

# Phenolic and Tannin-Based Adhesive Resins by Reactions of Coordinated Metal Ligands. II. Tannin Adhesive Preparation, Characteristics, and Application

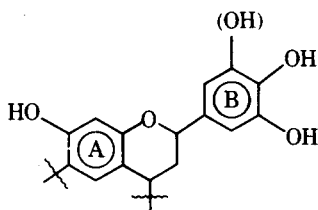
A. PIZZI, *Composite Products Division, National Timber Research Institute, Council for Scientific and Industrial Research, Pretoria, Republic of South Africa*

## Synopsis

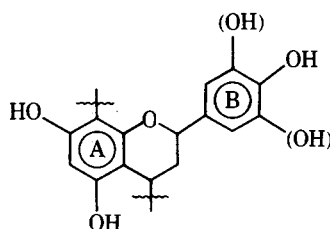
The accelerating effect due to bivalent metal ions observed in simple phenol-formaldehyde reactions are also observed in tannin-formaldehyde resins. Tannin steric hindrance prevents the retarding effect of trivalent metallic ions on tannin-formaldehyde reactions. Small amounts of metal ions do not significantly increase flavonoid B-ring participation to the crosslinking of tannin-formaldehyde networks. Improved plywood strength and shorter pressing times are obtained by the addition of metal ions to tannin/formaldehyde resins. These results are due to faster curing promoted by the presence of the metal ions.

## INTRODUCTION

The accelerating or retarding effect of metallic ions on phenol/formaldehyde reactions<sup>1,2</sup> could be applied to condensed tannins of the flavonoid type with some degree of success. Such tannins, including mimosa (wattle), quebracho, pine, hemlock, and mangrove tannins, are phenolic in nature and as such should undergo similar catalytic reactions with formaldehyde to those of simple phenols. The commercially available tannin extract of the bark of the black wattle tree (*Acacia mearnsii*, formerly *mollissima*) and the laboratory extract of *Pinus patula* bark were used for this study. The structure of the main polymeric constituents of wattle and pine tannins may be represented as follows:



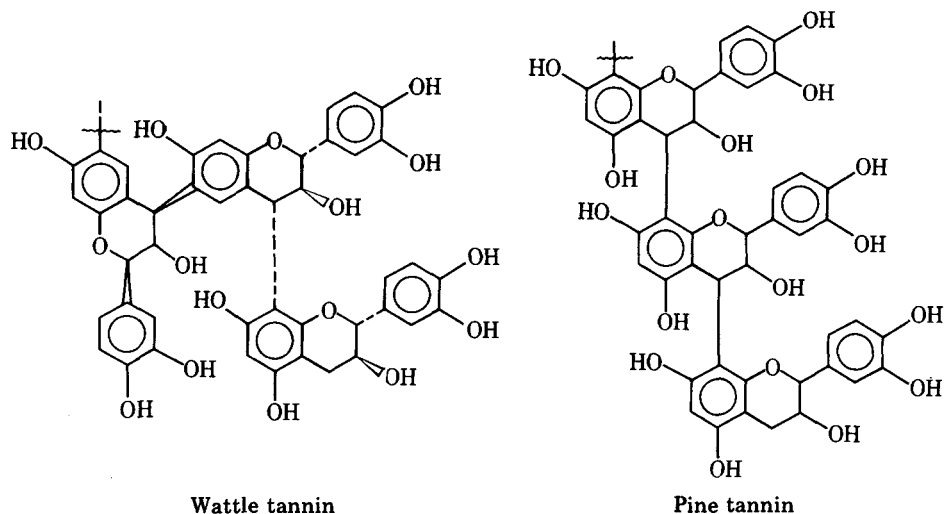
Wattle tannin unit



Pine tannin unit

These flavonoid units are repeated 2 to 11 times in the case of wattle and more than 10 times in the case of pine. In wattle tannins the resorcinolic flavonoid units are linked 4,6<sup>3</sup> with each other, while in pine the phloroglucinolic flavonoid units are linked 4,8.<sup>3</sup> As a general rule, resorcinolic flavonoid units are always

linked 4,6 and phloroglucinolic ones are linked 4,8 in any type of condensed tannin<sup>3</sup>:



