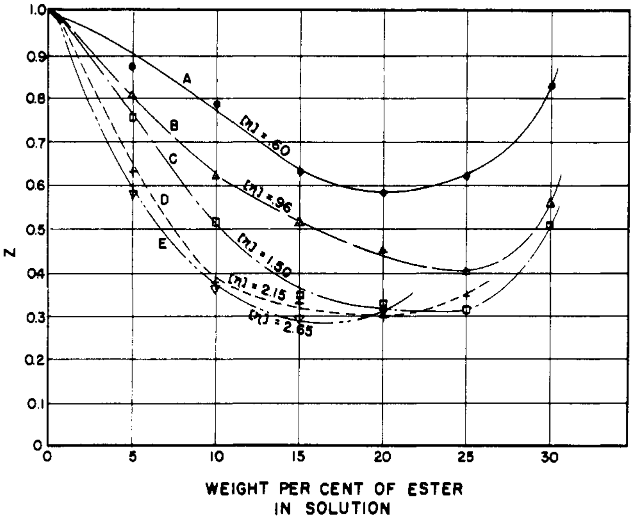

Figure 7. Relationship of Z with concentration for samples of cellulose acetate of different intrinsic viscosities

Using solvent of acetone containing 2.5% of water

There are factors which affect concentrated solution viscosities without affecting intrinsic viscosities. They would, of course, also affect *Z*. Some of these factors are methods of acetylation, salts in the product, or differences in raw materials. The relationship of *Z* to concentration is useful in comparing the viscosity behavior of different cellulose acetates in concentrated solutions. It may also point to the manufacturing variables which affect the viscosity properties of the product.

CONCLUSIONS

The $^{1}/_{6}$ power of the concentrated solution viscosities of secondary cellulose acetate in acetone was found to be approximately a linear function of intrinsic viscosity and concentration. A coefficient was introduced into the Baker-Philippoff equation to give an equation which would approximate the experimental data. This coefficient varies with both intrinsic viscosity and concentration.

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Viscosities of Solutions of Pine Wood Lignin from Kraft Black Liquor

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The lignin studied was a commercial pine wood lignin (Indulin A, Polychemicals Division, West Virginia Pulp and Paper Co.), recovered by acidification of kraft black liquor from the pulping of pine woods of the Southeast. A typical analysis as offered by the manufacturer is: moisture 4.3%, ash 0.4%, methoxyl 13.9%, and sulfur 1.4%. Four fractions of the lignin prepared by fractionation with acetone and with methanol, and a chemically modified form were also studied. The commercial lignin was fractionated according to the procedure outlined in Figure 1.

An oxidized lignin was prepared by passing oxygen gas through an aqueous alkaline solution of the commercial lignin. A solution containing 20% of the commercial lignin was prepared in which 4 moles of alkali were used to each 840 grams of the lignin. The solution was heated to 70° C. and oxygen gas was passed in for 11.5 hours at a rate of 0.04 cu. foot per minute per 1000 grams of lignin. When oxygen addition had been completed, the mixture was heated to 90° C. and 12*N* sulfuric acid was added with good stirring until a pH of 2.0 was obtained. The acidified mixture was allowed to cool to 70° C. and then filtered. The oxidized lignin cake was washed with water until the wash water had a pH of 4.5. The lignin was then dried to constant weight at 105° C.

PREPARATION OF PYRIDINE SOLUTIONS FOR VISCOSITY TESTS

After being dried to constant weight, the lignin and lignin fractions were stored in ground-glass weighing bottles, which were kept in desiccators containing both concentrated sulfuric acid and sodium hydroxide pellets as desiccants. The pyridine used to make the test solutions was Baker's analyzed reagent grade (J. T. Baker Chemical Co., Phillipsburg, N. J.).

TESTS OF VISCOSITY OF LIGNIN-PYRIDINE SOLUTIONS

The viscometers used in the tests were the Cannon-Fenske-Ostwald Type 50 (Cannon Instrument Co., State College, Pa.), standardized by the instrument company under the direction of M. R. Cannon. They held a charge of approximately 7.0 ml. and had a driving head of approximately 9.0 cm., and the working diameter of the lower reservoir was 3.0 cm. Their suggested range of operation was 0.8 to 3 centistokes. The viscosities of the pyridine solutions were determined at 20.00° ± 0.01° C. by the testing procedure recommended by the Cannon Instrument Co.

