Laminating Wood Adhesives by Generation of Resorcinol From Tannin Extracts

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Synopsis

Resorcinol has been generated *in situ* by high levels of sulfitation of the tannin extract of the black wattle tree (*Acacia mearnsii,* formerly *mollissima*). Consequently, weather and boil-proof tannin-based cold-setting adhesives for wood, satisfying the requirements of international standards, have been prepared and optimized by halving the amount of resorcinol chemical added to the tannin. Sulfitation afforded also considerable improvement of the "drying out" time characteristics of these adhesives.

INTRODUCTION

The chemistry and characteristics of condensed tannins of the flavonoid type regarding their application as exterior wood adhesives as well as the main types of products obtained by their reaction with formaldehyde have already been reported.[1–3]

Adhesive "drying out" time is the period of time between spreading of the adhesive on the substrate and the drying out of thin resin film applied. "Drying out" is not due to too fast adhesive setting. The need of sometimes using tannin-based adhesives in hot and dry climatic conditions, where faster solvent evaporation renders the problem noticeable, prompted the development of adhesives systems of unaltered pot life that were, however, capable of extended drying out times. The use of humectants, such as glycols, starches, and especially carboxymethylcellulose,[4] give lengthening of drying out time, but they constitute only "cosmetic" measures. The problem can be solved more effectively by structural modifications of tannin at molecular level. It is in the course of this study that resorcinol was generated *in situ* from the tannin extract, allowing considerable reduction of the resorcinol chemical to be added to wood laminating tannin-based cold-setting adhesives.

The tannin extract of the bark of the black wattle tree (*Acacia mearnsii,* formerly *mollissima*), commercially available, was used for this study.

The structure of the main polymeric constituents of wattle tannins, repeated

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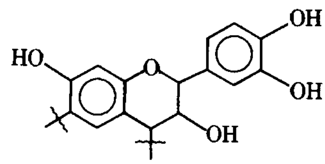
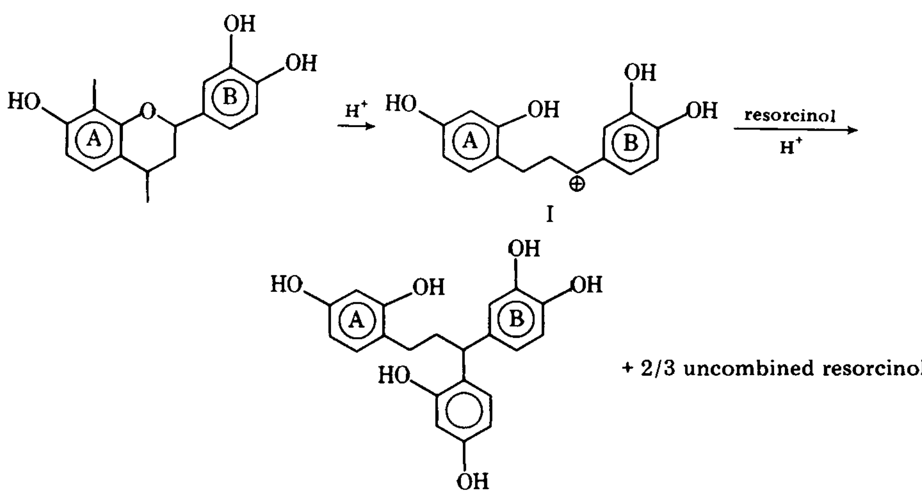
2 to 11 times, may be represented as follows:



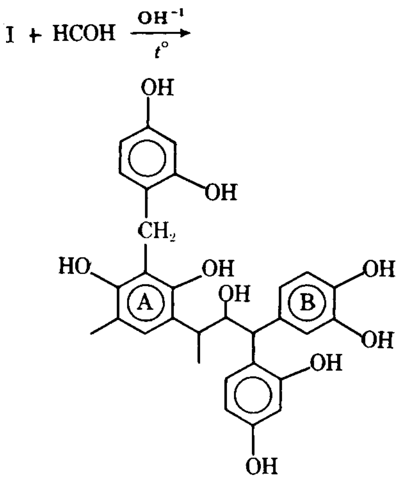
Condensed tannins macromolecules in water are more colloidal suspensions[5] than true solutions, with the —OH groups trying to keep the molecules in solution, while the ether group on the heterocyclic hydropyranic ring tends to push the tannin molecule out of solution.[5] In effect, the wood substrate, independent of evaporation effects and being more hydrophilic than the tannin resin, will remove a considerable amount of solvent from the adhesive with consequent drying out of the glue line before adhesive setting. The joint produced will be poor if the glue line is dried out before the end of assembly. The problem is not important in the case of thermosetting adhesives, where application of elevated temperature during curing mobilizes the moisture absorbed by the wood, which allows the necessary mobility of the adhesive to give a good joint. It is of more concern in the case of cold-setting adhesives. The solution to the problem consists of eliminating the ether group and introducing further hydrophilic groups in the tannin molecule. Care must be taken not to increase hydrophilicity excessively as this results in rapid deterioration of the cured adhesive in the presence of water. The opening of the flavonoid heterocyclic ring can be achieved by two different routes:

(1) Acid Hydrolysis in Presence of Resorcinol[7]



I

Adhesive I has already been reported as giving strength results just satisfying the British Standard BS1204.[6] The results obtained with this adhesive have been reported as being considerably lower than other tannin-based cold-setting adhesives reported.[7] It was noticed that in mixture I about ⅔ of the amount of resorcinol added was unbound to the flavonoids, indicating ring opening in only part of the flavonoids. The system was then corrected according to the following modification:

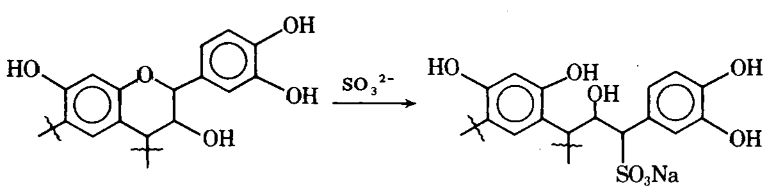


\+ a mixture of resorcinol/flavonoids condensates

II

Mixture II is an adhesive that can cure at room temperature once paraformaldehyde hardener is added.

(2) Sulfitation[8,11,13]



III

Compound III can be used instead of untreated tannin extract to manufacture successfully all the types of cold-setting adhesives already reported.[2,3] Sulfitation affords a better and more consistent control of the opening of the flavonoids heterocyclic rings and consequently should be the preferred reaction.

The newly created linked resorcinol (A ring) in mixture III should allow a decrease in the amount of resorcinol chemical added by increasing the level of sulfitation. Namely, a 3% sulfitation level (3% Na_2SO_3 on tannin extract w/w) corresponds to the formation of 1.0% resorcinol on tannin extract, as shown in Table I. In theory it should then be possible to reduce the amount of resorcinol on extract (33 resorcinol solid:66 extract solid w/w) in a standard tannin-based adhesive according to Table II.

Cold-setting laminating wood adhesives prepared using a heavily sulfited extract could then be very inexpensive, owing to the lower resorcinol added, and would constitute a considerable advance on any cold-setting adhesive for wood presented up till now.[1,3] Application of such a system of generating resorcinol *in situ* in the adhesive was also attempted for thermosetting plywood and particle-board adhesives.

TABLE I
Theoretical Amount of Resorcinol Produced in Wattle Extract by Different Levels of Substitution

Ne_3SO_3 On extract, w/w %	Free resorcinol on extract, %
3	1.0
5	4.2
7	6.1
12	10.4
20	17.4
37	32.3

EXPERIMENTAL

Adhesive Resins Preparations

Adhesive 1—Acid Hydrolysis in Presence of Resorcinol Preparation. For 3 hr, 614 parts of wattle extract 58.3% solution, 5 parts commercial defoamer, 4 parts water, 180 parts technical 33% resorcinol, and 43 parts tricloracetic acid were mixed and refluxed, then 20 parts 40% NaOH was added, followed by 22 parts paraformaldehyde and 18 parts 40% NaOH solution 5 min later. The mixture was then refluxed for 50 min, cooled, and stored.