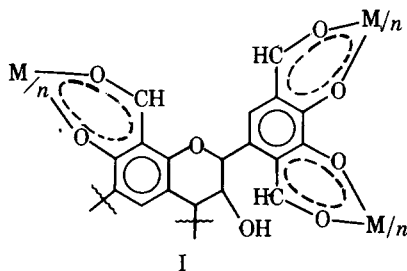
The nucleophilic centers on the A-rings of any flavonoid unit tend to be more reactive than those found on the B-ring. This is due to the vicinal hydroxyl substituents, which merely cause general activation in the B-ring without any localized effects on those found in the A-ring. Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages to reactive positions of the flavonoid molecules, mainly the A-rings. The reaction positions available on the A-rings are the 8-positions of all the resorcinolic flavonoid units (wattle) and the 6-position of all the phloroglucinolic flavonoid units. Resorcinolic A-rings (wattle) show reactivity towards formaldehyde comparable to that of resorcinol.<sup>4</sup> Phloroglucinolic A-rings (pine) behave instead as phloroglucinol.<sup>5</sup> The B-rings do not participate in the reaction except at high pH values (pH 10), where the reactivity towards formaldehyde of the A-rings is so high that the tannin-formaldehyde adhesives prepared have unacceptably short pot-lives. In general tannin adhesives practice, only the A-rings are used to crosslink the network. However, because of their size and shape, the tannin molecules become immobile at a low level of condensation with formaldehyde, so that the available reactive sites are too far apart for further methylene bridge formation. The result is incomplete polymerization and therefore weakness.

In the past, bridging agents with longer molecules,<sup>4,6</sup> like phenolic or aminoplastic resins, have been used to solve this problem by helping to bridge distances too large for interflavonoid methylene bridges. Hillis et al.<sup>7,8</sup> have shown that while catechol and the catecholic B-rings of the flavonoid unit do not react with formaldehyde at pH lower than 10, the addition of zinc acetate to the reaction mixture induces the B-rings to react with formaldehyde at lower pHs, the optimum being in the pH range 4.5–5.5, as shown by the higher amount of formaldehyde consumed.<sup>7,8</sup> This finding implies that in the presence of zinc acetate, further crosslinking of the tannin-formaldehyde network could be achieved through B-ring participation to the reaction. This could eliminate the need of increasing crosslinking by addition of synthetic phenolic or aminoplastic forti-

fiers. The accelerating or retarding effect that bivalent and trivalent metallic ions have on the reaction of phenols with formaldehyde has already been reported.<sup>1,2</sup> Although Hillis et al. use an equal amount in mass of zinc acetate and flavonoid tannin to increase B-ring crosslinking,<sup>7,8</sup> the catalytic effect on the rate of reaction is also present when much larger quantities of metal salts are used.<sup>2</sup>

The use of small amounts of metallic ion catalysts could probably give both an increase in crosslinking, hence an increase in strength, and an increase in the rate of the reaction, allowing faster crosslinking and consequently more economical plywood pressing times. The study was started by comparing the effect which different bivalent and trivalent metallic ions give in accelerating the reaction of tannins with formaldehyde. The values obtained were compared with values obtained by resorcinol-formaldehyde,<sup>2</sup> catechol-formaldehyde,<sup>2</sup> and phenol-formaldehyde<sup>1</sup> reactions. In the case of tannins, different degrees of chelation, and consequently different degrees of crosslinking, could be obtained according to (1) the quantities of metal and formaldehyde present, (2) the accessibility of the ligands reactive positions, (3) the steric hindrance of metal and ligands, and (4) the extent of the stresses on the chelate ring formed, which could lead to some of the metallic ions having a different behavior to that observed in simple phenols.

