The Chemistry and Development of Tannin/Urea–Formaldehyde Condensates for Exterior Wood Adhesives

A. PIZZI,* *Department of Chemistry, University of the Orange Free State, Bloemfontein, Republic of South Africa*

Synopsis

Novolak-like materials were prepared by condensation of urea–formaldehyde resins with resorcinol and/or resorcinolic A-rings of polyflavonoids such as condensed tannins. The copolymers formed were used as thermosetting and cold-setting exterior-grade wood adhesives. Condensation of tannins with small amounts of urea–formaldehyde resins can prevent the water deterioration normally experienced by the latter resins. Conversely, urea–formaldehyde resins improve crosslinking and strength of wood tannin–formaldehyde networks.

INTRODUCTION

Cold-setting and thermosetting tannin-based wood adhesives prepared by alkali- or acid-catalyzed polymerization of condensed tannins with formaldehyde have already been described as substitutes for synthetic phenolic resins.[1-9] A few of these adhesives[3,4] comply with the requirements of internationally recognized standards for weatherproof and boilproof wood adhesives. The distinguishing characteristic of many of these tannin-based adhesives is the necessity of increasing crosslinking by means of small amounts of simple phenolic polymers.[6] The use of commercial urea–formaldehyde resins, readily available and relatively inexpensive, in place of specially manufactured phenolic polymers as fortifiers for tannin-based adhesives would present economical and handling advantages. Urea–formaldehyde resins are not weatherproof and boilproof. However, there are positive indications that by copolymerizing small amounts of these resins with condensed tannins, the former are sufficiently shielded from the effect of cold and boiling water to prevent their normally experienced deterioration.[3]

This paper deals with the chemistry and development of new types of tannin-based adhesives for exterior-grade wood products. Urea–formaldehyde and resorcinol-terminated urea–formaldehyde resins are used to increase crosslinking of thermosetting tannin–formaldehyde networks. Tannin/urea–formaldehyde (UF)/resorcinol copolymers as well as resorcinol-terminated urea–formaldehyde resins are used for the preparation of weatherproof and boilproof tannin-based cold-setting adhesives. The primary object is the preparation of adhesives that are stable in the presence of moisture and heat and consequently are suitable for exterior use, which nevertheless use as "backbone resins" condensed tannins and the relatively inexpensive urea–formaldehyde resins as compared to the more

* Present address: National Timber Research Institute, Council for Scientific and Industrial Research, Pretoria, Republic of South Africa.

0021-8995/79/0023-2777$01.00

expensive resorcinol–formaldehyde resins that could solely be used for this purpose before.

The commercially available tannin extract of the bark of the black wattle tree (*Acacia mearnsii,* formerly *mollissima*) was used for this study. Different commercially available urea–formaldehyde resins were also used with comparable results.

The structure of the main polymeric constituents of wattle tannin may be represented as follows:
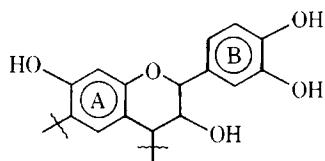
This flavonoid unit is repeated two to 11 times, and the different units are linked 4,6 with each other with the exception of the lower terminal unit:
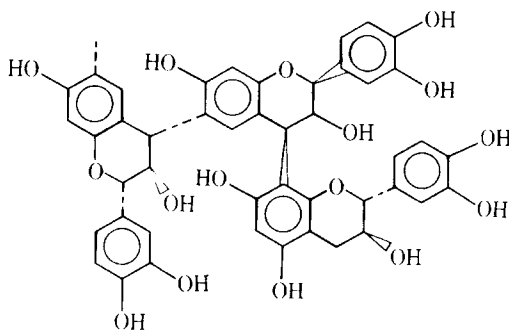
The latter flavonoid unit is very different from the other ones as the reactive A ring is phloroglucinolic in nature rather than resorcinolic as in the other units. The phloroglucinolic unit shows an 8-link with the resorcinolic unit that precedes it, indicating a condensation pattern 4,8 for phloroglucinolic units rather than 4,6 as in the case of the other resorcinolic units.[8]
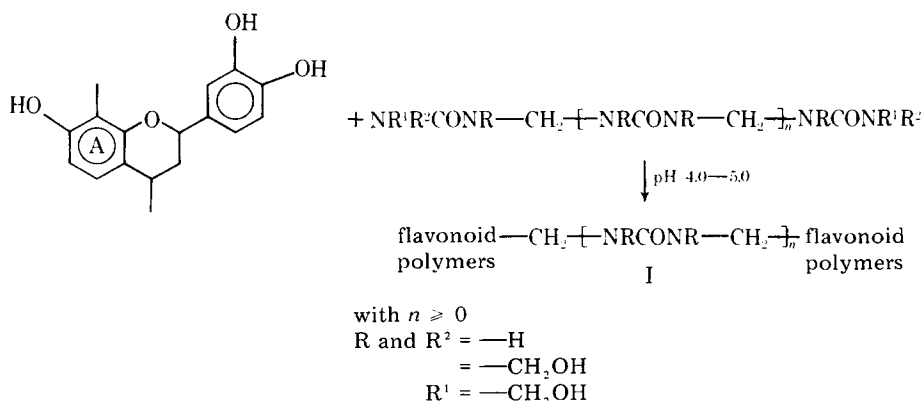
The nucleophilic centers on the A rings of any flavonoid unit tend to be more reactive than those found on the B ring. This is due to the vicinal hydroxyl substituents which merely cause general activation in the B ring without any localized effects as those found in the A ring. Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages to reactive positions of the flavonoid molecules, mainly the A rings. The reactive positions available on the A rings are the 8-position of all the resorcinolic flavonoid units, the 6- and 8-positions of the resorcinolic upper terminal flavonoid unit and the 6-position of the phloroglucinolic lower terminal unit. The resorcinolic A-rings show reactivity toward formaldehyde comparable to that of resorcinol.[6,7,9] Assuming the reactivity of phenol to be 1 and that of resorcinol 10, the resorcinolic A rings have a reactivity of 8 to 9. However, because of their size and shape, the tannin molecules become immobile at a low level of condensation with formal-