Adhesive 2-1—Basic Preparation. To 614 parts of wattle extract 58.3% solution and 5 parts of commercial defoamer 18 parts of sodium sulfite (5% sulfitation level on wattle extract solids) dissolved in 30–80 parts water were added. The mixture was then refluxed for 3 hr, under continuous mechanical stirring, then 180 parts technical 99% resorcinol were added followed by 15 parts of 40% caustic soda solution 5 min later. After another 5 min, 84 parts of 38% formalin solution (or 32 parts paraformaldehyde and 50 parts water, added separately) and 15 parts 40% caustic soda solution were added. The mixture was then refluxed for 50 min, cooled, and stored. The entire reaction was carried out under continuous mechanical stirring.

Adhesive 2-1—Variation of Level and Duration of Sulfitation. The level of sulfitation and the refluxing time of the preparation reaction of adhesive 2-1 were varied in order to establish the optimum conditions of preparation. Respectively, 2½, 5, 7½, 10, 12½, and 15% sodium sulfite w/w on wattle extract solids were used. Three adhesives were prepared for each sulfitation level at 1½, 3,

TABLE II
Theoretical Requirements of Resorcinol

Na_2SO_3, %	Resorcinol chemical added, w/w % on resorcinol and extract	Sulfited extract, w/w % on resorcinol and extract
0	33.0	66.0
3	32.4	67.6
5	29.5	70.5
7	28.0	72.0
12	23.5	76.5
20	16.0	84.0
37	1.1	98.9

and 6 hr reflux. The level of formaldehyde was varied accordingly. The scheme conditions are shown in Table III.

Adhesive 2-1—Decrease of Adhesive Resorcinol Content. The best formulation obtained in the previous experiment, namely, 10% sulfitation level and 6 hr reflux, was repeated, decreasing the percentage of resorcinol content on wattle extract solids (*not* on total resin solids) from the original 50.3% to 43.9, 38.3, 33.0, and 27.4%. This is equivalent to a reduction of resorcinol content on total resin solids from 29.1 to 26.4, 23.8, 21.2, and 18.3%, respectively. Results and conditions are shown in Table III.

Adhesive 2-2. The same quantities of chemicals and the same process of adhesive 2-1 were also used for adhesive 2-2; the only difference was in decreasing the 38% formalin solution content down to 56 parts (or 21 parts paraformaldehyde). The percentage of formaldehyde on wattle extract solids is, in the case of this adhesive, identical to the wattle commercial adhesive control used.

Adhesive 2-2—Decrease of Adhesive Resorcinol Content. A few extracts at 10% sulfitation level and 6-hr of reflux treated as adhesive 2-2 above (56 parts 38% formalin solution) were prepared by decreasing the percentage of resorcinol content on wattle extract solids (*not* on total resin solids) from 59.3% (180 parts) to 43.9, 38.3, 33.0, and 27.4%. This is equivalent to a reduction of resorcinol content on total resin solids from 30.5% to 27.9, 25.2, 22.6, and 18.7%, respectively. The amount of formaldehyde was also decreased accordingly. Results and conditions are shown in Table III.

Adhesive 2-3—Substitution of Formaldehyde by a Urea–Formaldehyde Resin in Adhesive 2-2 Preparation. Urea–formaldehyde resin (UF, Kauresin K285, BASF) was used in place of formalin solution (as paraformaldehyde) according to the directives for this type of adhesive already reported.[1] Namely, in the basic preparation of adhesive 2-2 already described, the 38% formalin solution was substituted with 120 parts 63.8% urea–formaldehyde resin. Results and conditions are shown in Table III.

PREPARATION OF GLUE MIXES AND TESTING

The 200 parts liquid of every cold-setting adhesive prepared were added to 20 parts 96% paraformaldehyde powder (Degussa N), 10 parts 200-mesh coconut shell flour, 10 parts 180-mesh wood flour, and 1 part commercial wetting agent. Enough caustic soda, 25% solution, or glacial acetic acid was added to each glue mix to correct the pH to the values shown in Table III. Enough water was added to each adhesive glue mix to adjust the viscosities of the glue mixes within the range of 2.6–3.0 Pa sec (1 Pa sec = 1000 cP). All the adhesives prepared were tested on beech strips of 10–12% moisture content at 40°C for 4 hr, according to British Standard BS1204, 1965, parts 1 and 2,[6] and the South African Bureau of Standard provisional specification for synthetic resin adhesives SABS 1973.[9]

