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# THE FORMULATION AND INDUSTRIAL APPLICATION OF NATURALLY OCCURRING POLYPHENOL (TANNIN) ADHESIVES IN THE WOOD BASED PANEL INDUSTRY 1/

by

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CONTENT

## SUMMARY

The present stage in applying naturally occurring polyphenol adhesives in plywood and particle board production and their commercial use after the Second World War is outlined in view of different countries. Tannin properties of different resources viz: wattle, hemlock bark, chestnut, etc. and the various possibilities of use with synthetic resins are described including the properties of the panel products bonded with tannin adhesives. The final chapters cover production problems and influence of commercial use of tannin adhesives in Australia.

## 4. THE PRESENT STAGE OF APPLYING NATURALLY OCCURRING POLYPHENOL (TANNIN) ADHESIVES IN THE WOOD BASED PANEL INDUSTRY IN DEVELOPING COUNTRIES

Although a patent was taken out by McCoy(20) in 1918 for the use of tannin as a condensing agent and reactant in the phenol-formaldehyde reaction, it was not until after World War 2 that tannin was adopted commercially for bonding wood.

In 1950 Dalton (10) reported on the reaction of extracts of six tree species with formaldehyde to form resins and on their adhesive properties, and in 1953 (11) on the adhesive properties of *Eucalyptus crebra*, *Pinus radiata* and commercial wattle (mimosa) extracts which had been treated with sulphites in order to reduce viscosity.

Dalton's work did not achieve commercial success but it did stimulate interest in tannin adhesives for bonding wood. In 1952 MacLean and Gardner (21) proposed the use of hot water extract of western hemlock (*Tsuga heterophylla*) bark in blends with phenol-formaldehyde resin for an exterior grade plywood glue. Other pioneering work on the formulation of tannin adhesives was reported in 1954 by Knowles and White (18) for commercial wattle and quebracho extracts.

In 1957 Plomley, Gottstein and Hillis (25) reported briefly the development of exterior type adhesives for plywood based on commercial mangrove and wattle tannins. Commercial wandoo extract was also studied. In 1958 Herrick and Bock (15) reported plywood adhesive formulations based on blends of western hemlock tannin with polymethylol phenol as crosslinking agent. In the same year Booth, Herzberg and Humphreys (7) reported on the adhesive properties of *Pinus radiata* bark extracts prepared at ambient temperature, which were used in experimental hot-press plywood and particle-board adhesives.

In 1960 the wattle tannin formulations developed by Plomley, Gottstein and Hillis were taken up commercially in Australia for the production of exterior grade plywood. This development was reported to the International Consultation on Plywood and Other Wood-Based Panel Products held by FAO in Rome in 1963.

In 1960 Herzberg (17) reported the extension of earlier studies on cold water extracts of *P. radiata* bark as adhesives for exterior grade plywood. Hall, Leonard and Nicholls (14) published on various *P. radiata* bark extracts prepared at elevated temperatures and used for bonding particleboard.

A number of reports of laboratory work on tannin adhesives were made by Narayanamurti and others between 1957 and 1969. Some of the polyphenolic materials from which adhesives were prepared were tamarind (*Tamarindus indica*) seed testa extract, cashew (*Anacardium occidentale*) kernel testa extract, cutch from *Acacia catechu* wood, tea (*Thea sinensis*) waste extract and areca (*Areca catechu*) cutch. George (13) states that none of these adhesives is suitable for commercial application in plywood manufacture without further development. In recent years in India there has been considerable interest in wattle tannin adhesives for bonding panel materials and they have been used commercially for plywood manufacture (45).

Studies of extracts of *Pinus ponderosa*, tanoak (*Lithocarpus densiflorus*) and Douglas fir for bonding particleboard were reported by Anderson, Breuer and Nicholls (1) in 1961, and extracts of white fir (*Abies concolor*) and of *P. ponderosa* bark in 1974 by Anderson and others (2,3).

In South Africa there has been a successful commercial development of a chemically modified wattle tannin (8), which is used largely for bonding particleboard. Wood adhesives from wattle bark extract have been the subject of a recent report by Saayman and Oatley (38).

In spite of these and other widespread investigations of many different tannins as adhesives, information available to the World Consultation on Wood-Based Panels, 1975, gave the following picture of the application of tannin adhesives (45):-

> "The quantities used are, up to the present time, relatively small - Australia reports about 700 tons per year for plywood, particleboard and water resistant cartons. Finland uses 2500 tons per year of quebracho in plywood manufacture, the quebracho making up 10% to 20% of the total glue solids. A new particleboard plant in Argentina plans to use 100% quebracho adhesive. India is gluing plywood with tannin. However, at the present time the total quantity of tannin adhesive used is minute compared to the world consumption of synthetic resins in the panel products industry."

To this should be added the quantity of chestnut wood tannin reported by Kulvik (19) as having been used to modify commercial phenol-formaldehyde adhesives in Malaya. According to Kulvik more than

3000 metric tons had been produced of 42% solids resin with a weight ratio of chestnut tannin to phenol of 33 to 67, or about 600 tons of tannin.

A more recent estimate suggests that present world consumption of wattle tannin for adhesives could be 4000 to 5000 tons. This is still a relatively small quantity and not all would be used in panel products.

## 2. ADHESIVE PROPERTIES OF TANNINS

The reaction of the polyphenolic substances of plant extracts with formaldehyde to form resins is the basis for their use as adhesives. It follows therefore that the search for tannins for adhesives should be concentrated on the condensed tannins rather than on the hydrolysable tannins. The Stiasny test (44), which involves the reaction of an aqueous solution of tannin with formaldehyde under hot acid conditions and the determination of the weight of tannin formaldehyde precipitate may be used to indicate those tannins which have potential as adhesives. This test will be preferred to the hide powder test (37) which is indicative of tanning properties and has little relevance to adhesives.

Tannins vary widely in adhesive properties, as is shown for example in Table 1, in which the bond strengths of mangrove, wattle and wandoo adhesives with klinki pine (*Araucaria klinkii*) veneers are compared (28). Dry tests of standard plywood test specimens bonded at 140°C press temperature with wattle tannin adhesive without fortifying resin gave significantly higher mean failing loads and wood failure at 290 lb/in.$^2$ and 47% than unfortified mangrove and wandoo adhesives, for which failing loads and wood failures were 221 lb/in.$^2$ and 0% and 165 lb/in.$^2$ and 5% respectively. The differences between species were more marked when specimens were tested wet after immersion in boiling water, failing load and wood failure for wattle tannin being 236 lb/in.$^2$ and 100% compared with 123 lb/in.$^2$ and 0% for mangrove tannin. The wandoo specimens delaminated during the boiling water treatment.