dehyde so that the available reactive sites are too far apart for further methylene bridge formation. The result is incomplete polymerization and therefore weakness. Bridging agents with longer molecules, such as phenol/formaldehyde condensates, have been shown capable of bridging the distances that are too large for methylene bridges.

Thermosetting Adhesives

The following two approaches have been used to prepare thermosetting urea–formaldehyde tannin-based adhesives.

1. Urea–formaldehyde/flavonoids condensates set and cured by addition of formaldehyde at elevated temperature:

$$+ NR^1R^2CONR{-\!-}CH_2{-\!\!\!\!\!\!+\!\!-}NRCONR{-\!-}CH_2{-\!\!\!\!\!\!+\!\!}_n NRCONR^1R^2$$

$$\downarrow pH\ 4.0{-\!-}5.0$$

flavonoid$-\!-$CH$_2\!\!-\!\!\!+\!\!-$NRCONR$-\!\!-$CH$_2\!\!-\!\!\!+\!\!-$ flavonoid
polymers   polymers

                I

with $n \geqslant 0$
R and $R^2 = {-\!-}$H
        $= {-\!-}$CH$_2$OH
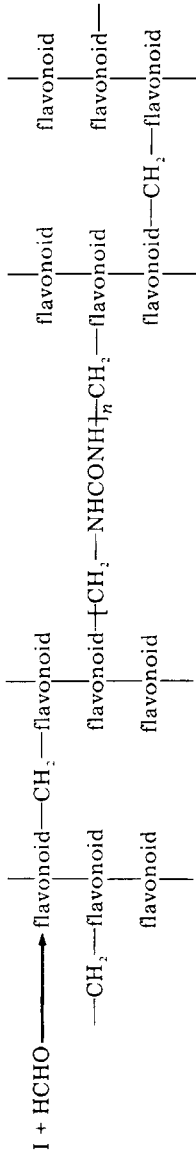$R^1 = {-\!-}$CH$_2$OH

Resin I is an adhesive that can be set and cured at elevated temperatures by addition of paraformaldehyde (see Scheme I):

2. Preparation of resorcinol/urea–formaldehyde condensates and curing of their mixture with flavonoid polymers by addition of paraformaldehyde at elevated temperatures:
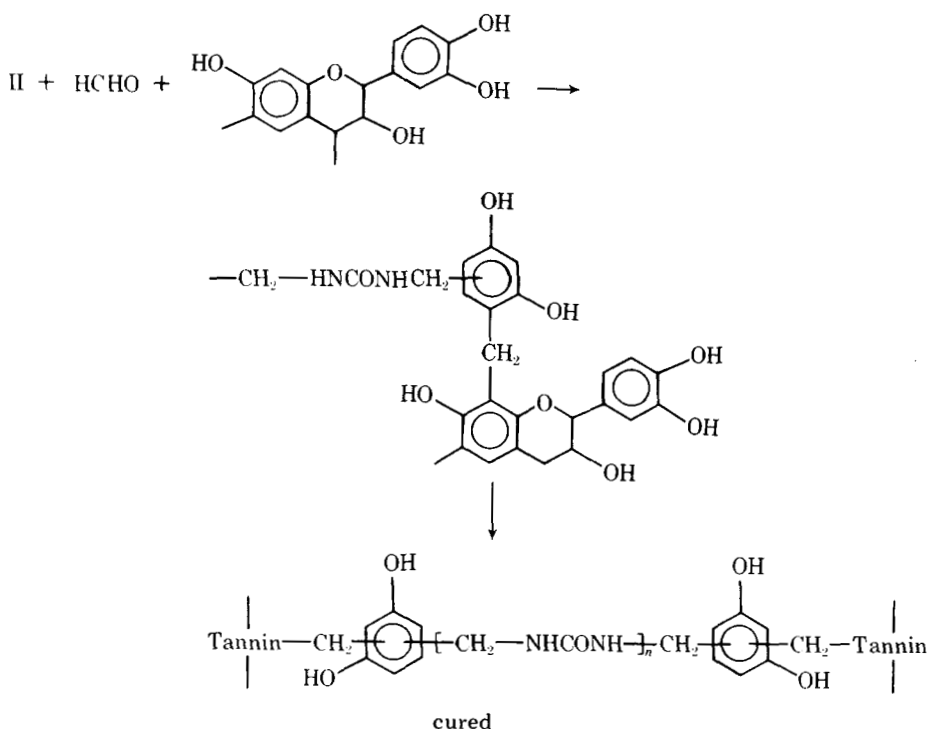

II
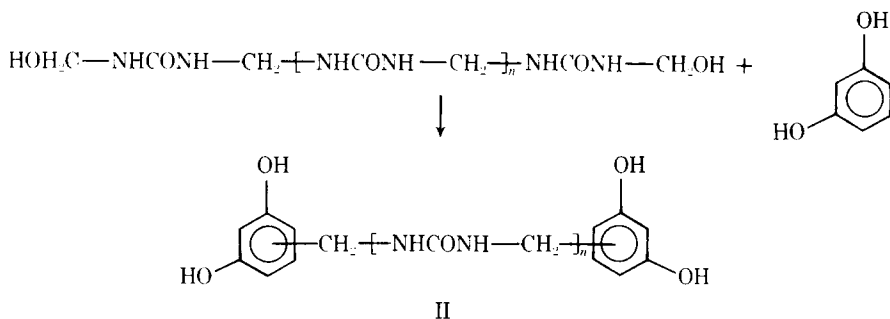
Polymer II, alone or when mixed with flavonoid polymers (tannin), is an adhesive that can be cured at elevated temperatures by addition of paraformaldehyde.