The requirements of the BS1204, 1965, for close contact joints are the following:

Dry	Shear strength, psi
24-hr cold water soaking	500
6-hr boiling	325

The requirements of the more modern SABS provisional specification are the

TABLE III
Properties of Tannin-Based Cold-Setting Adhesives

Adhesive type	Na_2SO_3 on extract solids, %	Sulfitation time, hr	HCHO content on extract solids in resin preparation, %	Resorcinol content, on extract solids, %	Corrected glue mix, %	Viscosity 50% resin solids 25°C, cP	Pot-life, min	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %
1	—	—	6	50.3	7.60	3150	125	723	29	530	66	538	42
2-1	2½	1½	9	50.3	7.61	2020	120	804	49	578	94	697	76
2-1	2½	3	9	50.3	7.60	2420	100	800	29	654	89	613	31
2-1	2½	6	9	50.3	7.59	1900	106	806	6	647	75	725	49
2-1	5	1½	9	50.3	7.59	1500	113	719	8	610	46	625	27
2-1	5	3	9	50.3	7.59	740	94	788	3	586	71	649	52
2-1	5	6	9	50.3	7.58	800	99	754	2	663	67	642	34
2-1	7½	1½	9	50.3	7.59	500	116	761	11	543	3	611	11
2-1	7½	3	9	50.3	7.60	520	107	703	1	658	12	645	8
2-1	7½	6	9	50.3	7.60	490	103	814	94	625	96	552	56
2-1	10	6	9	50.3	7.61	560	105	829	86	622	100	556	76
2-1	12½	6	9	59.3	7.60	520	111	846	41	689	91	611	42

2-1	15	6	9	50.3	7.60	640	105	869	30	705	95	593	19
2-1	10	6	7.9	43.9	7.40	—	103	773	77	588	64	607	61
2-1	10	6	7.1	38.3	7.41	—	96	678	99	526	46	604	48
2-1	10	6	6.3	33.0	7.41	—	99	813	58	587	55	517	100
2-1	10	6	5.6	27.4	7.39	—	124	789	70	572	31	535	14
2-2	10	6	6	50.3	7.91	175	295	838	98	604	94	546	90
2-2	10	6	5.25	43.9	8.01	305	296	799	93	678	87	643	80
2-2	10	6	4.75	38.3	8.01	260	309	806	98	645	67	622	95
2-2	10	6	4.25	33.0	8.00	350	314	785	95	637	81	642	70
2-2	10	6	3.75	27.4	8.01	550	298	876	94	600	76	523	85
2-3 (UF)	10	6	−(UF)	50.3	7.46	–	149	792	75	598	75	536	88
Unsulfited wattle cold setting (commercial control)	—	—	6	50.3	7.63	1150	156	753	88	654	62	583	85
Commercial PRF	—	—	—	—	8.5	—	—	791	90	659	98	609	81

same as regards the joints' tensile strength but require additionally a minimum of 75% average wood failure for both cold and boiling water tests.

The beech strips specimens were glued with an open assembly time of 15 min and a closed assembly time of 30 min, clamped under constant pressure (100 psi) for 4 hr, cured at 40°C, and aged for five days more at ambient temperature before testing.

The "drying out" times of all the adhesives were measured in a room humidity controlled and temperature controlled (25°C) by spreading an even adhesive coat, by hand roller, on freshly cut pine slats 5 cm × 40 cm and 2.5 cm thick. The spread was maintained constant at 200 g/m^2. Time to touch dryness was measured with a stopwatch and reported (See Table IV).

