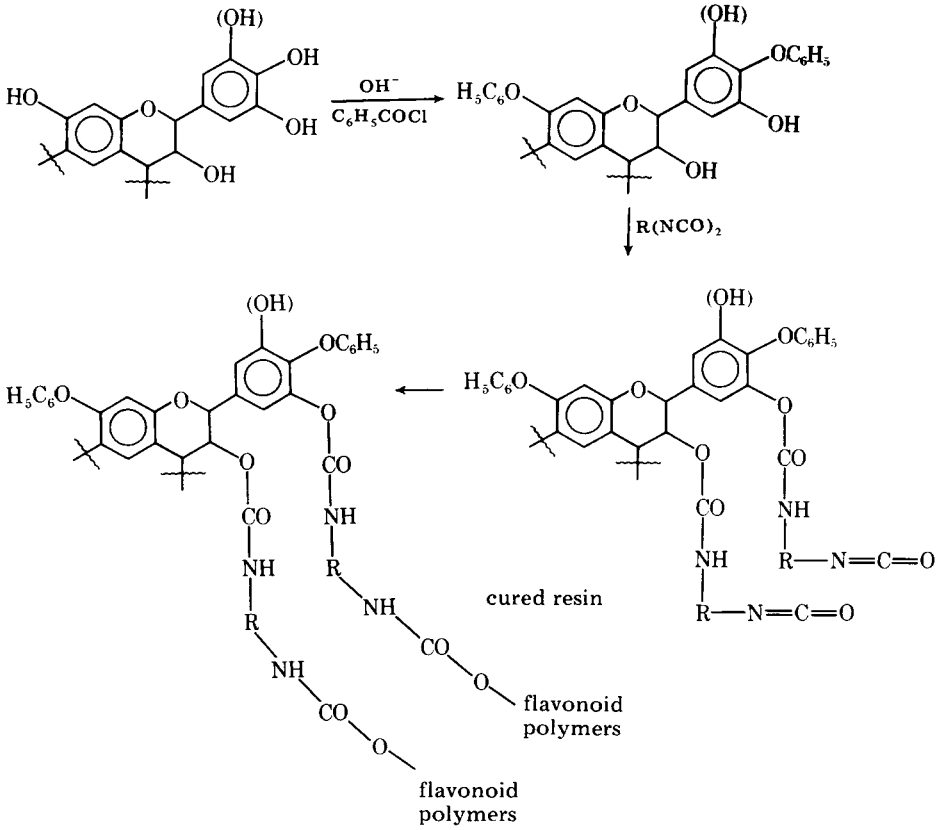
Tannin-Based Polyurethane Adhesives

Surface coatings of the polyurethane type with good resistance to weathering have been developed from diisocyanates with partially benzoylated wattle tannins as hydroxyl source.[1]

Tannins are polymers of flavonoid constituents which contain a high proportion of hydroxyl groups.[4] This high proportion of hydroxyl groups is undesirable in the production of tannin-based urethanes and needs to be reduced in order to limit reactivity with isocyanates. Benzoylation by the Schotten–Baumann method is used to reduce the number of reactive hydroxyl groups in the flavonoid molecule. Partially benzoylated tannins, prepared from the tannin extract, precipitate leaving untreated carbohydrates in aqueous solution.[4] Partial benzoylation confers solubility in the highly polar tannins in those solvent systems (e.g., cyclohexanane–butyl acetate; cyclohexanane–methyl ethyl ketone–acetone) required for reaction with diisocyanates.[4] The reactions involved are:



As economics is against condensed tannins being used in this type of adhesives, a further approach can be pursued. A small amount of a tannin-based cold-setting adhesive was added to a commercial polyurethane adhesive to increase the polyurethane strength and water resistance. The tannin-based cold-setting adhesive used has already been reported.[3] Other types of tannin-based cold-setting adhesives, already reported, can also be used.[2,3]