I + HCHO $\longrightarrow$

flavonoid—CH$_2$—flavonoid

—CH$_2$—flavonoid

flavonoid

flavonoid

flavonoid—[CH$_2$—NHCONH]$_n$—CH$_2$—flavonoid

flavonoid

flavonoid

flavonoid

flavonoid

flavonoid—CH$_2$—flavonoid

flavonoid—

cured resin

Scheme I

The reactions involved are the following:

II + HCHO + ⟶

—CH₂—HNCONHCH₂—

Tannin—CH₂—[—CH₂—NHCONH—]ₙ—CH₂—CH₂—Tannin

cured

In the preparation of adhesive 1, when small amounts of a urea–formaldehyde (UF) resin are added to a solution of wattle extract, copolymerization takes place immediately, at ambient temperature, giving a soft gummy mass easily redissolved by fast stirring and the addition of small amounts of water. In adhesive 1 the crosslinking of the prereacted condensates is due to the formation of methylene bridges among the flavonoids already UF-linked and between these and unreacted flavonoid units.

In adhesive 2, the crosslinking and curing of the resin are due to the formation of methylene bridges among the resorcinolic terminal groups of resin II and among these and the A-rings of the flavonoids, both of which compete for the formaldehyde.

Cold-Setting Adhesives

The following approaches were used to prepare cold-setting urea–formaldehyde/tannin-based adhesives.

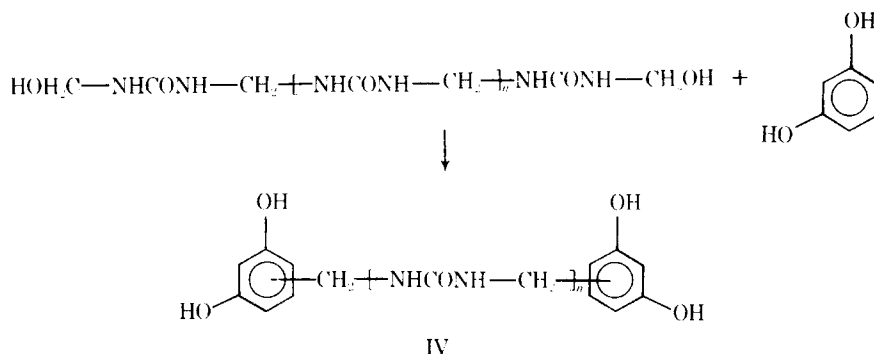3. Simultaneous formation of resorcinol–UF–resorcinol and flavonoid–

UF–flavonoid condensates.   The reactions involved are the following:
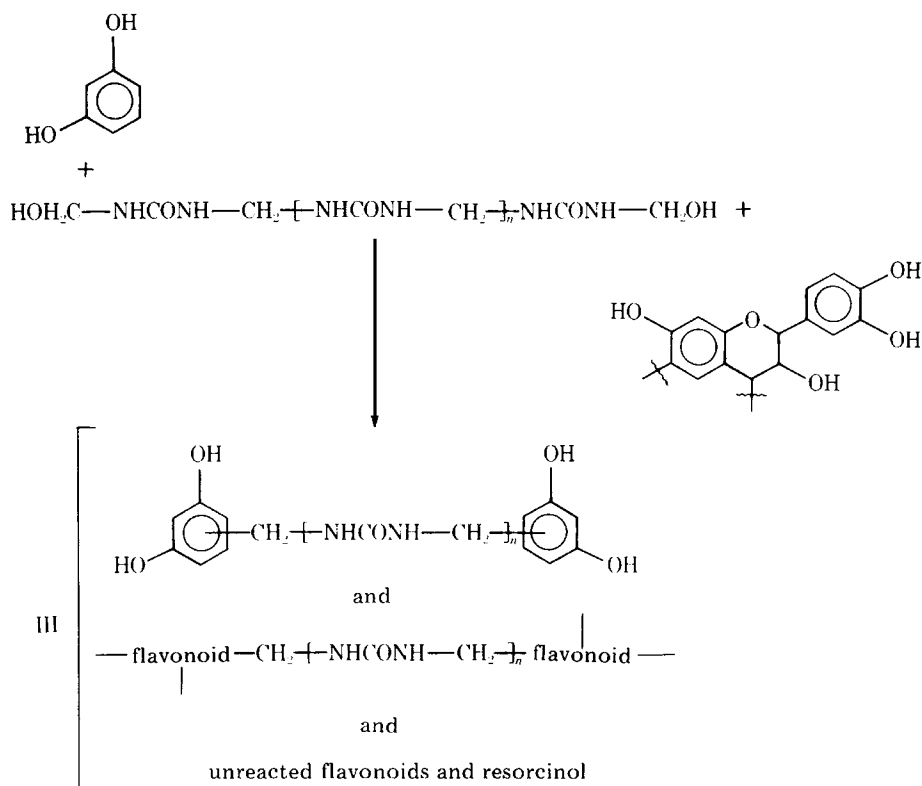
Mixture III is an adhesive that can be set and cured by addition of paraformaldehyde at ambient temperature:

$$III + HCHO \rightarrow \text{cured resin}$$
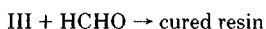
4.   Preparation of resorcinol–UF–resorcinol condensates and their subsequent addition to unreacted flavonoid polymers.   The reactions involved are the following:


The mixture of resin IV and unreacted flavonoid polymers is an adhesive that

can be set and cured at ambient temperature by addition of paraformaldehyde:

<div align="center">IV + unreacted flavonoid polymers + HCHO → cured resin</div>
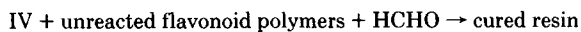
5.   Grafting of resorcinol on a tannin–UF resole.   The reactions involved are the following:

HOH$_2$C—NHCONH—CH$_2$—[NHCONH—CH$_2$—]$_n$NHCONH—CH$_2$OH   +

HOH$_2$C—HNCONH—[CH$_2$—HNCONH]$_n$

V

VI
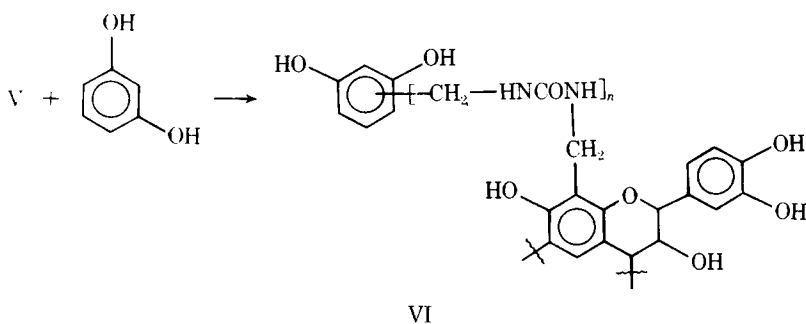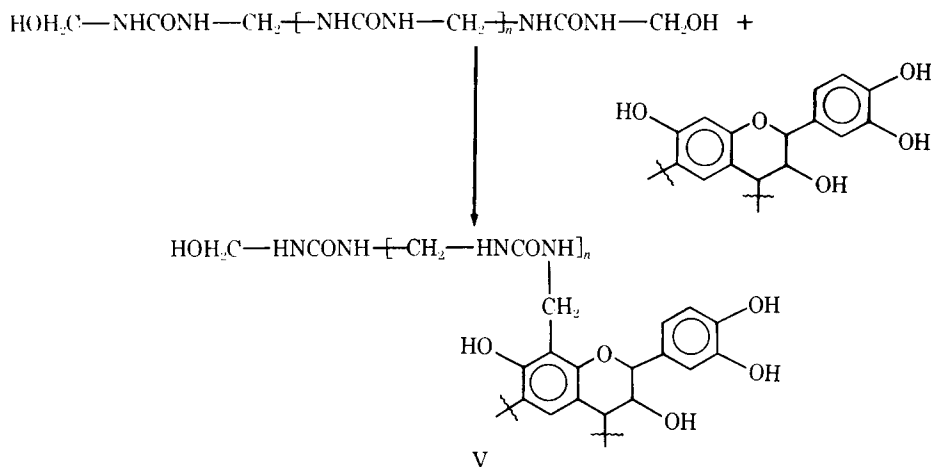
(plus small amounts of resorcinol–UF–resorcinol and flavonoid–UF–flavonoid condensates, uncombined resorcinol and uncombined flavonoids.)

Mixture VI is an adhesive that can be set at ambient temperature by addition of paraformaldehyde as follows:

<div align="center">2VI + HCHO</div>
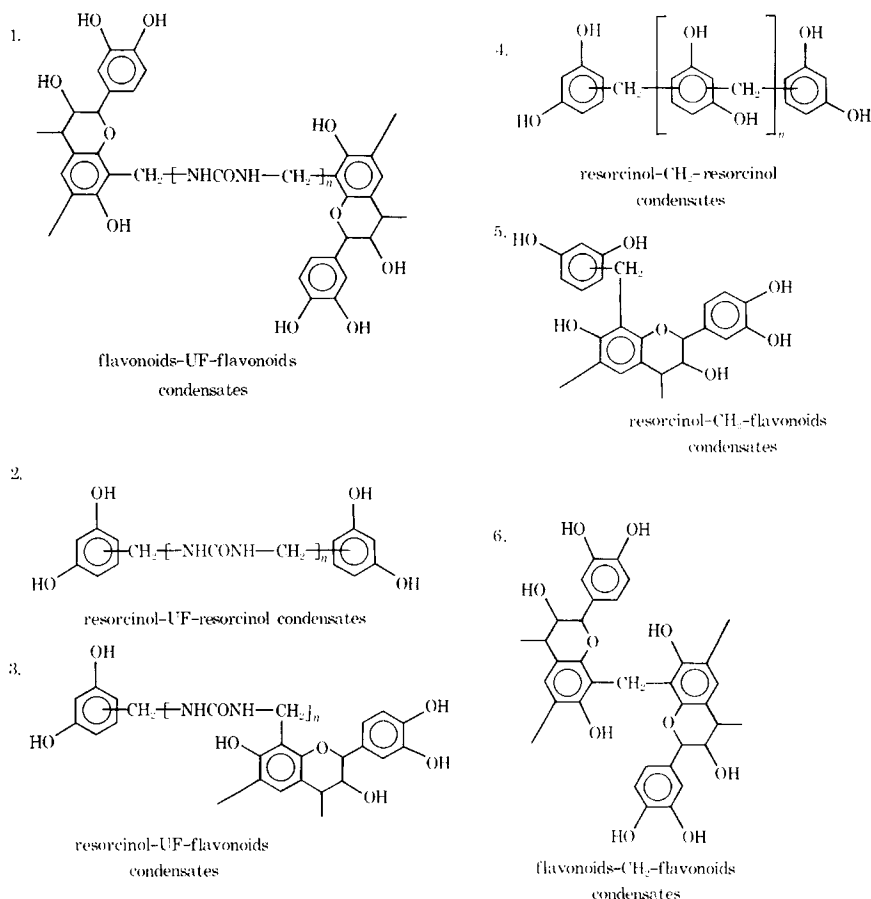

<div align="center">cured resin</div>
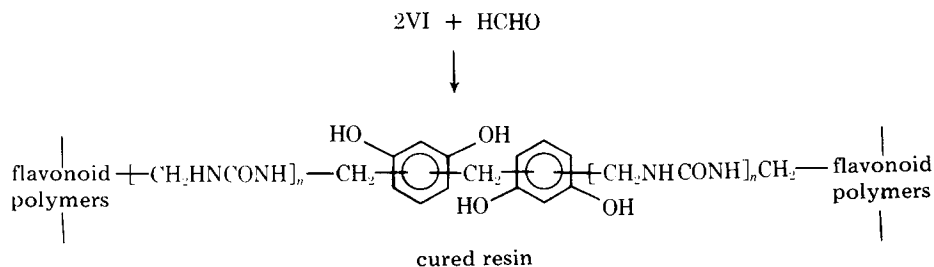
All the resins described can be prepared using different conditions of appli-

cation, and the number of products formed which are involved in the mechanism of curing are not as simple as implied by the formulae given.

The list of compounds listed in Table I can be formed in all the cold and thermosetting adhesives prepared, though in different proportions according to the process used. Furthermore, the presence of some of these compounds can

TABLE I
Polymers Formed by Reaction of Resorcinol, Urea–Formaldehyde Resins, and Condensed Flavonoids (Tannins) (Uncombined Resorcinol is Always Present)

1. flavonoids–UF–flavonoids condensates

2. resorcinol–UF–resorcinol condensates

3. resorcinol–UF–flavonoids condensates

4. resorcinol–CH_2–resorcinol condensates

5. resorcinol–CH_2–flavonoids condensates

6. flavonoids–CH_2–flavonoids condensates

7. Combination of 4 and 5 above (resorcinol–CH_2–resorcinol)$_n$$CH_2$–flavonoids condensates

8. Combination of 3 and 4 above (resorcinol-CH_2-resorcinol)$_n$-UF-flavonoids condensates

9. Combination of 2 and 5 above (resorcinol-UF-resorcinol)$_n$-CH_2-flavonoids condensates

10. Combination of 2 and 3 above (resorcinol-UF-resorcinol)$_n$-UF-flavonoids condensates

only be deduced or proved by indirect means.   By comparing the results obtained with cold-setting adhesives prepared according to different methods and/or conditions, it is possible to deduce which of the molecular species involved mostly contribute to the preparation of good tannin-based adhesives.

EXPERIMENTAL

Preparation of Thermosetting Adhesives

Adhesive 1. One hundred parts by mass of a 50% aqueous solution of wattle extract was mixed with 0.25 part of a commercial defoamer and 8.6 parts of a 63.8% commercial urea–formaldehyde resin syrup.   A soft gummy mass was formed which was easily redissolved by addition of 5–10 parts water and further stirring.   This resin can be stored in spray-dried powder or liquid form before compounding the adhesive glue mix.

Adhesive 2.   Forty parts by mass of a 63.8% commercial urea–formaldehyde resin solution was mixed with 4 parts methanol, 25 parts water, and 30 parts 99% resorcinol.   The mixture was mechanically stirred for 1–15 min at ambient temperature, and 825 parts of a 50.2% aqueous wattle extract solution mixed with 2 parts commercial defoamer was then added and stirring continued at ambient temperature for another 10–15 min.

Preparation of Cold-Setting Adhesives

The quantities of chemicals used are the same for all the three types of cold-setting adhesives prepared, in parts by mass, as follows: wattle extract 59.2% solution, 95; commercial defoamer, 0.3; methanol, 3.4; water, 7.2; urea–formaldehyde 63.8% syrup, 20.3; resorcinol, 26.3; caustic soda 40% solution, 7.9; glacial acetic acid (adhesive 4-3 only), 10.0.

Adhesive 3.   The wattle extract aqueous solution is mixed with methanol, water, and resorcinol at ambient temperature.   Urea–formaldehyde (UF) resin syrup and caustic soda solution are added and the mixture brought to reflux for 1 hr.   The adhesive mixture is then cooled and stored.