Satisfactory bonds, both dry and wet after immersion in boiling water, can be obtained with unfortified wattle tannin adhesive and lower density species at normal plywood and particleboard hot press temperatures if the gluing conditions are carefully controlled. This is possible in the laboratory, but is difficult to achieve consistently under factory conditions. The chemical modification of tannins and the addition of synthetic resins to adhesive formulations have as their main aims the improvement of bond quality and the development of greater tolerance of the normal manufacturing conditions used for panel products.

There is some evidence that the conditions which are generally used for bonding panel products with synthetic resin adhesives may not be optimum for tannin adhesives and that different conditions may be required for the latter to achieve their maximum potential. The optimum glue line moisture content for bonding differs considerably for tannin and synthetic resin adhesives, as will be discussed later. There are also the indications given by the performance of wattle tannin adhesives when cured by radio-frequency heating and by the improved veneer bonding results obtained with a western hemlock extract at 180°C compared with 160°C.

In a limited laboratory study (32) of fortified and unfortified wattle tannin formulations for laminating timber using radio-frequency heating to cure the adhesives, high failing loads and wood failures were obtained for all formulations in dry block shear tests. There were relatively small differences between the fortified and unfortified adhesives. The wood failures in the dry block shear test were a little lower for the unfortified formulation and the percentage delamination after vacuum-pressure soak and redrying was slightly higher. A comparison of these results with adhesion tests using veneers and hot pressing at 140°C to 160°C suggests that the bond quality obtained with unfortified wattle tannin is improved by radio-frequency heating.

In studies of the adhesive properties of western hemlock bark extracts Steiner and Chow (43) obtained results which suggested that under normal plywood pressing and bonding conditions (temperature 160°C) aqueous hemlock bark extractives do not provide satisfactory bond durability. When the press temperature was raised to 180°C high wood failure and much improved durability were obtained. This result appeared to correlate well with thermal softening and differential thermal analysis results.

## 3. PHYSICAL AND CHEMICAL PROPERTIES OF TANNINS IMPORTANT IN ADHESIVE FORMULATION

### 3.1 Viscosity

The viscosity pH curves of aqueous tannin solutions can differ greatly in form, as is shown in Fig. 1 for wattle, mangrove (28) and quebracho (29) tannin solutions at 35% solids concentration and at pHs between 4 and 13.

The viscosity of the wattle tannin solution is relatively low at about 1 P (Poise) between pH 4.5 and 9.5 and then increases to about 6 P at pH 12.

The viscosity curve for mangrove tannin is characterised by a very high peak in viscosity between pH 8 and 11. Between pH 4.5 and 8 viscosity varies from about 6 P to 4 P. It is lowest at about 2 P between pH 11 and 13.

The viscosity of the quebracho (non-sulphited) solution varies between 17 P and 22 P between pH 4 and 9 with a maximum at about pH 8, after which it decreases rapidly to about 2 P at pH 10 to 12.

The viscosity of a 35% solution of a hot water extract of *Pinus radiata* bark (not shown in the Figure) increased from 2 P at pH 3.5 to a maximum of 10 P at about pH 7.3 and then decreased to 2 P at pH 11 (33).

High viscosity may prevent the use of tannins at normal adhesive concentrations within certain pH ranges. Wattle tannin solution has a relatively low viscosity between pH 4.5 and 10, but the viscosity of quebracho is very high except at pH 10 to 13. Formulation of mangrove tannin adhesives between pH 8 and 11 would obviously be difficult.

There are ways of overcoming these problems for particular applications. For example, small decreases in solids concentration can produce asignificant decrease in viscosity, but dilution with water can only be used to a limited extent without causing bonding troubles. For spray application in particleboard manufacture wattle tannin solution viscosity can be reduced by raising the temperature, but this procedure requires separate application of paraformaldehyde.

The most effective method of reducing viscosity is by treatment with sodium sulphite and/or sodium metabisulphite. In 1953 Dalton (11) reported that tannin solutions after heating with sulphites have low viscosities and are suitable for the preparation of adhesives to be spread mechanically. The conditions for treatment with sulphite were determined for extracts from *Eucalyptus crebra* and *Pinus radiata* bark and for commercial mimosa extract.

Sulphite treatment has been used for *P. radiata* bark extracts by Hall, Leonard and Nicholls (14) for *Abies concolor* bark extracts by Anderson, Wong and Wu (2) and for *P. ponderosa* bark extracts by Anderson, Wu and Wong (3).

The addition of chemical compounds such as phenol, urea, alcohols, aldehydes, ketones etc. has been found to increase solubility and reduce viscosity of quebracho solutions (29). Phenol and urea are also effective in reducing the viscosity of solutions of other tannins, such as wattle and radiata. Adhesion tests with *P. radiata* tannin showed that phenol in amounts up to 5% of dry tannin had no harmful effect on the bonding of coachwood veneers (33). Addition of 10% of urea to quebracho tannin solutions increased gelation time considerably and affected bonding, unless the formaldehyde concentration was increased (29).

## 3.2 Rate of reaction of tannins with formaldehyde

The rate of reaction between tannins and formaldehyde varies with pH and with kind of extract. Dalton determined the gelation rate for wattle tannin and a number of other extracts between pH 0.5 and 9 (10). He found that the minimum reaction rate for all the tannins examined was between pH 3 and 4.5 and drew attention to the fact that the point of minimum reactivity for polyhydric phenols was determined by Little and Pepper as being at pH 3.0. The considerable differences in reactivity between the tannins was shown. He also studied the gelation of sulphite treated wattle and radiata tannins with paraformaldehyde between pH 4 and 9 (11).

The reaction rates with formaldehyde of wattle, mangrove and radiata (non-sulphited) tannins at 60°C and between pH 4 and 7.5 were determined by Plomley (28). At an arbitrary pH 6 the gelation times for 30% solutions of wattle, mangrove and radiata tannins were approximately 56, 13 and 3 min respectively. The influence of pH on the gelation time of a 35% solution of wattle tannin and 3% formaldehyde at 90°C is shown in Fig. 2. Steiner and Chow (43) found that hemlock bark extract-formaldehyde systems appear to closely follow the gelation time character of wattle bark extract and PRF (phenol resorcinol-formaldehyde) resin rather than PF (Phenol-formaldehyde). Relative gelation times only were given.

Soluble inorganic salts at concentrations of from 2.5% to 10% of the weight of dry tannin have been shown to produce a marked decrease in gelation time of wattle tannin-formaldehyde (26).