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EXPERIMENTAL

Adhesive 1. Thirty parts by weight wattle extract powder (bark extract of *Acacia mearnsii,* commercially available) was dissolved in 300 parts water, and 30 parts benzoyl chloride was added. Twenty-five parts of potassium hydroxide 20% solution was immediately added and the reaction mixture shaken vigorously. A light-brown solid settled out after a few minutes. The solid material was filtered, washed, and dried, giving a light-brown powder (35 parts). Twenty parts of this dibenzoylated flavonoid was dissolved in 20 parts of a mixture of cyclohexanane:methyl ethyl ketone:acetone 1:1:1 and then reacted with 50 parts of a commercially available diisocyanate (Desmodur 44 V20, Farbenfabriken Bayer AG, Leverkusen) using an isocyanate:hydroxyl ratio of 1:1:1.0 (wt:vol). The pot life of the adhesive was approximately 2 hr.

Adhesive 3. Fifty parts of a mixture of commercial tannin-based cold-setting adhesive for wood already reported (adhesive 2.1, ref. 2) and its hardener was added to 150 parts of a commercial polyurethane) adhesive for shoes (Aquaset, Bally shoes adhesives).

The two adhesives were applied according to British Standard BS1204, 1965, for synthetic resin adhesives for wood and to beech strips 125 × 25 × 3 mm in dimension, and such strips were glued in pairs at ambient temperature (25°C) with an overlap of 25 × 25 mm and clamped for 16 hr. The samples were tested dry and after 24 hr of cold-water soaking, and 6 hr boil (20 samples each). A commercial polyurethane adhesive was also used as control. The results and the requirements of the British Standard BS1204, 1965,[5] and of the more modern South African Bureau of Standards SABS provisional specification[6] are shown in Table I.

CONCLUSIONS

The results in Table I show that polyurethane adhesives can be produced by using wattle tannins as the hydroxyl source for the isocyanate. Furthermore, small amounts of tannin/formaldehyde cold-setting adhesives can be used to upgrade the performance of commercial polyurethane adhesives in the same way as synthetic phenol/formaldehyde resins are sometimes used for the same purpose. In the latter case it must be noted that the tannin also accelerated the setting of the polyurethane adhesive; an exothemic reaction between the tannin of the tannin/formaldehyde adhesive and the polyurethane takes place, indicating the probable formation of a tannin polyurethane copolymer though it is not certain to what extent this takes place.

Notwithstanding the compliance of adhesive 1 to British Standard BS1204, 1965, this adhesive shows poor or no wood failure, casting doubts on its usefulness as an exterior wood adhesive, although adhesive 1 could be used for applications other than for wood. The need for benzoylation, industrially impractical, and the small proportion of wattle tannin in the end product renders this adhesive industrially uneconomical, especially as other less expensive natural hydroxyl group sources are already available.

Adhesive 2 is more interesting as, notwithstanding the wastage of reactive isocyanate groups due to the presence of water in the tannin/formaldehyde fortifying resin, the expected upgrading effect of the polyurethane adhesive does take place. This is particularly evident from the increased percentage wood failure in all the tests and to much better results of both strength and percentage wood failure in the 6-hr boil test. Adhesive 2 satisfies the requirements of British Standard BS1204, 1965, for synthetic resin adhesives for wood but not the requirements of the SABS provisional specification. Increases of the ratio of tannin/formaldehyde adhesive:polyurethane adhesive up to 1:1 can be tolerated according to the type of polyurethane adhesive used. It is possible, though, that such an adhesive may be useful in fields other than wood.

TABLE I
Results of Tannin-Based Polyurethane Adhesives After Five Days of Aging[a]

	Compression Strength, psi		
	dry	24-hr cold soak	6-hr boil
Adhesive 1	684 (9)	515 (0)	409 (0)
Adhesive 2	925 (36)	608 (32)	545 (74)
Commercial polyurethane adhesive	916 (14)	576 (0)	433 (0)
BS1204, 1965 requirements	—	500 (—)	325 (—)
SABS provisional requirements	—	500 (75)	325 (75)

[a] % Wood failure in brackets.

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