Adhesive 4.   Different preparation procedures were used for this adhesive. The quantities of chemicals used are the same as those for adhesive 3.   For *adhesive 4-1,* resorcinol, methanol, water, urea–formaldehyde syrup, and caustic soda solution are mixed together and mechanically stirred at ambient temperature for 1 hr.   This mixture is then added to the wattle extract solution and stored before the preparation of the glue mix.   For *adhesive 4-2,* resorcinol, methanol, water, urea–formaldehyde syrup, and caustic soda solution are mixed and refluxed under stirring for 30 min (86°C).   The wattle extract solution is then added and the mixture refluxed for another 30 min, then cooled and/or stored before the preparation of the glue mix.   For *adhesive 4-3,* resorcinol, methanol, water, urea–formaldehyde syrup, and glacial acetic acid are mixed and heated under stirring for 30 min (77°C).   A mixture of wattle extract solution, defoamer, and caustic soda solution is then added and the mixture refluxed under stirring for 30 min (95°C).

Adhesive 5.   The proportions of chemicals are the same as those for adhesive 3.   Wattle extract solution, methanol, water, and urea–formaldehyde resin syrup

are mixed under mechanical stirring for 1½ hr at ambient temperature (adhesive 5-1) or at reflux (adhesive 5-2). The refluxed material gelled in the vessel. To the ambient temperature material resorcinol and caustic soda solution are then added and the mixture refluxed for 30 min, cooled, and/or stored before the preparation of the glue mix. Adhesive 5-2 gelled in the vessel before the addition of resorcinol.

Characterization of Isolated Resin Fractions

Resins II and IV and their variations produced in acid or alkaline conditions were acidified, when necessary, to litmus pink with 50% trichloroacetic acid. The mixture was then diluted with acetone. After about 150% dilution, the higher aminoplastic condensates formed precipitated out of solution and the liquid, containing the simpler aminoplastic–resorcinol condensates, was decanted and separated by TLC on Kieselgel PF254 using a 70:30 benzene–acetone solvent. The TLC separation yielded two fractions, which were then scraped off the plates and washed with acetone. The acetone solution was dried on a rotary evaporator and the residues analyzed by mass spectrometry. The samples were analyzed with an electrical field quadrupole mass spectrometer with 2-sec scanning over a 10-min period. A series of maximum quantity peaks were noticeable over the total scanning period. A few of them in both TLC fractions corresponded to spectra of resorcinol/formaldehyde polymers already reported.[4,6] In both TLC fractions two maximum quantity peaks were noticeable over the total scanning period: one peak at about 2 min, corresponding to M+ 182, and one peak at about 4 min, corresponding to M+ 212. A third peak after 5 to 5½ min and corresponding to M+ 242 was present only in the lower Rf TLC band. The mass spectra corresponding to higher molecular ions quantities for each of the five compounds were printed. On the basis of (i) fragments detected by mass spectrometry, (ii) the orientation of the substitution in model reactions of resorcinol with formaldehyde,[4,6] and (iii) the relative quantities of the compounds in the two chromatographic bands, the following structures were assigned:
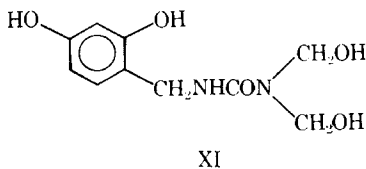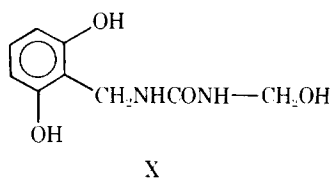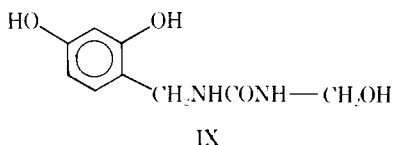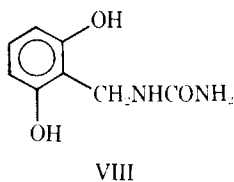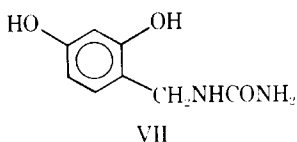
Variation in the position of the residual methylol groups of compounds IX, X, and XI cannot be ruled out.

From the mass abundances derived from the MS spectra it appeared that compound VII was more abundant than compound VIII. Compounds IX and X were about $1/3$ of the abundance of compounds VII and VIII, respectively. Compound XI was present only in traces and only in the lower Rf band.

(Dihydroxybenzyl)urea(VII) and (VIII): higher and lower Rf bands: M+ 192(53), *m/e* 165(48), 150(3), 149(20), 138(17), 123(39), 122(92), 73(7), 44(26), 43(100).

(Dihydroxybenzyl)methylolurea IX and X: higher and lower Rf bands: M+ 212(4), *m/e* 195(2), 182(4), 182(2), 165(11), 150(4), 149(23), 138(4), 123(33), 122(25), 86(4), 73(10), 44(14), 43(100).

(Dihydroxybenzyl)dimethylolurea XI: higher and lower Rf bands: M+ 242(5), *m/e* 212(4), 183(4), 182(15), 165(7), 150(3), 149(17), 138(4), 123(24), 122(21), 86(4), 85(4), 73(10), 44(36), 43(100).

The same five compounds were isolated from all the different variations of resins II and IV prepared.

Preparation of Glue Mixes

The glue mixes were prepared by mixing the components shown in Table II. Enough water was added to both glue mixes to reach an initial glue mix viscosity of 2500–3500 centipoises at 22°C.