The kinematic viscosity in centistokes for the pyridine solvent and the lignin solutions was obtained by multiplying the efflux time in seconds by the calibrated viscometer

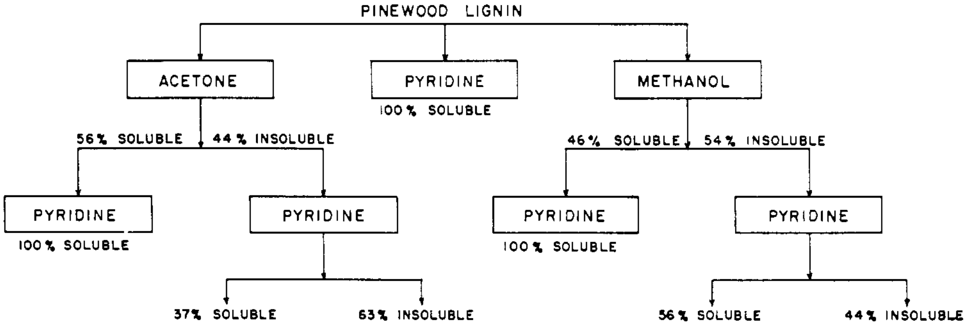

Figure 1. Solvent fractions of pine wood lignin

Table I. Viscosity of Pine Wood Lignin Solutions

Lignin Material in Solution	Lignin Concn., G./100 G. Soln.	Specific Gravity of Soln.	Flow Time of Liquid in Viscometer, Sec.	Viscosity				$\frac{\ln Nr}{C^a}$
				Centistokes	Centipoises	Relative	Specific	
None	None	0.9836	505	0.975	0.969	...	...	...
Pine wood lignin	0.31	0.9852	524	1.011	0.996	1.038	0.038	0.127
	0.45	0.9853	528	1.019	1.004	1.046	0.046	0.108
	0.81	0.9867	547	1.056	1.042	1.083	0.083	0.095
	1.07	0.9875	558	1.077	1.064	1.105	0.105	0.098
	1.43	0.9888	580	1.119	1.106	1.149	0.149	0.098
	1.96	0.9899	612	1.181	1.171	1.212	0.212	0.097
	2.58	0.9915	653	1.260	1.249	1.293	0.293	0.099
Methanol-soluble fraction	0.36	0.9854	523	1.009	0.994	1.036	0.036	0.109
	0.57	0.9857	525	1.013	0.999	1.040	0.040	0.069
	0.98	0.9868	539	1.040	1.027	1.067	0.067	0.069
	1.36	0.9878	545	1.052	1.039	1.079	0.079	0.057
	1.77	0.9888	560	1.081	1.069	1.109	0.109	0.059
	2.35	0.9902	578	1.116	1.105	1.145	0.145	0.060
Methanol-insoluble pyridine soluble	0.22	0.9848	519	1.002	0.987	1.028	0.028	0.134
	0.37	0.9850	526	1.015	1.000	1.042	0.042	0.106
	0.59	0.9862	530	1.023	1.009	1.050	0.050	0.083
	0.75	0.9861	540	1.042	1.028	1.069	0.069	0.090
	1.03	0.9867	552	1.065	1.051	1.093	0.093	0.084
Acetone-soluble fraction	0.34	0.9819	518	1.000	0.985	1.026	0.026	0.087
	0.55	0.9855	524	1.011	0.996	1.038	0.038	0.071
	0.97	0.9867	538	1.038	1.024	1.065	0.065	0.070
	1.18	0.9876	550	1.062	1.049	1.089	0.089	0.073
	1.60	0.9883	563	1.087	1.074	1.115	0.115	0.071
	2.22	0.9896	584	1.127	1.115	1.156	0.156	0.070
Acetone-insoluble pyridine-soluble	0.12	0.9846	518	1.000	0.985	1.026	0.026	0.247
	0.22	0.9859	524	1.011	0.997	1.038	0.038	0.178
	0.71	...	544	1.050	...	1.077	0.077	0.109
	1.06	0.9874	558	1.077	1.063	1.105	0.105	0.099
	1.40	0.9881	574	1.108	1.095	1.137	0.137	0.094
Oxidized	0.54	0.9867	554	1.069	1.055	1.086	0.086	0.160
	0.88	0.9874	577	1.114	1.100	1.131	0.131	0.139
	1.04	0.9888	617	1.191	1.178	1.210	0.210	0.183
	1.53	0.9903	679	1.310	1.279	1.330	0.330	0.187

