

The Chemistry and Development of Tannin-Based Weather- and Boil-Proof Cold-Setting and Fast-Setting Adhesives for Wood

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Synopsis

Condensed tannins, being phenolic in nature, can be chemically modified to undergo reaction with formaldehyde in such a way that the adhesives formed harden at ambient temperature in industrially meaningful times. Resorcinol, *m*-hydroxyaniline, and their condensation products with formaldehyde and/or tannin resoles have been used for this purpose. The optimum conditions of application, such as paraformaldehyde amount, pH, and open and close assembly times, were used when comparing the different resins prepared. Results satisfying the requirements of international standard specifications and comparable to those of phenol/resorcinol/formaldehyde cold-setting resins were obtained.

INTRODUCTION

The use of polyflavonoid of vegetable origin as thermosetting adhesives for wood products is not new. However, no formulation passing the requirements of international standards has been advanced for tannin-based weather- and boil-proof cold-setting wood adhesives.

This paper deals with the development of tannin-based weather- and boil-proof cold-setting adhesives and of very fast-setting tannin-based adhesives for wood, named in this paper simply as fast-setting adhesives. As previously reported,⁵ the main problem of simple tannin/formaldehyde mixtures used as adhesives is the limited intermolecular crosslinking. In the case of cold-setting adhesives, another problem is added to the previous one: the chemical species used to increase the crosslinking must be highly reactive to give an adhesive capable of curing at ambient temperature in a reasonable time.

This paper deals with such chemical modifications of tannins that they can be set and cured by formaldehyde at ambient temperature. The commercially available tannin of the wattle tree (*Acacia mearnsii*), extracted by cold leaching, was used for this study.

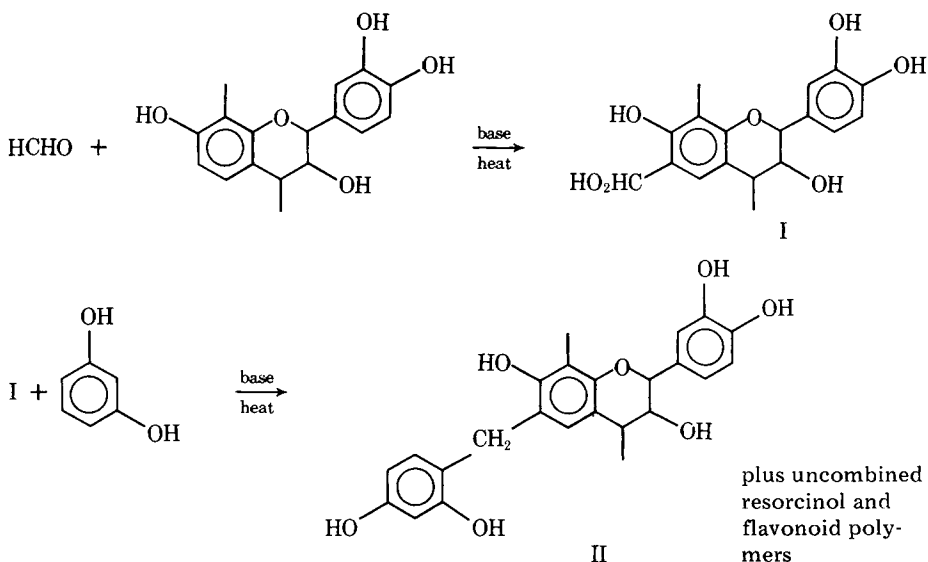
Cold-Setting Adhesives

Four different approaches were used:

1. **Grafting of Resorcinol on a Tannin/Formaldehyde Resole.** The

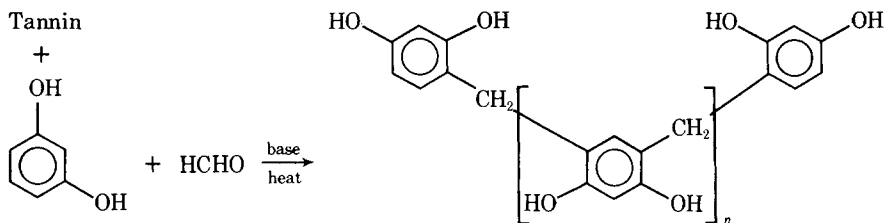
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reactions involved are as follows:



Mix II is an adhesive that can be set at ambient temperature by addition of para-formaldehyde.