DISCUSSION

The results shown in Table III indicate that resorcinol chemical, albeit still linked to the modified flavonoid polymer skeleton, is truly liberated during sulfitation of flavanoid extracts such as wattle tannin. Wattle extract sulfited at the 7½ and 10% levels appears to be optimal, as at this level of sulfitation the highest specimens shear strength and especially percentage wood failure were obtained. However, levels higher than 5% are not recommended for the less fortified thermosetting adhesives for plywood,[10] while unfortified thermosetting adhesives for particle board do not tolerate more than 2½% sodium sulfite.[11] The anomalous behavior of the thermosetting adhesives, in which sulfitation also generates resorcinol, are due to their low or nonexistent level of fortification with synthetic resins, causing a lower degree of crosslinking which allows the strong hydrophilic effect of the sulfonic group to induce rapid deterioration of the cured network in water.

The results in Table III also indicate that increasing the level of sulfitation generates a progressively increasing amount of resorcinol chemical *in situ* in the wattle tannin extract. Hence, good cold-setting adhesives satisfying the relevant British and South African standards specifications can be obtained by increasing the level of sulfitation and respectively decreasing the percentage of resorcinol added to the extract. Attention must be drawn in particular to the strength and wood failure results obtained with the adhesives in which resorcinol addition has been decreased from 50.3% to 43.9, 38.3, and 27.4% on extract solids (cf. 2-2, Table III). These levels of resorcinol addition appear to confirm the amounts of resorcinol generated during sulfitation, which have been postulated in Tables

TABLE IV
Average "Drying Out" Times

Adhesive Type	Glue mix drying out time, min		Adhesive without hardener, drying out time, min	
	Edge	Center	Edge	Center
1	40	121	—	—
2-1	40	106	85	125
2-2	79	139	—	—
2-3	83	132	—	—
Unsulfited wattle control	44	106	63	98

I and II. This means that weather- and boil-proof cold-setting adhesives for laminated wood with an added resorcinol content as low as 10–11% of total liquid adhesive (instead of the original 18%) can be obtained when using wattle tannin extract. Such a low level of resorcinol addition is unthinkable even in synthetic, oil-derived, phenol/resorcinol/formaldehyde resins.

The considerable decrease in the viscosity of the adhesives that is caused by sulfitation is also interesting. This is due to the tannin extract being transformed from its original hydrocolloidal suspension to a completely true solution as a consequence of the introduction of the highly hydrophilic sulfonic group. Increased molecular mobility, owing to the opening of the sterically hindered flavonoid configuration, also contributes to the reduction in viscosity. The importance of reduced viscosity lies in the possibility of using glue mixes of higher resin solids, affording considerably lower volume shrinkage of the adhesive during curing. Therefore, these adhesives can present better gap-filling properties. From Table III, it is noticeable that the viscosity increases with decreasing amounts of resorcinol. Free, uncombined resorcinol chemical, like all low molecular weight aromatic compounds, decreases the viscosity of tannin solutions.[11] Therefore, progressive substitution of the amount of resorcinol chemical added, by the generated resorcinol linked to the flavonoid polymer skeleton, causes viscosity increases.

Sulfitation appears also to lengthen considerably the "drying out" time of tannin-based adhesives (cf. control and adhesive 2-2, Table IV). This is caused by the presence of the sulfonic group, which is able to maintain water in the glue line for longer times. The apparent exception to such a finding is adhesive 2-1, which presents "drying out" times comparable to unsulfited tannin adhesives. This is explained by its higher formaldehyde content during resin manufacture (50% higher than control and adhesive 2-2). Hence, adhesive 2-1 is composed of condensates that have considerably higher molecular size. The influence of the molecular size is also reflected in adhesive 2-1 shorter pot lives.

The absence of effects owing to generation of the more reactive phloroglucinol during sulfitation of the 5% of wattle flavonoids A rings that contain phloroglucinol, as well as the absence of the considerable shortening of pot life which its presence would cause, is again a clear indication, contrary to more established opinions,[12] that the phloroglucinol positions capable of reaction with formaldehyde are, at least in wattle tannins, blocked by other flavonoids.[13]

CONCLUSIONS

Resorcinol, an expensive and scarce benzene derivative, can be obtained easily by sulfitation from a natural tannin extract (such as wattle extract, *Acacia mearnsii,* commercially available) though still linked to the tannin polymer. The latter disadvantage has no consequence when the resorcinol is needed for adhesive or resin manufacture. Sulfitation also improves considerably the "drying out" time characteristics of tannin-based adhesives without jeopardizing their exterior grade quality.

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