[a] Concentration, g./100 g. solution.

constant. The viscosity in centipoises was obtained by multiplying the centistoke values by the density of the solutions. The densities of the solvent and solutions at 20.00° ± 0.01°C. were determined with a 25-ml. pyrometer. Throughout this work the concentration of solution is stated as grams per 100 grams of solution, which is very close to that of grams per 100 ml. of solution commonly used in viscosity studies, because the density of the pyridine is so near unity.

COMPARISON OF VISCOSITIES OF PINE WOOD LIGNIN SOLUTION

The laboratory-determined concentration, specific gravity, and viscometer flow time of the lignin solutions tested, with five calculated viscosity relationships, are given in Table I. The relative viscosity, N_r and the specific viscosity are relations of the viscosity of the solution to that of the solvent (Equations 1 and 2).

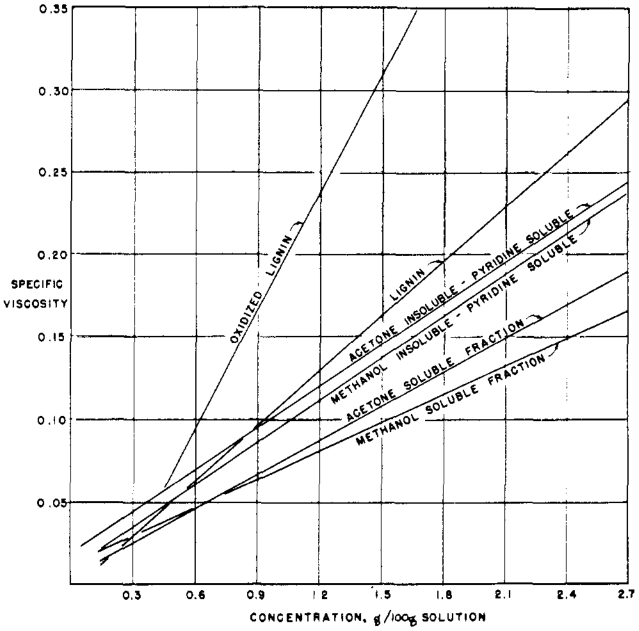

Figure 2. Specific viscosity vs. concentration of pyridine pine wood lignin solutions

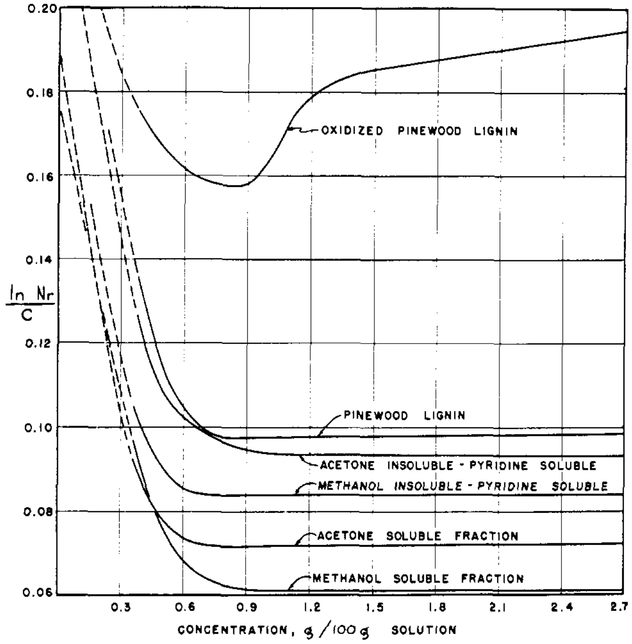

Figure 3. Logarithm of relative viscosity vs. concentration of pyridine pine wood lignin solutions