2. **Simultaneous Synthesis of Resorcinol/Formaldehyde and Flavonoid/Formaldehyde Condensates.** The reactions involved are as follows:

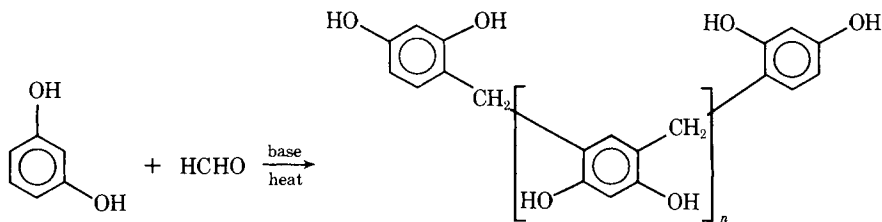


III with $n \geq 0$, IV ($-\text{CH}_2\text{-flavonoid polymer-CH}_2\text{-}$), uncombined resorcinol, and uncombined flavonoid polymers

lows:

The mixture of III, IV, uncombined resorcinol, and uncombined flavonoid polymers (mix V) is an adhesive that can be set in the cold by addition of para-formaldehyde.

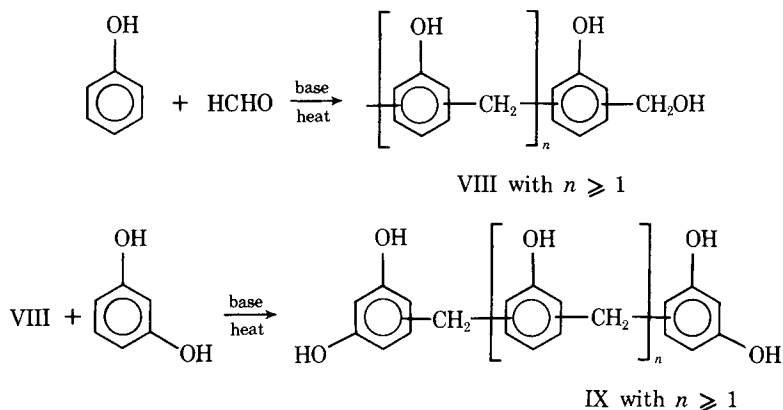
3. **Synthesis of Stable Resorcinol/Formaldehyde Condensates and Subsequent Addition to Flavonoid Polymers.** The reactions involved are as follows:



VI with $n \geq 0$ and uncombined resorcinol

The mixture of VI and uncombined resorcinol is then mixed with a solution of untreated flavonoid polymers to give an adhesive that can be set at ambient temperature by addition of paraformaldehyde.

4. **Synthesis of Stable Phenol/Resorcinol/Formaldehyde Resins and Subsequent Addition to Flavonoid Polymers.** To decrease the amount of resorcinol necessary in case 3 above, a phenol/resorcinol/formaldehyde polymer was prepared and then mixed with untreated flavonoid polymers:



Compound IX is then mixed with untreated flavonoid polymers to form an adhesive that can be set at ambient temperature by addition of paraformaldehyde.

Fast-Setting Adhesives

m-Hydroxyaniline was used, in combination with tannins, to produce very fast cold-setting adhesives. Two different approaches were used:

5. **Grafting of *m*-Hydroxyaniline on a Tannin/HCHO Resole.** The reactions involved are the same as in case 1 above, with the resorcinol substituted by *m*-hydroxyaniline.

6. **Synthesis of a Stable *m*-Hydroxyaniline/Phenol/Formaldehyde Resin and Subsequent Addition of Flavonoid Polymers.** The reactions involved are the same as in case 4 above, with the resorcinol substituted by *m*-hydroxyaniline.

In both adhesives 5 and 6, reaction of methylol groups and/or formaldehyde with the amino group of *m*-hydroxyaniline is also possible.^{7,8}

EXPERIMENTAL

Resin Preparation

Adhesive 1. A mixture of 90 parts of a 66.7% aqueous solution of commercial wattle extract, 9.6 parts of a 38% formalin solution, 30 parts methanol, and 0.3 part of a commercial defoamer was prepared at ambient temperature. The mixture was brought to reflux (76°C) in 10–15 min and held refluxing for 120 min at pH 4.5. Then 30 parts 99% resorcinol in 30 parts water were added,

dropping the temperature to 62°C; and 2.4 parts of a 25% aqueous solution of sodium hydroxide were added. The mixture was again brought to reflux in 5 min and held refluxing for 60 min. The excess methanol was then distilled off till the resin was in a 80/20 water/methanol solution, and the mixture was then cooled and stored.

