer chromatography. Phenyl- $\beta$ -D-glucopyranoside and phenyl- $\beta$ -D-galactoside were purchased from Mann Research Laboratories, New York, N.Y.

**Planting and Treatment Logistics.** Three containers constructed of <sup>3</sup>/<sub>4</sub> in. plywood and having dimensions of 31 × 31 × 99 cm were filled to a depth of 91 cm with a top soil from Contra Costa County, Calif. This soil had the following properties; pH 5.9, 0.65% organic carbon, 75%

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