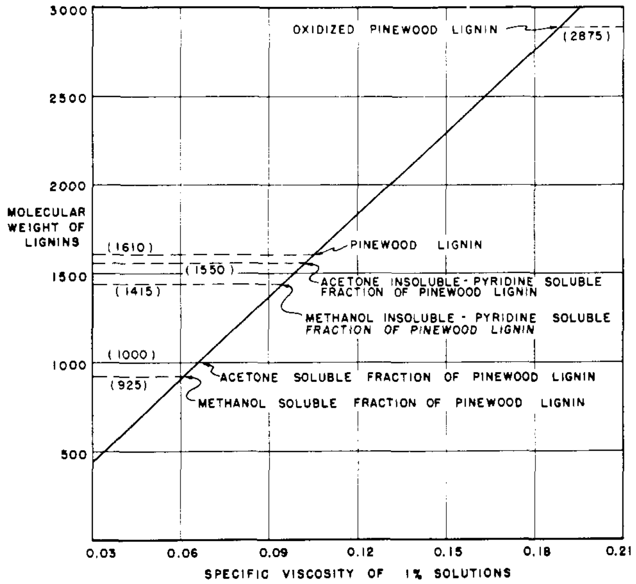

Figure 4. Empirical relations of molecular weight of lignins to specific viscosity of 1% solutions

Prepared from data of Staudinger and Dreher (*5*), assuming all values were straight-line functions

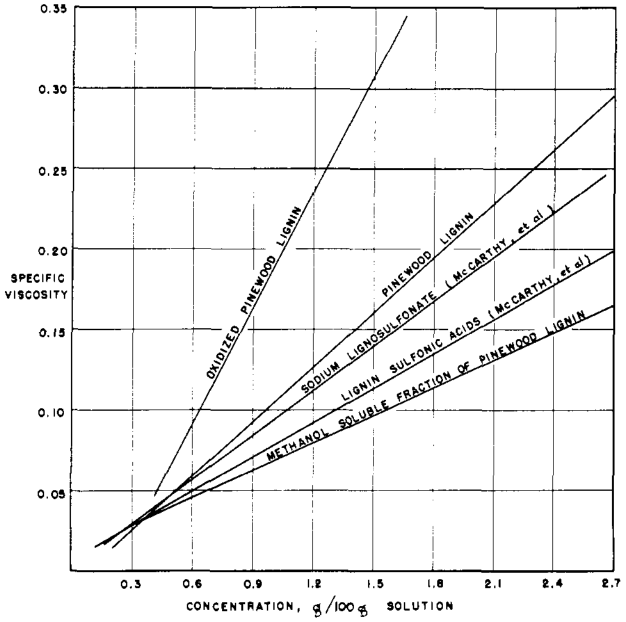

Figure 5. Specific viscosity vs. concentration of pyridine-lignin and water-lignosulfonate solutions

$$\text{Relative viscosity } (N_r) = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}} \qquad (1)$$

$$\text{Specific viscosity } (N_{sp}) = N_r - 1 \qquad (2)$$

For comparative purposes the specific viscosities of the solutions of lignins are plotted against concentrations in Figure 2, and in Figure 3 the logarithms of the relative viscosities divided by the concentration are plotted against concentration.

The differences in the viscosities of the lignin materials shown in Table I and Figures 2 and 3 suggest differences in chemical structure. These may be due entirely to differences in molecular weights. In general, the materials of lower molecular weight are more soluble in organic solvents than homologous materials of greater weight. This could explain the lower viscosities of the solutions of the solvent-separated lignins and the greater viscosities of the solutions of the oxidized lignin. One theory of the oxidation of such lignins from kraft liquors proposes that oxidation occurs between the mercaptan groups of each of two molecules of lignin and thus molecules of greater size are formed. The lower viscosities of the solutions of the pyridine-soluble portions of the acetone- and methanol-insoluble fractions of the lignin would be expected. If solutions were prepared of the pyridine-insoluble materials of these fractions, their viscosities would probably be greater than that of the unchanged pine wood lignin in the same solvent.