3.3 The amount of formaldehyde required for crosslinking

The amount of formaldehyde required for crosslinking is relatively small for most tannins. For wattle tannin Parrish (24a) calculated that 3% to 4% of formaldehyde on extract weight was necessary. Plomley (28) found that the minimum requirement for wattle tannin used to bond experimental particleboards was between 6% and 8%. In later tests (33), 4% was found to be the minimum for the satisfactory bonding of coachwood veneers, but a study of the rate of gelation with varying concentrations of formaldehyde indicated a minimum of 6%.

The minimum amount of formaldehyde required for crosslinking mangrove tannin, based on adhesion tests with veneers, was found by Brandt (9) to be 5% for an aqueous extract and 4% for an aqueous alcoholic extract. Plomley, Gottstein and Hillis (27) found a minimum of 4% for an aqueous extract of mangrove tannin.

Working with cold aqueous extracts of *P. radiata* bark Hersberg (17) concluded that maximum adhesive bond strength is developed if at least 6% paraformaldehyde is incorporated in the resin.

In tests of adhesives based on sulphite treated hot water extracts of western hemlock bark, MacLean and Gardner (21) found a minimum requirement of 6% hexamine, equivalent to 7.7% formaldehyde. In contrast to this and to the results obtained for other tannins, which have been referred to, Steiner and Chow (43) reported that amounts of 15% and 20% of paraformaldehyde were required to obtain maximum durability with two different cold water extracts of western hemlock bark.

## 4. DEVELOPMENT OF ADHESIVE FORMULATIONS BASED ON COMMERCIAL WATTLE TANNIN

It has been mentioned above that although satisfactory bonds can be obtained with simple tannin formulations under laboratory conditions, it has not been possible yet to achieve consistently high bond strengths with such formulations under factory conditions. Up to the present the adhesive formulations which have been commercially successful are those involving either the addition of synthetic resin (usually in relatively small proportions) to the adhesive mixture immediately before use or prior reaction of tannin with synthetic organic compounds. These procedures lead to an increase in bond strength above that of the tannin alone, and also important they increase the adhesives' tolerance of gluing conditions and reduce bond variability.

### 4.1 Adhesive formulations based on mixtures of tannin and synthetic resin

The wattle tannin adhesives developed by CSIRO in Australia for plywood and particleboard manufacture are examples of this type of formulation. For practical purposes all the reaction between tannin, resin and formaldehyde takes place in the hot press. Control of curing time and usable life of the adhesive is obtained by control of pH together with the use of paraformaldehyde as the source of formaldehyde. The pH selected for a formulation is that which will give a short curing time and will also provide a sufficiently long pot life at ambient temperature. For example, Fig. 2 shows that at pH 7 and 90°C the gelation time of a wattle tannin solution with formaldehyde is about 4 minutes and is approaching a minimum value. Fig. 3 shows that at pH 7 and 25°C the gelation time of a 48% solution of wattle tannin with formaldehyde is 3½ h and with paraformaldehyde about 14 h. Thus, at about pH 7 a wattle tannin adhesive containing paraformaldehyde can be expected to have a pot life at 25°C and a curing time at hot press temperatures of 140°C and above which will satisfy usual plant requirements.

It is possible to use formaldehyde solution in wattle tannin adhesives, as has been done for reasons of economy, but careful control of pH is necessary to prevent premature gelation. The use of paraformaldehyde is generally to be preferred.

In Australia wattle tannin adhesives have been formulated for wood bonding over a pH range of 6.7 to 8.0, the hot-press curing time and the usable life of the adhesive at ambient temperature decreasing with increase in pH.

4.2 <u>The development of fortifying resins for blending with tannin adhesives</u>

At an early stage of CSIRO's investigations of tannin-formaldehyde adhesives it was observed that bond failure tended to be cohesive (failure within the glue) and that wood failure was usually low. This type of failure was more apparent in bonds made with mangrove and wandoo tannin than with wattle tannin adhesives. It was found that the bond could be improved greatly by incorporating in the adhesive relatively small proportions of certain synthetic resins ("fortifying resins"). The amount of resin needed to achieve a satisfactory bond varied with kind of tannin, kind of synthetic resin and wood density. With klinki pine (*Araucaria klinkii*) for example, wattle tannin formulations required the addition of only 10% of fortifying resin in order to yield acceptable failing loads and wood failure, whereas adhesives based on mangrove and wandoo extracts required three times as much or even more to reach the same level of bond strength (Table 1).

In addition to its contribution to bond strength, properties which seemed necessary in a fortifying resin were compatibility with the tannin solution at the required pH and a sufficiently fast rate of polymerization.

The first fortifying resins tried in the laboratory were commercial RF (resorcinol formaldehyde) and PRF resins, which were effective but too costly for use in plywood applications. A PF resin was developed for mangrove tannin plywood adhesives (27), but it had too short a storage life for Australian conditions and at that early stage of its development tended to be somewhat unstable in blends with tannin.

The results obtained with wattle tannin, which required smaller amounts of fortifying resin than mangrove tannin, made possible the development of a more costly fortifying resin, namely the low resorcinol PRF resin which has been used commercially in Australia for some 16 years (28). Although its storage life at ambient temperatures is limited, it is satisfactory when cold storage is used.

Phenol-formaldehyde fortifying resins have been used in India. One resin is described as having a pH of 8.5 and a storage life of 20 to 30 days at 25°C (46).

Formulations for PRF and PF fortifying resins for blending with wattle tannin adhesives for the manufacture of marine grade plywood and shuttering (form) board have been reported by Saayman and Oatley (35). In recent tests emulsified PF resin has given promising results in the bonding of veneers and experimental particleboard (33). Polymethylol phenol preparations have been used as fortifying resins and crosslinking agents for western hemlock tannin adhesives by Herrick and Bock (15). Combinations of urea and formaldehyde with tannin have been reported (18,34).

(i) Plywood Adhesives

A plywood adhesive formulation similar to those in commercial use in Australia is as follows:-

| | Parts by weight |
|---|---|
| Wattle tannin | 90 (oven dry weight) |
| Water | 113 |
| Sodium hydroxide | 0.9 |
| PMF fortifying resin | 10 (oven dry weight) |
| Wood flour | 10 |
| Walnut shell flour | 10 |
| Paraformaldehyde | 4 to 6 |

The pH of the formulation is about 7 and the useful life (time at 25°C to reach twice the initial viscosity) is approximately 4 h.

The proportion of fortifying resin in the above formulation gives a satisfactory bond with a wide range of Australian veneer species. However, experience has shown that 10 parts of resin is unnecessarily high for a number of species and can be reduced substantially. For greater economy a plywood manufacturer can vary the amount of fortifying resin in the formulation to suit the species being bonded.

The pH of the adhesive can be varied according to the hot-press curing time and pot life required; a pH range of about 6.8 to 7.5 has been used for plywood.