In structure I, all the possibilities of metal-ligand coordination are shown, but it is possible that only some, rather than all of them, are allowed:



The adhesive preparations were then done according to the two following approaches.

1. *Preparation of unfortified tannin-formaldehyde adhesives with metal salts added to simple tannin/formaldehyde mixtures.* This approach was used to see if increased flavonoid B-ring/formaldehyde crosslinking could eliminate the need for fortifiers.

2. *Preparation of fortified tannin-formaldehyde adhesives with added metal salts.* A tannin/urea-formaldehyde copolymer already reported<sup>4,6</sup> was used. With this approach only the accelerating effect of the metal ion is exploited, while relying on the fortification of the tannin/formaldehyde network to achieve sufficient crosslinking and strength.

Sulfited tannins were also used to try to decrease the effect of tannins' steric hindrance on the action of the metal ions.

## EXPERIMENTAL

### Preparation of Sulfited Tannins

Sodium sulfite (5 g) was added to 180 g of a 55% wattle extract solution; the mixture was refluxed for 3 hr, then cooled and stored.

### Gel Times of Tannin/Formaldehyde Mixtures

To 10 g of a 58% wattle extract (containing 80% flavonoids) aqueous solution or to 10 g of a 58% pine extract (containing 83% flavonoids) aqueous solution in a test tube, were added 0.3 g 96% paraformaldehyde powder and the different salts indicated in Table I; the test tube containing the mixture was then immersed in a boiling water bath (96°C) and gently and rapidly stirred with a thin stainless-steel coil using an upward-downward motion until gelation occurred. Ten measurements for each specimen were used. The gel time values are shown in Table I.

### Gel Times of a Wattle Tannin-Urea-Formaldehyde Adhesive<sup>4,6</sup>

To 100 g of a wattle extract 55% aqueous solution were added 8.6 g of 63.8% urea-formaldehyde resin (Kaurit K285, BASF). The mixture was vigorously stirred after addition of 5 g water to dissolve the soft gummy mass of the copolymer formed. To 11 g of this solution were added in a test tube 0.3 g of 96% paraformaldehyde powder and different salts as indicated in Table I. The test tube containing the mixture was then immersed in a boiling water bath (96°C) and gently and rapidly stirred with a thin stainless-steel coil using an upward-downward motion until gelation occurred. The gel time calculated from the start of immersion of the test tube in boiling water to gelation was measured. Ten measurements for each specimen were used. The gel time values are shown in Table I.

### Preparation of Glue Mixes

Two series of glue mixes were prepared. The first series, identical to the glue mixes used to measure the gel times, was used to evaluate the total contribution to the fully cured strength of simple tannin-formaldehyde networks of the different metal ions under study. The strength results obtained by testing (see Testing) according to British Standard BS1204, 1965, Part 2,<sup>9</sup> for synthetic resins adhesives are shown in Table I.

The second series of glue mixes was used for plywood panel manufacture.

TABLE I  
Effect of Different Metallic Catalysts on Tannin-Formaldehyde Mixtures and Adhesives