Cold-Setting Adhesives

For all the resins prepared, to 100 parts by mass of resin solids was added 16 parts of a 96% paraformaldehyde powder of medium-high reactivity, 7 parts of 200 mesh coconutshell 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 2500–3500 centipoises. To all the adhesives, with the exception of adhesive 5-2 that gelled in the vessel, enough of a 40% aqueous sodium hydroxyde solution or glacial acetic acid was added before the addition of paraformaldehyde to obtain a glue mix of pH 8.1. The usable pot life of all the adhesives prepared was approximately 1 hr 20 min.

TESTING

Thermosetting Adhesives

Triplicate plywood panels 60 × 60 cm in dimension were prepared using sapele mahogany veneers in the following conditions: press temperature, 125°C;

TABLE II
Glue Mixes

Thermosetting adhesives	Parts by mass	
	Adhesive 1	Adhesive 2
Adhesive 1, liquid as from resin preparations	100	—
Adhesive 2, liquid as from resin preparations	—	100
96% Paraformaldehyde, 180 mesh	4.8	7
Coconut shell flour, 200 mesh	7.9	11.4
pH Adjusted to	4.9	6.5

pressing time 6 min pressure 250 psi; pre-pressing time, 10 min at 79 psi; open assembly time, 10 min; closed assembly time, 4 hr; glue spread, 180 g/m² s.g.l. (74 lb/MDGL); panel construction, 5 ply, each 1 mm thick.

After manufacture the plywood panels were hot-stacked overnight in an insulated box, then trimmed and cut into four 12.5 × 12.5 cm squares. Nine squares for each of the triplicate panels were used to knife test the panels—three dry, three after 24 hr of cold water soaking, and three after 72 hr of boiling. The knife test was evaluated in terms of British Standard BS 1088, 1957, 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 no glue line shall have an overall quality of less than 2 and the average value for all glue lines tested shall not be less than 5. The plywood knife test results are shown in Table III.

Cold-Setting Adhesives

All the adhesives prepared were tested on beech strips of 10% to 12% moisture content, for gap-filled and close-contact joints, according to the British Standard BS 1204, 1965, parts 1 and 2, for synthetic resin adhesives and the South African Bureau of Standards (SABS) provisional specification for synthetic resin adhesives. The requirements of BS 1204, 1965, are the following: 24-hr cold water soaking, 500 psi for close-contact joints and 400 psi for gap-filled joints; 6-hr boiling, 325 psi for close-contact joints and 225 psi for gap-filled joints.

The SABS provisional specification takes into account only-close contact joints; the shear strength requirements are the same as for BS 1204, 1965, but as an additional requirement a minimum of 75% wood failure in the cold soaking and boiling test are 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 16–24 hr, cured at 24–26°C, and aged for a further five days at ambient temperature before testing. One hundred and twenty glued beach strip specimens for each of the adhesives were tested: 60 for close-contact and gap-filled joints, respectively; 20 dry, 20 cold water soaked for 24 hr, and 20 boiled for 6 hr. The results are shown in Table IV. In the same table, for comparison, are shown the results obtained under the same conditions with a commercial phenol/resorcinol/formaldehyde cold-setting adhesive.

DISCUSSION AND COMMENTS

The results shown in Tables III and IV indicate that adhesives 1, 2, 3, 4, and 5 give good results. Both thermosetting adhesives give good results, though the use of adhesive 1 is preferable for economic reasons (absence of the expensive

TABLE III
Thermosetting Adhesives. Plywood Knife Test Results, Adhesives 1 and 2

Adhesive type	Dry average		24-hr cold soak average		72-hr boil average	
	Outer glue lines	Inner glue lines	Outer glue lines	Inner glue lines	Outer glue lines	Inner glue lines
1	10	10	9	10	10	9
2	10	10	10	10	10	9

TABLE IV
Cold-Setting Adhesives. Close-Contact and Gap Filled Joints Results—Adhesives 3, 4, and 5

Adhesive type	Close-contact joints						Gap-filled joints					
	Dry		24-hr cold soak		6-hr boil		Dry		24-hr cold soak		6-hr boil	
	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %	Shear strength, psi	Wood failure, %
3	786	88	671	83	639	91	654	91	546	100	562	100
4-1	542	4	668	42	633	83	—	—	—	—	—	—
4-2	687	65	596	85	585	75	614	79	532	84	544	82
4-3	576	3	458	14	511	20	—	—	—	—	—	—
5-1	817	78	668	83	545	98	661	75	593	80	515	100
Commerical phenol/res HCHO adhesive	829	100	665	94	697	96	729	89	567	96	552	95

resorcinol) and satisfy the requirements of the British Standard BS 1088, 1957. Cold-setting adhesives 3, 4-2, and 5 give excellent results and satisfy the requirements of the British Standard BS 1204, 1965, parts 1 and 2. Adhesives 4-1 and 4-3 give poorer results than adhesive 4-2. While pH and viscosity controls do not need to be strict for the two thermosetting adhesives, their importance must again be stressed as regards the three cold-setting adhesives. For the latter, starting glue mix viscosities of 2500–2800 centipoises and a 7.9–8.3 pH range are necessary. Lower pH will give poorer strength and wood failure results, while higher pH will considerably shorten the adhesive potlife. The pH range in which these tannin/urea–formaldehyde cold-setting adhesives are applicable is much wider than that needed for older tannin-based cold-setting formulations already reported.[4,5] Thus, their handling is easier. Potlife of the order of 1 hr 20 min to 1 hr 30 min is obtained with these cold-setting adhesives. Their potlife is shorter than that of older tannin-based formulations,[4,5] as the copolymers used have higher molecular weight and are of greater size; consequently a lower number of reaction steps is necessary to set the adhesive.