Glue spreads of 290 g to 390 g/m$^2$ double glue line have been used successfully under laboratory and factory conditions in mild climates, but for commercial production in a hot dry climate spreads up to 490 g/m$^2$ have been required. As with synthetic resin adhesives prepressing is beneficial.

Using the above formulation and hoop pine veneers at 5% moisture content total assembly times of 2 to 3 h may be used under mild climatic conditions. In warmer areas, especially in summer, open and closed assembly times must be reduced. Longer assembly times are possible with higher veneer moisture contents.

Pressing conditions are usually temperature 140° - 150°C and pressure 0.7 to 1.4 MPa[1)] depending on veneer density. For two 3 x 2.5 mm thick hoop pine panels per press opening a curing time of 7 min at 140°C may be used. (Two 3 x 2.5 mm thick hoop pine panels means two panels of 3-ply construction made up of 2.5 mm thick veneers.)

(2) Particleboard adhesives

A particleboard formulation for air spray application is as follows:-

| | Parts by weight |
|---|---|
| Wattle tannin | 95 (oven dry weight) |
| Water | 130 |
| Sodium hydroxide | 1.6 |
| PMF fortifying resin | 5 (oven dry weight) |
| Paraformaldehyde | 4 to 6 |

Viscosity at 25°C is 150-200 cp

As with the plywood formulation the present tendency is to decrease the proportion of fortifying resin. Under laboratory conditions boards complying with the specification for Standard Grade Particleboard (40) have been made using unfortified wattle tannin and radiata pine wood, which is the main species used for particleboard manufacture. However, for Flooring Grade Particleboard, Class 1 (40), for which wattle tannin adhesives are used in Australia, fortifying resin is considered necessary in order to obtain full properties at normal adhesive loadings and to provide greater tolerance of

1) 1 MPa (megapascal) = $1 N/mm^2$

manufacturing conditions.

Pressing temperatures of 160°C and above are used. Under factory conditions pressing times of about 9 min are usual for boards of 19 mm thickness, but under laboratory conditions with close control of moisture content or with the use of higher resin loadings at higher moisture contents a pressing time of 7 min can be achieved for the same thickness.

Compared with synthetic resin adhesives, higher mat moisture contents at pressing are necessary when using tannin adhesives; moisture contents of about 25% for surface layers and 17% for core have been used.

4.3 The western hemlock bark tannin formulation of Herrick and Bock

A somewhat different formulation was developed by Herrick and Bock (15) for a western hemlock (*Tsuga heterophylla*) extract, which was prepared as a dry sodium salt. The adhesive pH was about 10.5, a pH at which the pot life might be expected to be very short in the presence of either formaldehyde or paraformaldehyde. Formulation problems were overcome by using polymethylol phenol condensates with high methylol content but no free formaldehyde. These permitted the preparation of low viscosity adhesives with fairly high solids content. A formulation containing 60% bark extract and 40% polymethylol phenol reagent seemed to provide the best balance of curing time and adhesive strength and met commercial requirements for an exterior-type plywood adhesive.

4.4 Tannins as accelerators of PF resin cure

Tannins are added to alkaline PF resin adhesives in order to reduce bonding temperature or to allow shorter hot press cycles at the normal PF bonding temperature. It is commercial practice in Finland to us 10% to 20% of quebracho extract calculated on the weight of PF resin solids for this purpose (12). Other tannins, such as wattle tannin, also give this effect (33). Part of the formaldehyde requirement of the quebracho extract may be added as formaldehyde or paraformaldehyde, otherwise this requirement is provided by the PF resin.

4.5 Tannin based adhesives prepared by previous reaction with synthetic organic compounds

Two kinds of tannin adhesives of this category are used at the present time for the manufacture of panel products, one based on wattle tannin which is made in South Africa and the other based on chestnut tannin which was developed by a Norwegian company in Malaya.

The South African product is made by a process in which tannin is reacted in an aqueous medium with a substituted or unsubstituted aromatic compound including the grouping $-CH_2CO-$ at a temperature between 80°C and 98°C in the presence of a basic catalyst such as pyridine. This is followed by treatment with an alkali to raise the pH above 5.0, preferably to between 5.8 and 6.0. The aromatic compounds including the grouping $-CH_2CO-$ which are considered suitable are phenylacetate, acetophenone, phenoxyacetic acid, resacetophenone and roso-diacetophenone (8).

This adhesive is used in the same way as the CSIRO formulations and is reacted with formaldehyde, usually in the form of paraformaldehyde, in the hot press. It differs from commercial wattle tannin in several respects. The viscosity of aqueous solutions is somewhat lower, possibly due in part to hydrolysis of the gum normally present in wattle tannin. The pH of several samples examined ranged from 6.3 to 6.9. It is used without pH adjustment and in tests with formaldehyde at pH 6.8 and at 90°C gelation was found to be slightly faster than for commercial wattle tannin. The optimum amount of formaldehyde indicated by gelation tests with varying amounts of paraformaldehyde was 6% of the dry weight of material, the same as for commercial wattle tannin (33).

The wood-glue moisture relationship appears to be similar to the wattle tannin adhesives previously described and for particleboard manufacture higher mat moisture contents are used than in the case of PF resin adhesives.

In an adhesion test with coachwood veneers at 12% moisture content results were not significantly higher than for unfortified wattle tannin. Physical and mechanical properties of experimental particleboards pressed at 160°C were equivalent to those obtained with fortified wattle tannin adhesives (33).

## 4.6 Chestnut tannin-modified phenol-formaldehyde (PCF) adhesive

The development of this adhesive was reported at the World Consultation on Wood Based Panels in 1975 (19). In its manufacture chestnut wood tannin is added to the PF reaction mixture and it is claimed that the extract chemically replaces part of the phenol in normal alkaline phenol-formaldehyde adhesives, which are used in the manufacture of exterior grade plywood to meet BS 1455. It was found that the requirements of the standard could be met with an adhesive in which as much as 50% of the phenol was replaced by tannin. However, it appears that commercial practice is to use 33% replacement.

PCF adhesives are said to have approximately the same properties as the unmodified PF adhesive and the recommended glue mixture is 100 parts by weight of liquid adhesive and 30 parts of filler. The gluing conditions - glue spread, assembly time, prepressing time, hot pressing temperature and time are the same as for unmodified PF. The gelation time at 100°C is shorter with increasing replacement of phenol.

The advantage claimed for the PCF adhesive is that it is economical, the disadvantage that it is more sensitive to variations in conditions during plywood manufacture as compared with the pure PF adhesive. Stricter production controls and quality control are said to be necessary.