Adhesive 2, Case 1. A mixture of 259 parts of a 58% aqueous solution of commercial powder wattle extract (containing 6% moisture), 42.2 parts methanol, 0.8 part of a commercial defoamer, and 74.9 parts 99% resorcinol was prepared at ambient temperature. To this mixture 24.5 parts 38% formalin solution and 20 parts of a 45% aqueous sodium hydroxide solution were added still at ambient temperature. The mixture was brought to 70°C and held there for 1 hr, then cooled and stored.

Adhesive 2, Case 2. A mixture of 285 parts of a 52.5% aqueous solution of commercial powder wattle extract (containing 6% moisture), *no methanol*, 0.8 part of a commercial defoamer, and 74.9 parts 99% resorcinol was prepared at ambient temperature. To this mixture 24.5 parts of a 38% formalin solution and 20 parts of a 45% aqueous sodium hydroxide solution were added at ambient temperature. The mixture was then brought to 70°C and held there for 1 hr, then cooled and stored.

Adhesive 3. A mixture of 89.1 parts 99% resorcinol and 20.9 parts of a 38% formalin solution was prepared at ambient temperature, and then 5.0 parts of 40% aqueous sodium hydroxide solution were slowly added and the mix brought to reflux (93°C) and held refluxing for 60 min, cooled, and stored. 80 parts of the resorcinol/formaldehyde resin prepared were added to 180 parts of a 64% aqueous solution of commercial powder wattle extract (containing 6% moisture), 0.6 part of a commercial defoamer, 32.3 parts methanol, and 13.0 parts of a 45% aqueous sodium hydroxide solution.

Adhesive 4. A mixture of 40.3 parts 100% phenol and 35.2 parts of a 38% formalin solution was prepared at 25°C. Then 2.75 parts of a 40% aqueous sodium hydroxide solution were slowly added and the mix brought to reflux (91°C) and held refluxing for 60 min; then 18.8 parts 99% resorcinol were added dropping the temperature to 68°C. The mixture was brought again to reflux (93°C) for 60 min and then cooled and stored. 50 parts of the phenol/resorcinol/formaldehyde resin prepared were added to 182 parts of a 55% aqueous solution of commercial powder wattle extract (containing 6% moisture) and 23.7 parts methanol.

Adhesive 5. A mixture of 90 parts of a 66.7% aqueous solution of powder commercial wattle extract, 9.2 parts of a 38% formalin solution, 30 parts methanol, and 0.3 part of a commercial defoamer was prepared at ambient temperature, and the mixture was brought to reflux (75°C) and held refluxing for 120 min. Then a solution of 10 parts 99% *m*-hydroxyaniline in 60 parts ethanol and 2.4 parts 25% aqueous sodium hydroxide solution were added. The mixture was held refluxing for a further 60 min, then cooled and stored.

Adhesive 6, Case 1. A mixture of 12.8 parts 100% phenol, 3.2 parts methanol, and 3.9 parts water was prepared at ambient temperature and warmed, and 6.2 parts 96% paraformaldehyde and 4.0 parts of a 14% aqueous sodium hydroxide solution were added. The mixture was brought to reflux (90°C) and held refluxing for 1 hr; 22.7 parts *m*-hydroxyaniline were then added, the temperature was held refluxing for a further 1 hr, and the mixture was cooled and stored.

Then 15 parts of the *m*-hydroxyaniline/phenol/formaldehyde resin prepared were added to a solution composed of 10 parts commercial powder wattle extract (containing 6% moisture), 8.0 parts water, 2.8 parts methanol, 0.1 part of a commercial defoamer, 0.4 part of a commercial wetting agent, and 1.6 part of a 45% aqueous sodium hydroxide solution.

Adhesive 6, Case 2. A mixture of 12.8 parts 100% phenol, 3.2 parts methanol, and 3.9 parts water was prepared at ambient temperature. The mixture was warmed and 4.3 parts 96% paraformaldehyde and 2.5 parts of a 14% aqueous sodium hydroxide solution were added. The mixture was brought to reflux (90°C) and held refluxing for 1 hr; 8.2 parts *m*-hydroxyaniline were then added and the mixture was held refluxing for a further 1 hr and then cooled. Fifteen parts of the *m*-hydroxyaniline/phenol/formaldehyde resin prepared were added to a solution composed of 10 parts commercial powder wattle extract (containing 6% moisture), 8 parts water, 2.8 parts methanol, 0.1 parts of a commercial defoamer, and 0.4 part of a commercial wetting agent. To this mixture 1.6 part of a 45% aqueous sodium hydroxide solution were added.