Catalyst	Metallic ion/ flavonoid monomer, mol/mol	Average gel time, sec		Wattle tannin fully cured strength <sup>a</sup>						
		Wattle tannin	Pine tannin	Dry		24 hr soak		6 hr boil		
				Strength, psi	Wood failure, %	Strength, psi	Wood failure, %	Strength, psi	Wood failure, %	
No metal salts	—	366	65	324	674	83	523	44	435	20
Al <sup>III</sup> chloride + Na acetate	0.02	—	61	—	—	—	—	—	—	—
Co <sup>III</sup> acetate	0.02	—	53	—	—	—	—	—	—	—
Cr <sup>III</sup> acetate	0.02	244	55	—	685	75	482	37	476	18
Cr <sup>III</sup> sulfite + Na acetate	0.02	254	56	—	692	94	518	15	428	26
Fe <sup>III</sup> acetate	0.02	209	58	—	654	52	466	27	361	28
Fe <sup>III</sup> chloride + Na acetate	0.02	222	60	—	641	53	503	49	385	24
Pb <sup>II</sup> acetate	0.02	179	49	123	703	22	560	77	480	53
Mn <sup>II</sup> acetate	0.02	199	55	142	707	64	512	19	401	22
Mn <sup>II</sup> chloride + Na acetate	0.02	237	—	169	683	88	569	12	390	24
Mg <sup>II</sup> acetate	0.02	238	57	—	674	67	498	29	444	18
Mg <sup>II</sup> chloride + Na acetate	0.02	270	—	—	788	52	591	51	505	37
Ni <sup>II</sup> acetate	0.02	242	56	—	647	82	505	49	424	25
Ni <sup>II</sup> chloride + Na acetate	0.02	307	60	—	679	75	493	12	478	21
Zn <sup>II</sup> acetate	0.02	188	51	130	745	72	576	40	448	14
Zn <sup>II</sup> chloride + Na acetate	0.02	243	55	—	666	65	478	48	451	29
Zn <sup>II</sup> chloride	0.02	325	—	—	—	—	—	—	—	—
Zn <sup>II</sup> acetate + acetic acid (equal amount by mass of acetate)	0.02	257	—	—	730	71	478	13	431	28
Acetic acid	—	416	—	—	—	—	—	—	—	—
Zn <sup>II</sup> acetate	0.04	125	—	—	—	—	—	—	—	—
Zn <sup>II</sup> acetate + acetic acid (half amount by mass of acetate)	0.04	148	—	—	—	—	—	—	—	—

<sup>a</sup> Unfortified wattle tannins + metal ions; beech strip test BS 1204, 1965, Part I.

These glue mixes were prepared by mixing the following components, in parts by mass:

Glue mixes	1	2	3	4	5	6	7	8
Wattle extract, 57.7% solution	130	130	130	130	130	130	130	130
Urea formaldehyde, 63.8% resin	—	—	—	—	12	12	12	12
Zinc acetate (hydrated)	—	3	—	—	—	3	—	—
Lead acetate (hydrated)	—	—	5.1	—	—	—	5.1	—
Manganese chloride	—	—	—	3	—	—	—	3
Sodium acetate	—	—	—	1.5	—	—	—	1.5
Coconut shell flour, 200 mesh	14	14	14	14	14	14	14	14
Paraformaldehyde, 96% powder	10	10	10	10	9	9	9	9
Water	15	20	30	20	20	25	35	25

Small amounts of extra water were added to obtain an initial glue-mix viscosity of 2.5–5.5 Pa · sec (1 Pa · sec=10 poise) at 22°C.

Viscosity increase (pot life) at a constant temperature of 30°C in a water bath were measured with a Brookfield RVF viscometer every hour, or more frequently when necessary, for glue mixes 5 and 6. The viscosity curves obtained are shown in Figure 1.

## TESTING

### Evaluation of Fully Cured Adhesives Strength

All the first series of glue mixes prepared were tested on beech strips of 12% moisture content for close contact joints, according to British Standard BS1204, 1965, Part 2,<sup>9</sup> for synthetic resin adhesives. The beech strips, 3 × 25 × 150 mm, are glued in pairs with parallel wood grain and a glued overlap of 25 × 25 mm.