Although the PCF adhesive represents a useful application of a hydrolysable tannin in the adhesive field it may be questioned whether chestnut tannin is truly a replacement for phenol, which implies the provision of reactive groups. Apart from what is known of the chemical reactions of hydrolysable tannins, the bonding results reported and the stated higher sensitivity of PCF to manufacturing conditions suggest that chestnut tannin is acting mainly as an extender; any reaction that takes place probably results in an increase in the mass of the PF molecule without adding significantly to the number of reactive groups.

## 5. THE WOOD-GLUE MOISTURE RELATIONSHIP

The acceptance by industry of tannin adhesives as substitutes for synthetic resins depends very much on their not being significantly different in properties. It is necessary therefore that the basic extracts should have an adequate storage life. Adhesive formulations should have a sufficiently long working life to satisfy factory requirements and a suitable viscosity for application to veneers or wood particles with the usual equipment. When applied to the wood the adhesive should permit adequate assembly times and be capable of being cured under normal hot press conditions. Bonding should meet standards which have been established on the basis of the performance of synthetic resin adhesives.

Adhesive formulations based on wattle tannin meet these requirements under commercial conditions of manufacture of plywood and particleboard. However, in one respect they differ significantly from synthetic resin adhesives, namely in the wood-glue moisture relationship. It is considered that an understanding of this relationship is highly important for the successful use of tannin adhesives.

When glue is spread on wood water passes from the glue to the wood. The rate at which it loses moisture depends on the properties of both the wood and the glue, e.g. wood moisture content, density, anatomical structure, chemical composition and adhesive resin composition, viscosity and moisture content etc. This change in glue line moisture content can have important effects at all stages of the gluing process, particularly as it influences glue transfer, grip or prepress adhesion and resin flow in the hot press.

Observations made in the laboratory and under factory conditions have shown that tannin adhesives lose moisture more rapidly than synthetic resin adhesives such as PF when spread on veneers. In addition, it has been found that the optimum glue moisture requirements for hot-press bonding are higher for tannin adhesives than for PF (32). These two factors may explain some of the variability of results obtained in laboratory adhesion tests. Also, they can have a considerable influence on factory gluing procedures, especially at low veneer moisture contents. At low veneer moisture contents and with long assembly times, the adhesive may lose moisture too rapidly for satisfactory transfer to the unspread veneer or for sufficient flow in the hot press. In this situation slight changes in formulation resulting in lower viscosities, control of gluing, assembly and pressing conditions may be necessary in order to maintain bond quality. As shown in Table 2, fortifying resin has an ameliorating effect. (32 a)

In particleboard manufacture the mat moisture content at pressing has a marked influence on the physical and mechanical properties of the board. Modulus of rupture (MOR) tests on experimental particleboard specimens saturated with cold water under vacuum and pressure (VPS treatment) indicate that the optimum moisture content at pressing for unfortified wattle tannin is between 17% and 21%. The optimum for *P. radiata* bark extract, based on the results of dry MOR tests, was found to be about 35% (14).

## 6. PROPERTIES OF PANEL PRODUCTS BONDED WITH TANNIN ADHESIVES.

### Plywood

Wattle tannin-formaldehyde (wattle TF) adhesives have been used commercially in Australia for bonding exterior grade plywood since 1960. The tannin-formaldehyde bond complies with the specification for Type A bond quality of AS 087-1963 (38), which is described as capable of withstanding extreme exposure for a long period and suitable for permanent external sheeting. The method of test for Type A bond is described in AS 090 (39), which specified testing wet after 72-h immersion in boiling water or equivalent steam treatment.

Veneer species ranging from 0.513 to 0.881 kg/m$^3$ are bonded with wattle TF. The effect of the number and the location of glue lines in the cross-section on the bending properties has been studied on plywood bonded with wattle TF adhesive by Okuma (22), who found that the Young's modulus in bending of the TF glueline in plywood is larger than that of PF.

The bond durability of hoop pine and coachwood panels glued with 10% fortified wattle tannin adhesive has been tested by exterior exposure. There has been no bond failure after 15 years' exposure to Melbourne climatic conditions with a temperature range (highest monthly mean daily maximum to lowest mean daily minimum) of 26°C to 4.6°, mean relative humidity (3 pm) 40% to 66% and rainfall 761 mm.

At high veneer moisture contents, tannin adhesives tend to penetrate veneers. For this reason and because of their dark colour they are better suited for bonding rotary veneers than sliced decorative veneers.

__Particleboard__

In 1969 the properties of experimental single-layer flat-pressed boards made from commercially products *Pinus radiata* particles and two kinds of commercial tannins, wattle and quebracho (30). Boards bonded with these tannins at a level of 12% of extract on the weight of wood particles (oven dry weight basis) retained their integrity after immersion in boiling water for 72 h.

At a slightly higher addition of extract the swelling of boards immersed in boiling water for up to 90 h or saturated with cold water by prolonged VPS[2)] treatment was controlled to an acceptable level, and on redrying the boards returned to within 2 to 5% of the original thickness. The results of mechanical tests were comparable with those of UF bonded boards.

Further studies showed that boards of about 700 $kg/m^3$ density with 14% of tannin solids in the surface layers and 10% in the core complied with the mechanical property requirements of the proposed Standard for Flooring Grade Particleboard. Board thickness increase after 24 h VPS treatment was less than 12% (33).

Generally, the properties of wattle TF bonded boards are equivalent to those of alkaline PF boards at the same active adhesive content, allowance being made for the small proportion of material in commercial wattle tannin which does not take part in the condensation reaction with formaldehyde.

At the present time Flooring Grade particleboard made to the requirements of AS 1859-1976 (40) is bonded with either wattle TF or PF adhesives. The physical and mechanical properties necessary for

2) VPS is an abbreviation for vacuum-pressure soak treatment which involves immersing specimens in a tank of cold water in a pressure cylinder and applying an initial vacuum followed by a positive pressure to ensure saturation. The conditions are specified in Appendix C, AS 1859 as follows:
"C2.1 Pressure Soaking of Test Pieces. Prior to the loading of test pieces they shall be immersed in water at 20 ± 2°C and subjected to a negative pressure of 85 kPa for a period of 30 min followed immediately by the application of a pressure of 400 kPa for a period of 23 ± 1 h".

compliance with the standard are set out in Table 3 together with the test results obtained for two commercial TF and one PF board (42). The MOR after immersion in boiling water for 72 h and MOR after 24 h VPS treatment at 20°C are expressed as percentages of the dry MOR.

The surface water absorption of various commercial UF, TF and PF bonded boards is shown in Table 4. Board E exceeds the specification limit of 200 g/m$^2$ of surface in 2 h. However, these tests were made before AS 1859-1976 came into force and at the present time all boards on the market meet this requirement. The highest water absorption is shown by the PF bonded boards and the lowest by UF, TF bonded boards being intermediate but closer to the UF boards.