The molar ratios of the various ingredients used in each resin are shown in Table I, assuming a wattle "reactive" unit to have a molecular weight of 272 and taking into account that only 80% of wattle commercial extract is composed of flavonoids usable for adhesive.

Characterization Of Isolated Resin Fractions

Resins VI and IX were acidified with trichloroacetic acid and separated by TLC of kieselgel no. PF254 using a 70:30 benzene-acetone solvent for resin VI and 50:50 benzene-acetone solvent for resin IX. The fractions separated by TLC were then scraped off the plate and washed with acetone, the acetone solution dried on a rotary evaporator and the residues analyzed by mass spectrometry.

Resin V was also separated by TLC under the same conditions. And by comparison of plates developed with 1% formalin and 99% concentrated sulfuric acid, it showed the formation of the same polymers of resin VI with the formation also of reaction products between tannin and formaldehyde.

Resin VI was also separated in the different constituents by column chromatography using a 50:50 benzene-acetone solvent on 300-mesh silica gel. The different fractions were analyzed by both mass spectrometry and NMR. The different species isolated in the cases examined are shown in Table II.

Preparation of Glue Mixes

For all the resins prepared, to 100 parts solid resin 16 parts of a 96-97% powder paraformaldehyde of medium or high reactivity, 7 parts 200-mesh coconut shell flour, 7 parts 200-mesh wood flour, 1 part of a commercial wetting agent, and enough water to bring the viscosity of the glue mix to 2600-3000 centipoises were added.

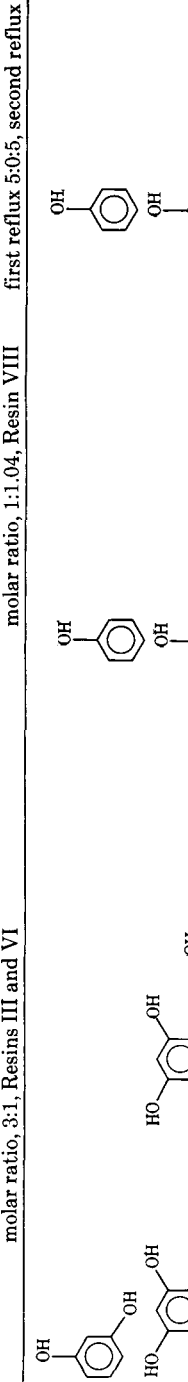
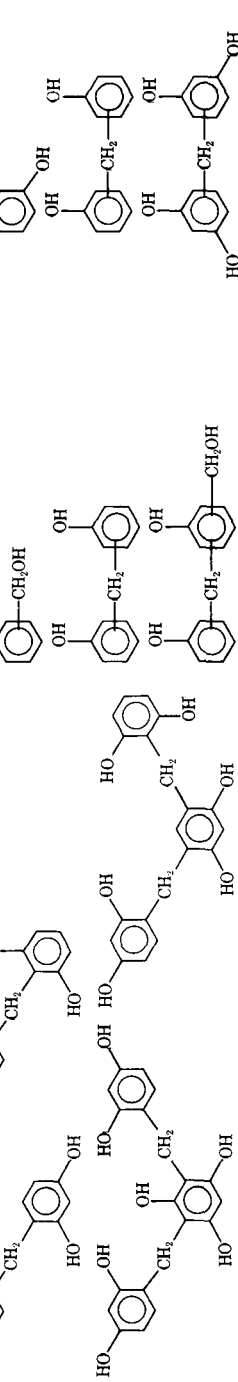
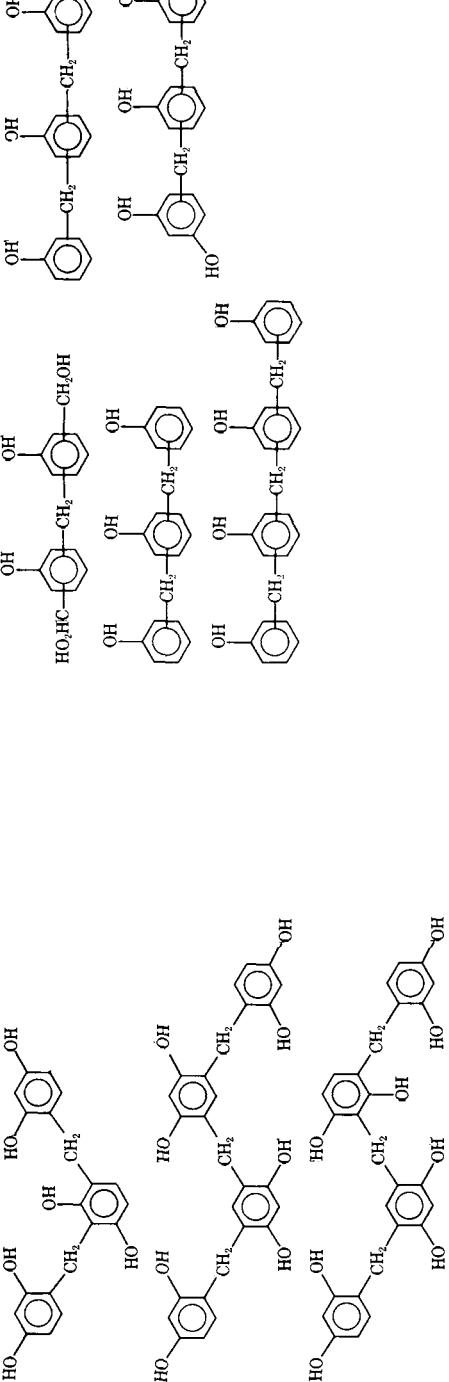
In the case of adhesives 1, 2, 3, and 4, enough of a 40% aqueous sodium hydroxide solution was added before the addition of paraformaldehyde to obtain a usable potlife of the glue mix of 2½-3 hr at 25-27°C.