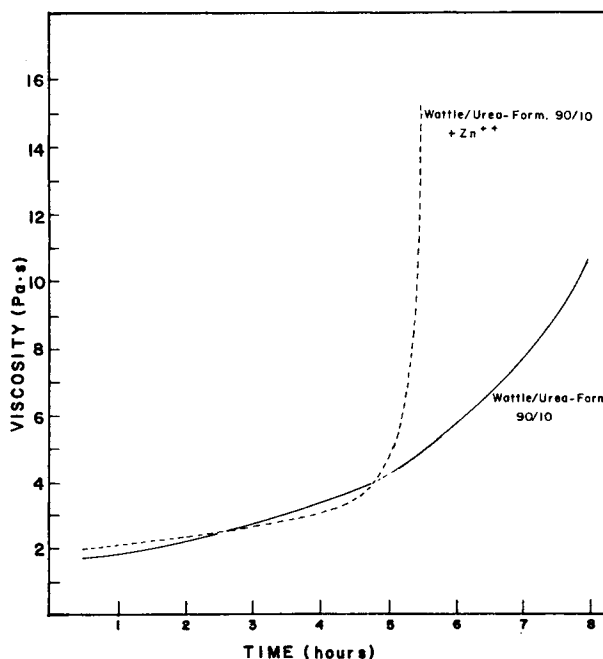


Fig. 1. Pot life of fortified wattle adhesives with and without  $Zn^{2+}$ .

The beech strip specimens glued with the glue mixes described were cured for 4 hr at 90°C and 12% equilibrium moisture content; the requirements of BS1204, 1965, Part 2, are the following:

Condition	Shear strength (psi)
Dry	—
24-hr cold water soak	500
6-hr boil	325

The results obtained are shown in Table I.

### Manufacture of Plywood Panels

Duplicate plywood panels, 9 mm thick, were prepared by using rough pine veneers under the following conditions:

Press temperature	125°C
Pressure	1.6 MPa (1 MPa = 145 psi)
Pressing time	2.5, 3.5, 4.5, 5.5, and 6.5 min
Veneer species	Pine
Veneer moisture content	5%–6%
Prepressing	None
Assembly time	20 min
Glue spread	230 g/m <sup>2</sup> single glue line
Panel construction	Three ply, each 3 mm thick
Panel size	50 × 50 cm

After pressing, the plywood panels were cooled without hot stacking, then trimmed and cut into 30 pieces 25 × 150 mm and 3 pieces 125 × 125 mm. The 25 × 150-mm pieces were used to determine shear strength dry, after a 24-hr cold water soak, and after a 6-hr boiling according to the South African SABS 929, 1971 Standard<sup>10</sup> for marine-grade plywood. The 125 × 125-mm pieces were used to knife test the panels dry, after a 24-hr cold water soak, and after a 72-hr boiling according to British Standard BS1088<sup>11</sup> for marine-grade plywood, in which a rating from 0 to 10 is assigned, 0 indicating complete glue failure and 10 complete wood failure, and stating that the average value for all glue lines tested shall not be less than 5. The South African SABS 929, 1971 standard<sup>10</sup> for shear strength of marine grade plywood has as sole requirement that the test specimen present a shear strength of more than 200 psi after 72 hr of boiling. The results of both tests are shown in Table II.

### DISCUSSION

The accelerating effect<sup>1,2</sup> of phenol-formaldehyde reactions caused by the presence of metal ions is maintained when the phenolic compound is a tannin (Table I). However, the retarding effect<sup>1,2</sup> caused by certain metal ions in the case of the reactions of simple phenols with formaldehyde is not maintained when using tannins as the phenolic compound (Table I, Cr<sup>III</sup>, Al<sup>III</sup>, Co<sup>III</sup>). The latter finding could be explained only in light of the higher steric hindrance of the tannin polymer due to its close tridimensional structure. The metallic ion can still probably form a complex with formaldehyde and the tannin phenolic nuclei; due to its charge, which is stronger than that of hydrogen ions, it will still accelerate the initial reaction of formaldehyde on the phenolic nuclei by forming a carbocation of stronger positive charge. The high steric hindrance of the tannin, though, should cause strong stresses on the partly aromatic etherocyclic ring

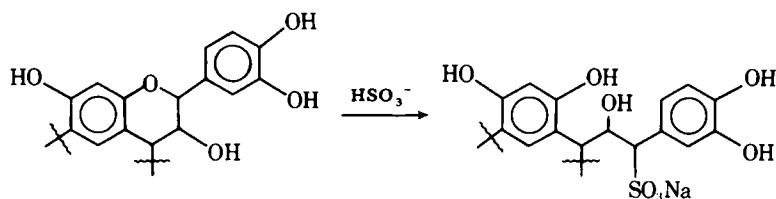
TABLE II  
Plywood Shear Strength and Knife Test Results