INDICATED MOLECULAR WEIGHT OF LIGNIN MATERIALS

In a study of lignins isolated from wood by phenol and resorcinol it was noted that the specific viscosities of the chloroform solutions of these lignins at concentrations of 1% or below were directly proportional to the concentrations and that viscosity-concentration curves were linear (*6*). The specific viscosities of these solutions at the lower concentrations were 0.030 to 0.065. More detailed studies of similar lignins in acetone, acetic acid, and dioxane solutions (*5*) confirmed the earlier work. The specific viscosities of 1% solutions of phenol lignin, acetylphenol lignin, *o*-cresol lignin, acetyl-*o*-cresol lignin, beechwood lignin, and a sodium lignosulfonate in acetone and acetic acid were from 0.030 to 0.065. These values corresponded very closely to that of cellopentaose acetate, whose molecular weight was 1542. A lignin obtained by digestion of spruce wood in concentrated formic acid gave a molecular weight of 1000 by freezing point depression of dioxane. The specific viscosity of a 1% solution of the same lignin in dioxane or formic acid was 0.065 to 0.070. By using the molecular weight of the formic acid spruce lignin as 1000 and its specific viscosity of 0.065, and assuming the weight-viscosity relationship to be a straight-line function, Figure 4 was prepared. From Figure 2 specific viscosities at 1% concentration were obtained and are indicated on Figure 4. The molecular weights as indicated in Figure 4 vary from 900 to 2900.

In a study of native black spruce lignin, the viscosities of some dilute solutions of the lignin in dioxane were determined (*2*). Various fractions of the lignin having molecular weights estimated at 2800 to 5800 were studied. The reduced viscosities (specific viscosity per unit concentration) of 1 and 2% solutions varied from 0.05 to 0.10. Calculations of the reduced viscosities of the pine wood lignin-pyridine solutions from the curves of Figure 2 give values of 0.06 to 0.23. Assuming the specific viscosity-concentration relationships for the native black spruce lignin-dioxane solutions and the pine wood lignin-pyridine solutions are comparable, it appears that the two lignins are of about the same molecular weight.

The viscosities of some dilute solutions of purified (by exhaustive dialysis) sodium lignosulfonates and lignin sulfonic acids from a sulfite waste liquor have been determined (*1*). The specific viscosity-concentration relationship of these aqueous solutions was shown to be a lineal function. A plot of this viscosity-concentration relationship is shown in Figure 5, with similar plots of like values of solutions of three pine wood lignins. The two types of lignins appear to have molecular weights of the same magnitude. Estimated molecular weights of 3000 to 20,000 have been obtained for lignosulfonates from spent sulfite liquors by calculations from light-scattering measurements (*3*) and determinations of diffusion coefficients (*4*).

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Weathering of Poly(vinyl Chloride)

Effect of Composition

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Plasticized poly(vinyl chloride) (PVC) is being used in an increasing number of outdoor applications, particularly in the outside telephone plant, where it appears as extruded wire coatings, injection molded parts, and dispersion coatings on textiles. Serviceable outdoor compositions are possible through the judicious choice of stabilizers and pigments (*8*). The series of colored poly(vinyl chloride) coatings used on the two new types of outdoor telephone wire known as B Urban and B Rural Wire are practical applications of these principles (*20*). On the basis of a 4-year study in Florida, a minimum outdoor life of 10 years has been predicted by Griesser and Higgins (*15*) for properly pigmented materials.

Poly(vinyl chloride) plastics are not inherently weather-resistant and derive their properties in this respect mainly through formulation. The purpose of the present studies has been to assess the effects of weathering on various resins, plasticizers, and light absorbers. Through work of this kind, it is hoped to accumulate technical data useful in formulating outdoor compositions designed for specific applications.

The formulations reported here are not intended for any specific applications, however, and should be viewed only as vehicles in which the variables are being investigated. As the samples weathered, their attrition was followed primarily by the measurement of physical properties. Natural weathering was used exclusively, with diverse climates, to obtain the maximum possible effect.

MATERIALS

The mixing procedures were essentially those followed in the previous investigation (*8*). Compositions were mixed on hot rolls and press-molded to test sheets 0.030 inch thick, except where noted. Three series of experimental compositions were studied in which the resin, plasticizer, and organic ultraviolet absorber were varied.