The pH needed for the glue mixes to have such a potlife was 7.49-7.55 when a high-reactivity powder paraformaldehyde (namely, 96% Degussa) was used

TABLE I
Molar Ratios of Resins

Adhesive	Commercial wattle extract (MW 272)	Wattle tannin (MW 272)	Formaldehyde (MW 30)	Resorcinol (MW 110)	<i>m</i> -Hydroxyaniline (MW 103)	Phenol (MW 94)
Resin 1	1.25	1.0	0.69	1.53	—	—
Resin 2,1	1.25	1.0	0.70	1.53	—	—
Resin 2,2	2.2	1.0	0.71	1.53	—	—
Resin 3	0.76	0.61	0.33	1.0	—	—
Resin 4	1.66	1.33	1.04	0.395	—	1.0
Resin 5	1.25	1.0	0.66	—	0.51	—
Resin 6,1	0.89	0.71	1.75	—	1.53	1.0
Resin 6,2	0.59	0.47	1.01	—	0.55	1.0

TABLE II
Characterization of Isolated Resin Fractions

Resorcinol-formaldehyde molar ratio, 3:1, Resins III and VI	Phenol-formaldehyde molar ratio, 1:1.04, Resin VIII	Phenol-resorcinol-formaldehyde molar ratio first reflux 5:0:5, second reflux 5:2:5, Resin IX
		

and 7.87–7.93 when a medium-reactivity powder paraformaldehyde (Synthite 97% OP) was used. In the case of adhesive 6, enough 40% aqueous sodium hydroxide solution was added before the addition of paraformaldehyde to reach pH 9.0–9.1, and a medium reactivity paraformaldehyde was used. In the case of adhesive 5, enough 40% aqueous sodium hydroxide solution was added before the addition of paraformaldehyde to reach pH 7.9, and a medium reactivity paraformaldehyde was used.

Testing

All the adhesives prepared were tested on beech strips of 12–14% moisture content, for gap-filled and close-contact joints, according to British Standard BS1204 1965, parts 1 and 2, for synthetic resin adhesives, and the South African Bureau of Standards provisional specification for synthetic resin adhesives.

The requirements of the BS1204 1965 are the following:

	<u>Close-contact joints</u> shear strength, psi	<u>Gap-filled joints</u> shear strength, psi
Dry	—	—
24 hr Cold water soaking	500	400
6 hr Boiling	325	225

The SABS provisional specification, instead, takes into account only close-contact joints. The shear strength requirements are the same as for BS1204 1965, but as an additional requirement a minimum of 75% wood failure is required. The beech strips were glued with an open assembly time of 15 min and a closed assembly time of 30 min clamped under constant pressure for 24 hr, cured at 24°–27°C, and aged for a further five days at ambient temperature before testing. The results are shown in Table II.