From the physical and mechanical properties shown in Table 3 there is small difference between TF and PF bonded panels except in absorption of water. The adhesive concentrations in surface and core layers of the boards are probably similar for the different resins.

Accelerated ageing tests of commercial particleboards bonded with UF, TF and PF adhesives have been carried out by Stashevski (41). In one study specimens of flooring boards were subjected to humidity cycling at 40°C, each cycle consisting of exposure to 25% relative humidity (RH) for one week followed by one week at 86% RH. These cycling conditions were used in an attempt to simulate the board moisture variations which may occur with seasonal changes. After 50 cycles the MOR for the TF and PF boards had not decreased and the tensile strength perpendicular to the plane of the board (IB) showed a small decrease only. The MOR and IB values of the UF boards decreased to a small proportion of the original values.

In a second study boards were immersed in water at 40°C for 24-hr and then redried at 40°C and 25% RH for 6 days. This cycle was repeated up to 15 times. The effects of cycling were similar for TF and PF boards which were much superior in performance to the UF bonded boards.

## 7. PROBLEMS IN THE PRODUCTION OF EXTRACTS FROM DIFFERENT WOOD SPECIES

The commercial tannins are produced primarily for the leather industry, though they do find uses in other industries, such as oil drilling. At the present time no commercial tannin is produced specifically for adhesives. For this reason the quality of extracts is usually evaluated by the hide powder test, a test which has little relevance to adhesive properties. The Stiasny test which measures the proportion of an extract which will react with formaldehyde, is a more useful test in relation to adhesives use. It gives an indication of quality of an extract, but not necessarily of its usefulness as an adhesive. At this stage the ultimate assessment is provided only by carefully conducted adhesion tests. The rate of reaction with formaldehyde and especially viscosity are other highly important properties of tannins.

There are three principal stages in the manufacture of commercial tannins:-

1. Reduction of the bark or wood to pieces of suitable size for extraction.

2. Extraction with hot water.

3. Concentration of the aqueous extract under vacuum.

In the manufacture of wattle (*Acacia mearnsii*) extract, for example, undried bark is delivered to the factory as soon as possible after it is stripped. Alternatively, bark is dried and extracted when convenient. Control of extract quality begins at harvesting and care is taken to prevent mould growth on green bark delivered to the factory or on the bark being dried.

On arrival at the factory the bark is reduced to small pieces preparatory to extraction. Extraction is usually carried out in batch type extraction units worked on the counter-current principle. A unit consists of a battery of 6 or more autoclaves which must be made of copper or stainless steel because of the reaction of tannin with ferrous metal. Extraction of tannin is effected by passage of water which has been preheated to about 100°C. Further heating is carried out in the autoclaves by injection of steam or is provided by heat exchangers between the autoclaves. The autoclaves are usually operated under a small positive pressure of steam.

The final liquor which has passed through the battery is transferred to a triple effect evaporator in which the bulk of the water is removed under vacuum. The liquor at about 50% solids is then passed to a vacuum pan, where the moisture is reduced to about 10%. Alternatively, concentrated liquor is spray dried.

Wattle tannin is relatively stable to heat and the extract, which in the course of manufacture is heated at about 100°C for some 8 hours in the autoclaves and experiences further heating in the concentration or drying processes, still has a viscosity comparable with synthetic resin adhesives and also has good adhesive properties.

Quebracho tannin which is produced from the wood of *Schinopsis* spp. is also relatively stable to heat and extraction is conducted at 115°C (23). There are two grades of commercial tannin, "ordinary", which is untreated, and "soluble", which has been treated with sodium sulphite. Aqueous solutions of the untreated tannin have very high viscosities, but this seems to be a natural characteristic and not largely the result of the heat treatment used in its manufacture. Like wattle these extracts are produced for the tanning industry. Because of the high viscosity of the ordinary extract below about pH 10.5, its use in adhesives is limited to acceleration of PF and UF resins and potentially to formulations at high pH, such as with polymethylol phenol as crosslinking agent. The "soluble" extract is a more suitable material for adhesives formulation because of its relatively low viscosity.

Mangrove tannin is extracted from the bark of *Rhizophora* and *Bruguiera* spp. The same general procedure is used in its manufacture, but some changes are necessary because of its considerable heat sensitivity. The problem in relation to the production of high quality mangrove extract in the delta region of Papua have been reported by Hillis (17a) and the properties of the extract in relation to the preparation of plywood adhesives were studied by Plomley, Gottstein and Hillis (27). At the Papua factory care was taken that the time from bark removal from the tree and commencement of extraction was 3-4 days. Such rapid treating procedure was considered necessary in that climate, if severe fungal infection and degrade were to be avoided. Because of the heat sensitivity of the tannin, mangrove bark was extracted at 60°C or below and concentrated under vacuum to the desired moisture content.

Variability in viscosity was a major problem in the mangrove extracts studied. This is shown in viscosity-solids concentration curves for a solid and a liquid extract at the natural pH (27); at an arbitrary viscosity of 67 P the solids concentration for the solid extract was 40% and for the liquid extract about 54%. A 40% solution of Borneo cutch (a mangrove extract) also at 25°C had a viscosity of 370 P. The very high viscosity between pH 8 and 11 limits the pH range available for adhesive formulation.

In plywood bonding tests wood failures were typically low, especially when specimens were tested wet after immersion in boiling water. It is significant that a carefully prepared, relatively low viscosity liquid extract did not give significantly higher bond quality than a high viscosity solid extract.

Studies of the extraction of coniferous barks and the adhesive properties of extracts have been reported by a number of workers. In 1953 Dalton (11) examined the adhesive properties of sulphited *Pinus radiata* bark extract. The conditions used for the preparation of the extract were not specified except that some sulphite was added to the tannin during its extraction from the bark. High viscosity, necessitating subsequent sulphite treatment, indicates that extraction was carried out at an elevated temperature. Failing loads of plywood specimens bonded with radiata TF and tested dry and wet after 6 h in boiling water were almost as high as the PF bonded controls, but wood failures were relatively low.

Booth, Herzberg and Humphreys (7) and Herzberg (17) reported adhesion studies of cold water extracts of radiata bark. Encouraging results were obtained in initial plywood and particleboard bonding tests. Under optimum conditions coachwood plywood specimens bonded with radiata TF gave satisfactory failing loads and generally high wood failures when tested dry. When tested wet after 6 h in boiling water wood failures were rather more variable. Cold water extraction overcame viscosity problems, but led to low tannin yields.