Glue mix	Metal ion species	Type of formulation	Pressing time, min	Shear strength BS						Knife test BS 1088		
				Dry		24-hr soak		72-hr boil		Dry	24-hr soak	72-hr boil
				Strength, psi	Wood failure, %	Strength, psi	Wood failure, %	Strength, psi	Wood failure, %			
1	—	Unfortified	6.5	200	29	135	48	113	77	6	5	3
2	Zn <sup>2+</sup>	Unfortified	6.5	215	61	166	23	141	47	7	7	7
3	Pb <sup>2+</sup>	Unfortified	6.5	265	72	197	52	182	61	7	7	7
4	Mn <sup>2+</sup>	Unfortified	6.5	207	74	180	44	131	61	8	7	7
5	—	Fortified	6.5	321	53	206	77	206	58	8	8	8
6	Zn <sup>2+</sup>	Fortified	6.5	428	66	279	59	224	41	9	9	9
7	Pb <sup>2+</sup>	Fortified	6.5	376	44	295	46	283	38	9	9	8
8	Mn <sup>2+</sup>	Fortified	6.5	439	61	338	52	270	54	9	9	9
5	—	Fortified	6.5	321	53	206	77	206	58	8	8	8
5	—	Fortified	5.5	321	25	234	29	232	36	8	8	8
5	—	Fortified	4.5	333	62	204	73	195	55	8	8	7
5	—	Fortified	3.5	258	13	177	25	164	17	7	6	6
5	—	Fortified	3	230	13	156	5	141	6	6	5	5
6	Zn <sup>2+</sup>	Fortified	6.5	428	66	339	91	262	47	10	9	9
6	Zn <sup>2+</sup>	Fortified	5.5	326	75	233	100	215	82	10	9	8
6	Zn <sup>2+</sup>	Fortified	4.5	317	38	222	43	222	21	9	9	9
6	Zn <sup>2+</sup>	Fortified	3.5	315	65	229	35	203	25	10	9	9
6	Zn <sup>2+</sup>	Fortified	3	312	20	210	39	213	19	9	8	7
6	Zn <sup>2+</sup>	Fortified	2.5	257	16	201	36	174	5	8	7	6
8	Mn <sup>2+</sup>	Fortified	3.5	266	47	199	29	234	28	8	8	8



containing the metal, with consequent instability of the ring and finally the ring opening. Once the metal-containing ring is open, the methylol-phenolic compound formed, no longer blocked by a slow exchange rate metal, is free to proceed in the reaction and to form methylene bridges. In this way the retarding effect of the metal ion, due to the formation of a stable ring, is lost, while its accelerating effect due to its strong charge is not. Consequently, all bivalent and trivalent metals function, to different degrees, as accelerators of the flavonoid tannin-formaldehyde reactions.

Proof that tannin steric hindrance is the cause of this peculiar behavior can be obtained by repeating the study using sulfited tannins (Table III). In these the tannin steric hindrance has been considerably reduced by opening of the tannin etherocyclic ring according to the following reaction:



The sulfited tannin will be faster reacting with formaldehyde than unsulfited tannin, as the A-ring will now behave more as a resorcinol nuclei than a 3-methoxyphenolic one. However, at the faster gel times obtained, it is possible to observe that bivalent metals will further accelerate the reaction (Table III,  $Zn^{II}$ ), while trivalent ones will slow it down (Table III,  $Cr^{III}$ ), in line with their observed behavior in the simple phenol-formaldehyde reaction.