These adhesives, on accelerated testing, satisfy the requirements for weatherproof and boilproof adhesives of the relevant British Standard specifications.[10,11] This again confirms previous indications that urea–formaldehyde resins are protected from water attack once they copolymerize with condensed flavonoids.[3] The quantity of urea–formaldehyde solids should not be more than 15%–20% of total resin solids.[3] Much lower amounts of urea–formaldehyde resins (as low as 1/2 the amounts presented) can also be used. The results obtained will still be acceptable but definitely worse than those now reported.

The resorcinol/urea–formaldehyde condensates isolated from resins II and IV indicate that resorcinol/urea–formaldehyde copolymers can be formed under acid and alkaline conditions. By considering resorcinol as a model compound for the resorcinolic A rings of the flavonoid, these condensates indicate that copolymerization of urea–formaldehyde resins and tannins by reaction of the methylol groups of the UF resin with the resorcinolic A rings of the flavonoids is also possible.

It is interesting to compare the results obtained with the different cold-setting adhesives prepared in order to deduce which of the condensates formed contribute the most to the effectiveness of a good tannin-based cold-setting adhesive. In adhesive 3 all the species listed in Table I are formed. Condensates 2, 3, 1, and 4 are the most abundant of the simpler molecular species (1–6), in the order given. Condensate 4 is formed according to two routes only, namely: (i) by reaction of resorcinol with small amounts of formaldehyde unbound to the urea–formaldehyde resin and (ii) by reaction of resorcinol with formaldehyde formed by some splitting of aminoplastic bonds in the urea-formaldehyde polymer during reflux. The amount of condensate 4 formed in the former case is much less than that formed in the latter one.

In adhesive 4-1 the main condensate formed is polymer 2 (Table 1). Small amounts of condensate 4, formed by reaction of resorcinol with unbound formaldehyde present in the urea–formaldehyde resin are also present.

In adhesive 4-2 all the species are again present, with 2 and 4 being the more abundant condensates, in the given order, followed by condensate 6. Noticeable amounts of condensates 8 and 9 are also present.

In adhesive 4-3 the same species observed in adhesive 4-2 are present, but the

molecular weight of the urea–formaldehyde resin is higher. This indicates that, in the acid conditions used, the urea–formaldehyde resin autocondensation reaction and the urea–formaldehyde/resorcinol condensation are in competition. Thus, it is logical to expect the urea–formaldehyde resin increasing in size before its autocondensation reaction is stopped by reaction with resorcinol. As a consequence of the urea–formaldehyde resin higher molecular weight and the lower number of urea–formaldehyde terminal sites available for reaction with resorcinol an higher amount of unbound resorcinol has been found in this resin.

In adhesive 5-1 condensate 3 is the more abundant, followed by 1, 4, 5, and 6. All the other condensates are present to some extent with the exception of condensates 2, 9, and 10.

Adhesive 5-2 gelled in the vessel during preparation before resorcinol was added. This indicates that the formaldehyde formed by splitting of aminoplastic bonds in the urea–formaldehyde resin during reflux is enough to gel an already polymeric material such as a polyflavonoid tannin. This is not the case with resorcinol or other phenols of similar reactivity that are not already in polymeric form and that use much higher amounts of formaldehyde to form firstly polymeric condensates and then gel (see adhesive 4-2).

From all this an interesting conclusion is that a certain variety of condensates is needed to have an acceptable tannin/urea–formaldehyde/resorcinol cold-setting adhesive. The condensates that appear to contribute the most are 2, 3, and 4. Condensate 5 is not present in great quantity in any of the three cold-setting adhesives presented, and its contribution cannot be judged. However, this latter condensate is known to contribute considerably, together with condensate 4, to the strength of older cold-setting tannin-based adhesive formulations already reported.[4,5] In short, an abundance of one or more of condensates 2, 3, 4, and 5 should be present in order to obtain good results with a tannin-based cold-setting adhesive.

It is useful to note that the adhesive formulations reported give good results when condensed flavonoid tannins of mainly resorcinolic nature, such as wattle (mimosa), sulfited quebracho, and mangrove extracts are used. The formulations presented are not applicable to condensed flavonoid tannins of mainly phloroglucinolic nature, such as pine extracts, as the phloroglucinolic A-ring, far more reactive than resorcinol, would substantially alter the balance of reactivities of the different chemical species needed. The much higher molecular weights of the latter tannins as well as higher quantities of detrimental impurities add to their more marked unsuitablity for wood adhesives. Hydrolizable or gallic tannins are also unsuitable for the formulations presented. They are only mixtures of simple chemical species such as pyrogallol, catechol, and ellagic acid that are not in polymeric form and lack the high reactivity toward formaldehyde of condensed tannins. They can still be used for partial substitution of the phenol in phenol/formaldehyde adhesives; but, not being polymeric in nature, they afford a considerable loss in the amount of formaldehyde necessary. However, the condensed tannins of resorcinolic nature to which the formulations presented are applicable contribute about 90% of the commercially available tannin in the world.

The results of these adhesives are comparable to those obtained with commercial phenol/resorcinol/formaldehyde adhesives. In the Republic of South Africa a few plants are starting to use some of the thermosetting adhesives pre-

sented.   While quite a few local plants have for the past few years been using older types of tannin-based cold-setting adhesives,[4,5] the adhesives presented in this paper are now starting to be used.   Their potlife, excellent gap-filling properties, and ease of handling renders them particularly suitable for use by small workshops and operators.

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