Hall, Leonard and Nicholls (14) gave particular attention to hot alkaline extraction. Evidence was obtained which supported previous observations of the deleterious effect of storing bark under damp conditions. It was shown that when bark is extracted with 2.0% sodium carbonate (oven dry bark basis) the yields of extract could be doubled by raising the temperature from 30°C to 60°C, but it was stated that increasing the temperature to 90°C was of no particular advantage and furthermore, the extract obtained at 60°C was as effective as either of the others as a bonding agent component. The effect of sulphite on an alkali extract was beneficial for viscosity and stability. In tests of the extracts as binders for experimental particleboards the best results were obtained with extracts made at 60°C with 2.5% carbonate or 2.0% carbonate with 0.5% sulphite either in the extracting solution or used as an after treatment, comparison being made with other sodium carbonate concentrations and with hot water extract.

Problems of viscosity and variability are important when it comes to establishing conditions for the manufacture of radiata extract. Low viscosity extracts can be prepared under mild conditions, but at the expense of yield, and high yield extracts prepared at elevated temperatures with or without alkali are invariably very high in viscosity. The high viscosity is due primarily to the fact that the bulk of the polyphenols in the outer bark are highly polymerised - mean molecular weight 25,000 to 35,000 compared with commercial wattle tannin, mean m.w. 1250 (22). Viscosity increases are likely to occur because the tannin is sensitive to heat and pH.

Viscosity can be reduced and stability improved by treatment with sulphite, but this does not eliminate variability. In addition to the effects of extracting conditions the quantity of tannin in the bark varies with height above ground; the bark in the lower portion of the tree is high in tannin content, whereas that of the upper portion of the tree is rather low (5). Because of this within-tree variation in bark tannin concentration, it has been suggested that the bark of the butt logs only should be used for extraction (6).

A considerable amount of research has been carried out on the extraction of western hemlock bark tannin. MacLean and Gardner (21) studied the adhesive properties of hot water extracts of bark removed hydraulically from sea-water floated logs. Adhesive formulations based on sulphited and unsulphited extracts with hexamine as the cross-linking agent were used to bond veneers at 140°C press temperature. Dry shear tests showed low wood failure and bond durability (boil test) was also very low.

Scott and Korach (36) found that yields of tannin were much improved, as compared to water extraction, and extraction times shortened, by using sufficient alkali to give a final extract solution pH of 6.5 to 7.5. The proportion of tannin to soluble solids was not affected at these low levels of alkalinity. Increase in temperature increased yield in less time, with no reduction in quality. Extract solids obtained were readily soluble in cold water and their solutions were stable on heating and at pH levels above 5.0.

Herrick and Bock (15,16) observed that viscosity or average molecular weight of western hemlock bark extract was dependent on the choice of extraction and processing conditions and to some extent was associated with certain variables in the bark. Extraction with weak bases such as aqueous ammonia gave products with reproducible, high reactivity in yields of 25% to 30% of the weight of dry bark. The ammonia extract was converted to a water-soluble form for adhesives use by treatment with sodium hydroxide. When this extract was used to bond experimental plywood at 140°C, tests showed that although bond quality appeared to be good in some cases, boiling water resistance was unsatisfactory.

A different picture of western hemlock extraction and extracts is given by Steiner and Chow (43). They concluded that increasing the extract yield by means of higher temperatures and pH does not necessarily lead to improved yield of quality tannin. The mildest extraction conditions (cold pressing) provided the lowest viscosities, while increasing the extraction temperature resulted in higher solution viscosities. The storage conditions of bark after peeling and the pH of extraction also influence the solution viscosity. This change in viscosity and yield at higher pH and temperature most likely reflects increased solubilities of bark carbohydrate and higher molecular weight tannin materials, in addition to self-polymerization of the tannins.

Further, the absorption-spectra data demonstrate that increases in either pH or temperature can significantly alter the chemical character of the extract and this change may be reflected in the potential use of the material as an adhesive. To maintain extract quality, storage at a pH below 5.3 at room temperature or lower is desirable. Because of the influence of heat, light and moisture on oxidation and polymerization processes, the period of time between the falling of a tree, removal of bark and subsequent extraction should also influence extract quality.

The curve for rate of reaction with formaldehyde between pH 1 and 11 of hemlock bark extract closely followed those of wattle tannin and phenol resorcinol formaldehyde. In exploratory bonding experiments with adhesives based on extracts carefully prepared at low temperatures, the results suggested that, under normal plywood pressing conditions (160°, aqueous hemlock bark extractives do not provide suitable bond durability. However, at 180°C bond quality improved greatly.

The use of bark extracts of *P. ponderosa*, tanoak, (*Lithocarpus densiflorus)* and Douglas fir (*Pseudotsuga menziesii)* for bonding particleboards was studied by Anderson, Breuer and Nicholls (1). Extraction was carried out with water and 2.0% sodium carbonate on weight of dry bark at 70° - 80°C. A mixture of 0.25% sodium metabisulphite and 0.25% sodium sulphite was added to the filtered extracts, which were concentrated under reduced pressure at 35° - 45°C. This method is derived from the studies of Hall, Leonard and Nicholls (14). Yield of extract from run of mill ponderosa bark was low and a 50% increase was obtained from bark from freshly felled trees. Tanoak bark extract was relatively unstable and within 24 hours exposure to air formed an insoluble surface film.

At the optimum moisture content for pressing a higher modulus of rupture (MOR) and a lower water absorption were obtained for experimental particleboards bonded with extract from fresh ponderosa bark than with extract from run of mill bark. Under optimum conditions the MOR of boards bonded with ponderosa and tanoak bark extracts closely approximated the MOR of UF bonded boards, but the latter had much lower water absorptions.

To sum up, the aim in extraction is to remove the maximum amount of tannin in its purest form and unchanged or with the least harmful effect on those properties which are important for its particular application. This applies generally, whether the extract is to be used for tanning of hides or for adhesives, but the properties may not be identical in both applications. For example, viscosity is less important for tanning than for adhesive use and a light colour which is important for tanning is of little significance where the objective is a structural adhesive. For the evaluation of a tannin as an adhesive it is essential that the extract be prepared under the best conditions which will cause the least change in physical and chemical properties, because only then can its maximum potential be assessed.

Control of extract quality begins at bark or wood harvesting - in the case of wattle tannin it may be said to begin in the plantation. The time elapsing between harvesting and drying or, in the case of green bark, extraction is important. Mould growth on stripped bark affects quality and yield on wattle and mangrove tannins. Radiata bark stored damp decreases considerably in yield, especially under warm temperature conditions.