The results shown in Table IV and Figure 2 indicate that the metal ions' accelerating effect has different intensities in different pH ranges. From Figure 2 it is noticeable that the accelerating effect of the metal ions will produce a flatter curve, with little difference in gel time at low and high pH but with considerable difference around the pH of minimum reactivity (Fig. 2). The lack of difference in gel time at low and high pH between tannins with or without metallic ions can be ascribed to the "drowning" of the metal ion effect by the enhanced reactivity, due to the pH, of the tannin-formaldehyde system.

The wattle tannin-formaldehyde "ultimate" shear strength results shown in Table I indicate that when taking into consideration both shear strength and percentage wood failure values, little significant variation between cured wattle-formaldehyde networks with or without metallic ions present occurs. Also, when significant differences can be observed (as in the case of  $Pb^{III}$ ), these are small. From this it is possible to conclude that the addition of small percentages

TABLE III  
Effect of Sulfitation on Wattle Tannin-Formaldehyde Mixtures

Catalyst	Metallic ion/ flavonoid monomer, mol/mol	Average gel time, sec
No metal salts	—	269
$Zn^{II}$ acetate	0.02	135
$Cr^{III}$ sulfate	0.02	308

TABLE IV  
Effect of pH on Gel Times of Wattle Tannin-Formaldehyde Mixtures

Catalyst	pH	Metallic ion/ flavonoid, mol/mol <sup>a</sup>	Average gel time, sec
No metal salts	4.7	—	366
	5.7	—	265
	7.0	—	92
	7.7	—	54
Zinc acetate	4.7	0.02	188
	5.7	0.02	151
	7.0	0.02	86
	7.7	0.02	57
Zinc acetate + acetic acid <sup>b</sup>	4.7	0.02	257
	7.0	0.02	115
	7.7	0.02	68
Acetic acid	4.7	—	416
	7.0	—	153
	7.7	—	60
Zinc acetate	4.7	0.04	125
	5.7	0.04	105
	7.0	0.04	85
	7.7	0.04	64
Zinc acetate + acetic acid <sup>c</sup>	4.7	0.04	147
	7.0	0.04	93
	7.7	0.04	74

<sup>a</sup> Molecular weight, 272.

<sup>b</sup> Zinc acetate/acetic acid, 50:50 (w/w).

<sup>c</sup> Zinc acetate/acetic acid, 66.6:33.3 (w/w).

of metal ion do not increase, or increase very little, the flavonoid B-ring cross-linking; fortification of tannin-formaldehyde networks cannot, consequently, be completely eliminated. High amounts of metal salts will considerably increase B-ring crosslinking, but the quantities of metal ions needed render this possibility uneconomical.

The plywood results shown in Table II indicate that when limited hotpressing times are involved, the contribution of the metallic ions is considerable. The panels glued with the adhesive containing the metal, both fortified and unfortified, are simply more cured and consequently present higher strength when using equivalent pressing times. However, it is noticeable that the effect is of greater magnitude at the faster pressing times used. In the case of Zn<sup>2+</sup>-fortified formulations, the more significant drop in strength occurs when passing from 3 to 2.5 min of pressing time. In the case of fortified formulations without any metal ions, the same significant drop occurs when passing from 4.5 to 3.5 min pressing time. This indicates that the presence of the metal ion is capable of shortening the pressing time of 1–1.5 min or between 20 and 30% of the original value. All the three metals used—Zn<sup>II</sup>, Pb<sup>II</sup>, and Mn<sup>II</sup>—appear to perform well, though, as expected, the Mn<sup>II</sup> being a milder accelerator than Zn<sup>2+</sup> does not perform as well at very short pressing times. Lead appears to be the best performer in the unfortified formulations.