DISCUSSION

The results shown in Table III indicate that adhesive 1, 2, and 3 give very good results. The results shown in Table III are the best obtained. Adhesive 2, case 1, performs best. It must be noted, however, that the presence of methanol can lead to problems when the adhesive is used on an industrial scale, when the beams assembled are of particularly big size (25–30 meters or longer), as with the long assembly times necessary, the methanol tends to slowly evaporate from the open glue lines with consequent glue line drying. In these cases the use of adhesive 2, case 2, is preferable.

The importance of strict viscosity and pH control must again be stressed, particularly in regard to the type of paraformaldehyde used; namely, the pH of the resin must be chosen according to the paraformaldehyde used in such a way that a potlife of roughly 3 hr is obtained. Much longer potlife is conducive to much poorer results, and a much shorter potlife would be industrially unrealistic.

Adhesive 6, case 1, is the best of the fast-setting resins. Adhesive 5, notwithstanding the reasonable results obtained, is not good because of the problems of solubility that *m*-hydroxyaniline presents in such a system and the formation in some cases of lumps in the adhesive.

The fast-setting adhesives can be used only with fast automatic processes as

TABLE III
Shear Strength and Wood Failure of Cold-Setting and Fast-Setting Tannin-Based Adhesives

Adhesive	Close-contact joints						Gap filled joints					
	Dry		24-hr Cold soak		6-hr Boiling		Dry		24-hr Cold soak		6-hr Boiling	
	Shear strength, failure, psi	Wood %	Shear strength, failure, psi	Wood %	Shear strength, failure, psi	Wood %	Shear strength, failure, psi	Wood %	Shear strength, failure, psi	Wood %	Shear strength, failure, psi	Wood %
Resin 1	799	100	614	74	570	87	740	53	494	95	443	8
Resin 2,1	974	95	664	100	641	98	692	100	579	100	496	100
Resin 2,2	671	81	678	78	609	89	626	100	543	100	532	100
Resin 3	684	70	584	97	629	89	—	—	—	—	—	—
Resin 4	389	10	346	10	520	38	—	—	—	—	—	—
Resin 5	680	13	520	7	495	16	—	—	—	—	—	—
Resin 6,1	610	68	522	81	644	92	—	—	—	—	—	—
Resin 6,2	452	32	378	47	407	93	—	—	—	—	—	—
Commercial phenol/res./form. adhesive	849	100	687	94	701	97	—	—	—	—	—	—
Commercial phenol/res./form. adhesive diluted 50:50 with gum arabic	437	5	77	0	0	0	—	—	—	—	—	—

their setting time varies, according to pH and paraformaldehyde type, from 3 to 40 min. Alternatively, separate application systems for fast laminating and finger-jointing can be used, with one surface being glued with a resorcinol/tannin-based adhesive containing excess paraformaldehyde and the other surface glued with a fast-setting adhesive to which paraformaldehyde has not been added.

Simple mixtures of resorcinol/tannin/paraformaldehyde, without any pre-reaction, have also been tried with the same proportions of chemicals, but these mixtures are unreliable, giving only in rare cases reasonable results. The results obtained both in strength and especially in potlife are never reproducible.

As can be seen from Table III the results of these adhesives are comparable to those obtained with the control, a phenol/resorcinol/formaldehyde cold-setting adhesive. Furthermore, diluting a commercial phenol/resorcinol/formaldehyde cold-setting adhesive with gum arabic in the proportions of 50 parts adhesive solids and 50 parts gum arabic by weight, the adhesive loses most of its strength indicating that the wattle extract is not an inert filler not participating to the reaction.

All the cold-setting adhesives in this paper can be set at temperatures as low as 18°C, but the results would be lower than those shown in Table II. All the cold-setting adhesives in this paper can be spray dried and can be presented as two component adhesives: one component being the resin, in liquid or powder form, and the other component being the hardener, in powder form, composed of paraformaldehyde and fillers.

In the Republic of South Africa, a few plants are already using some of these wattle-based cold-setting adhesives, as economically they are highly competitive with phenol/resorcinol/formaldehyde cold-setting adhesives of similar performance.

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