Tannins vary in their sensitivity to heat. Wattle and quebracho extracts, for example, are relatively stable to heat and they are extracted commercially at 100°C and above. On the other hand mangrove tannin is sensitive to heat and is therefore extracted commercially at 60°C or below. Even so, mangrove extracts were found to vary widely in viscosity, possibly mainly as a result of insufficient control of heating. In spite of large differences in viscosity, low wood failures were typical of adhesion tests carried out with both crude commercial and carefully prepared (low temperature, shorter heating time) extracts.

Conifer bark extracts present some additional problems. Generally these extracts are affected by extraction temperature and also by increase in pH above the natural pH, but because the bark contains a high proportion of high molecular weight tannin increase in extraction temperature and pH of solvent are required in order to obtain high yields. For such preparations treatment with sulphite during or after extraction is necessary in order to obtain stable, low viscosity extracts.

Studies of the alternative approaches of a low yield low viscosity extract made at ambient temperature and higher yield extracts prepared at higher temperature and pH are represented by work on *P. radiata* bark extract by Herzberg on the one hand and Hall, Leonard and Nicholls on the other. In plywood adhesion tests the low temperature extract gave high bond strength and wood failure with medium density veneers when tested dry, but wood failures were somewhat variable in the boil test. Hall, Leonard and Nicholls obtained results in particleboard tests apparently comparable with urea-formaldehyde resins, but the high optimum mat moisture content (about 35% at 160°C) would present manufacturing difficulties.

The extracts prepared from western hemlock bark at high temperatures and pH showed low wood failures and low durability in bending tests. Aqueous extracts prepared at ambient temperature were sensitive to increase in temperature and pH and results of plywood bonding tests indicated that these extracts did not provide high bond durability except at above normal pressing temperatures.

With many variables to influence properties a major problem in the commercial production of extracts for adhesives will be to maintain a consistent product. A suitable viscosity and good adhesive properties are probably the most important characteristics of an extract, but without uniformity the formulation of commercially acceptable adhesives will be extremely difficult. The uniformity of commercial wattle tannin has been a major factor in its successful application in wood adhesives.

## 8. FACTORS INFLUENCING THE COMMERCIAL USE OF TANNIN ADHESIVES IN AUSTRALIA

The wider use of tannins as the main components of adhesive systems undoubtedly depends at the present time more upon economics than on technology. Commercial experience over a number of years has shown that adhesives based on wattle tannin are effective substitutes for synthetic PF adhesives for the manufacture of exterior grade plywood and flooring grade particleboard. A number of other tannins have shown potential as adhesive bases in laboratory tests and some also in tests under factory conditions.

Although the first successful application of tannin adhesives was for exterior grade plywood, their potential is greater for particleboard manufacture, particularly for flooring and other uses for which a bond of high durability is required. Particleboard is a more favourable application for tannin adhesives than plywood because of the generally lower cohesive strength required. Also, the high reactivity of tannin adhesives and the lower water absorption of boards bonded at about neutral pH, when compared with boards bonded with alkaline PF adhesives, are considerable advantages.

In Australia the cost of wattle tannin, all of which is imported, has been the main influence limiting the wider use of tannin adhesives. In assessing costs some factors other than the basic costs of materials must be taken into consideration, first of all there is the additional work involved in preparing the adhesives for use, and secondly, the fact that the manufacturers of synthetic resin adhesives usually provide a technical service for their customers. Such a service is not provided for tannins, which means that the user must rely on his own technical resources to overcome any adhesive problems. Nevertheless, there is an increasing interest in tannin adhesives, especially for particleboard manufacture. The cost of imported tannin has not permitted its use in competition with UF adhesives, but the development of a domestic tannin producing industry could change this situation.

REFERENCES

(1) Anderson, A.B., Breuer, R.J. and Nicholls, G.A. (1961)
Bonding particle boards with bark extracts.
Forest Prod. J. 11 : 226-227.

(2) Anderson, A.B., Wong, A. and Wu, K-T (1974)
White fir bark and its extract in particleboard.
Forest Prod. J. 24 : 40-45.

(3) Anderson, A.B., Wu, K-T and Wong, A. (1974
Utilization of ponderosa pine bark and its extract in particleboard.
Forest Prod. J. 24 : 48-53.

(4) Anderson, A.B. (1975) - Bark extracts as bonding agents for particleboard.
World Consultation on Wood-Based Panels, New Delhi, India 1975.
Proc. Background paper No. 67. FAO.

(5) Anderson, H. (1952) - The tannins of certain eucalypt species and
*Pinus radiata*. J. Soc. Leath. Trades Chem. 36 : 211-217.

(6) Anderson, H. and Gilkens, A. (1958) - Investigations on the tannins
of *Pinus radiata* bark. Aust. J. Appl. Sci. 9 : 183-191.

(7) Booth, H.E, Herzberg, W.J. and Humphreys, F.R. (1958) -
*Pinus radiata* (Don) bark tannin. Aust. J. Sci. 21 : 19-20.

(8) Boxes and Shooks Ltd. (1971) - Improvements in or relating to
adhesives derived from tannins. British Patent 1,225,571 (March 17).

(9) Brandts, Th. G. (1952) - Mangrove tannin-formaldehyde resins as hot-press
plywood adhesives. Tectona 42 : 137-150.

(10) Dalton, L.K. (1950) - Tannin-formaldehyde resins as adhesives for wood.
Aust. J. Appl. Sci. 1 : 54-70.

(11) Dalton, L.K. (1953) - Resins from sulphited tannins as adhesives for wood. Aust. J. Appl. Sci. 4 : 136-145.

(12) Brlje, R.H. (1975) - El extracto de quebracho como materia prima para adhesives de paneles basados en madera. World Consultation on Wood-Based Panels, New Delhi, India 1975. Proc. Background paper No. 19. FAO.

(13) George, Joseph (1975) - Tannin adhesives for wood based panels. World Consultation on Wood-Based Panels, New Delhi, India 1975. Proc. Background paper No. 14. FAO.

(14) Hall, R.B., Leonard, J.H. and Nicholls, G.A. (1960) - Bonding particle boards with bark extracts. Forest Prod. J. 10 : 263-272.

(15) Herrick, F.W. and Bock, L.H. (1958) - Thermosetting exterior - plywood type adhesives from bark extracts. Forest Prod. J. 8 : 269-274.

(16) Herrick, F.W. and Conca, R.J. (1960) - The use of bark extracts in cold-setting waterproof adhesives. Forest Prod. J. 10 : 361-368.

(17) Hermberg, W.J. (1960) - *Pinus radiata* tannin-formaldehyde resin as an adhesive for plywood. Aust. J. Appl. Sci. 11 : 462-472.

(17a) Hillis, W.E. (1956) - The production of mangrove extract in the delta region of Papua. