## Tannin-Formaldehyde Exterior Wood Adhesives Through Flavonoid B-Ring Cross Linking

As reported by previous authors<sup>1</sup> the lack of strength of unfortified tannin-formaldehyde adhesives is caused by the low amounts of cross linking due to the formation of the early methylene bridges between the A rings of the long rigid flavonoid polymers and immobilizing the tannin-formaldehyde network while containing gaps too wide to be filled by other short methylene bridges, rendering useless any further reaction of formaldehyde on the flavonoid A rings. The problem of low crosslinking arises from the fact that in all industrially meaningful tannin-formaldehyde adhesives developed until now, only the highly reactive resorcinolic A rings of the flavonoids were utilized, the catecholic or pyrogollolic B rings presenting such a low reactivity that only in extreme conditions of pH, time, and temperature they would be able to condense with formaldehyde.

In the past the problem of low crosslinking has been overcome by the use of small amounts of longer crosslinking agents such as aminoplastic resins or simple phenolic polymers, with excellent results.

Fraser and coworkers<sup>2</sup> have shown that metallic bivalent ions are able to increase the amount of formaldehyde condensing with phenol in the preparation of phenolic resins during a short and finite period of time.

Hillis and Urbach<sup>3,4</sup> have also shown that formaldehyde uptake by catechin at pH 5.5 is much higher if zinc acetate is present and concluded that zinc acetate induces the catecholic B ring in catechin to react with formaldehyde at pH 5.5.

This finding was applied to wattle extract (bark extract of Acacia mearnsii) adhesives to try to form the following:



TABLE I Glue Mixes in Parts by Weight

	1	2	3
Wattle extract powder	58.5	58.5	58.5
Water	64.0	55.5	51.5
Defoamer	0.2	0.2	0.2
Zinc acetate	5.0	_	
Commercial urea-formaldehyde resin 63.8%	<del></del>	_	9.5
Paraformaldehyde 96% powder	7.0	7.0	6.3
Wood flour filler	2.0	2.0	2.0
Coconut shell flour filler	2.0	2.0	2.0
pH	5.0	5.0	5.0

Journal of Applied Polymer Science, Vol. 22, 2397–2399 (1978) © 1978 John Wiley & Sons, Inc.

0021-8995/78/0022-2397\$01.00

TABLE II Results from Glued Beech Strips	cold soak 6 hr boil	BS 1204 BS 1204 and SABS and SABS	3 require- 1 2 3 require- monte monte	651 >500 495 392 540 >325	85 >75 47 16 79 >75
	24 hı		1 2	713 583	90 31
	Dry	BS 1204 & SABS	require-	sinen.	ļ
			က	825	98
			73	683	64
	-		1	616	33
	Test		Glue mix No.	Shear strength, psi	% wood failure



obtained in all previous thermosetting wattle-based adhesives. Zinc acetate has been used to this effect, but all metallic bivalent ions could be used, though with less definite effects than the one mentioned. A control glue mix composed of only wattle extract and formaldehyde and a control glue mix of an already industrially successful aminoplastic fortified wattle-based adhesive were also tested.

## **EXPERIMENTAL**

Glue mixes in parts by weight were prepared as shown in Table I. These glue mixes were used to glue beech strips  $125 \times 25 \times 3$  mm glued overlap of  $25 \times 25$  mm, cured for 4 hr at 90°C at an equilibrium moisture content of 12%. The glued beech strips prepared and tested according to British standard 1204 part 2 for synthetic resin adhesives for wood<sup>5</sup> and SABS specification gave the results in Table II.

## DISCUSSION AND CONCLUSIONS

Notwithstanding a considerable improvement in strength and wood failure obtained by the use of zinc acetate on simple wattle extract formaldehyde glue mixes (compare results of glue mix Nos. 1 and 2), it is evident that fortified wattle-based adhesives, glue mix No. 3, are still the best. The zinc-acetate-wattle-formaldehyde resin does satisfy the requirements of BS 1204 that does not require wood failure, but does not satisfy the requirements of the more modern SABS specification in which % wood failure plays a more important part. It is evident from the results that a higher degree of cross linking has been obtained when using zinc acetate, but not high enough to be able to give the same degree of cross linking of fortified formulations.

## References

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Received June 15, 1977 Revised July 12, 1977

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