The effect of metallic ions on wattle tannins can also be observed in the case

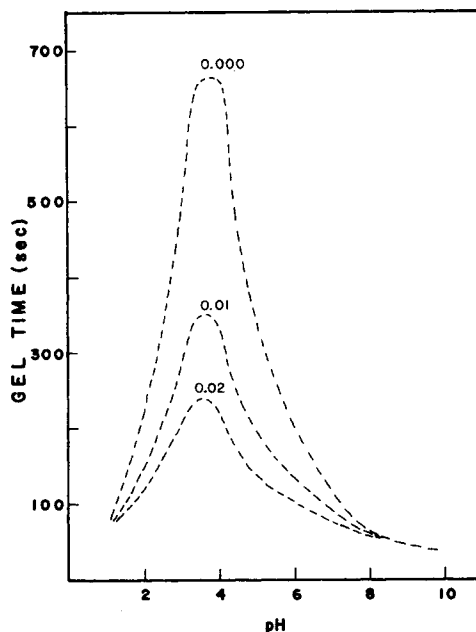


Fig. 2. Wattle tannin-HCHO gel times using different molar percentages of  $Zn^{2+}$ .

of pine tannins (Table I). The higher reactivity of their phloroglucinolic A-rings, though, does not allow very evident effects, as in the case of wattle tannins. More interesting, for the pine tannins, would be the trivalent ions retarding effect so as to allow their easier utilization and the lengthening of their pot life, as well as decrease of their precuring tendency due to their higher reactivity. As shown, the retarding effect is lost, and this avenue of exploitation is not possible for pine tannins.

Figure 1 indicates that the viscosity curve (pot life) of tannin-formaldehyde formulations is shortened by the addition of metal ions. The effect, though quite evident, is not so marked as to put in jeopardy the plant use of such formulations. As observed in Figure 1, pot lives of 5–5.5 hr are attainable, and these are more than sufficient for plant application.

Similar effects to those obtained by using metallic acetates are observed when using other anions of the same metal in conjunction with sodium acetate. The effects are less marked though.

In conclusion, a few factories in this country are using these formulations for industrial production with results comparable to those obtained with commercial synthetic phenol-formaldehyde adhesives and at substantial cost savings.

Acetic acid slows down the reaction by shifting the system towards pHs where reactivity is lower and by depressing the hydrolysis of the metals acetates. Acetic acid can consequently be used to increase pot life, though longer gel times also result.

Factory trials of the formulations presented gave equivalent strength and bond quality results for three- and five-ply pine plywood to those obtained for laboratory plywood panels. Slightly longer pressing times (8–10 min in the factory versus 6.5 min in the laboratory for three-ply plywood panels) were necessary to obtain statistically identical results. Short pressing times, though, also gave

acceptable results. In practice, a few factories manufacturing plywood, using low-density wood veneer, are able to use unfortified wattle tannin-formaldehyde-metallic ions adhesives with good results. Other factories, instead, prefer to use wattle tannin-urea-formaldehyde adhesives with or without metallic ions according to their production speeds.

### References

1. D. A. Fraser, R. W. Hall, and A. L. J. Raum, *J. Appl. Chem.*, **7**, 676 (1957).
2. A. Pizzi, *J. Appl. Polym. Sci.*, **24**, 1247 (1979); A. Pizzi, *J. Appl. Polym. Sci.*, **22**, 2397 (1978).
3. D. G. Roux, D. Ferreira, H. K. L. Hundt, and E. Malan, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **28**, 335 (1975).
4. A. Pizzi and H. O. Scharfetter, *J. Appl. Polym. Sci.*, **22**, 1745 (1978).
5. H. Scharfetter, A. Pizzi, and D. du T. Rossouw, I.U.F.R.O. S5.04-07, *Conference on Wood Gluing*, Mérida, Venezuela, October 1977.
6. A. Pizzi, *Adhes. Age*, **20**, 12, 27 (1977).
7. W. E. Hillis and G. Urbach, *J. Appl. Chem.*, **9**, 474 (September 1959).
8. W. E. Hillis and G. Urbach, *J. Appl. Chem.*, **9**, 665 (December 1959).
9. British Standard BS 1204, 1965, Part 2 for synthetic resin adhesives.
10. South African Bureau of Standards, SABS 929-1971, Standard for marine craft plywood.
11. British Standard BS 1088, 1957, for marine craft plywood.

Received December 19, 1978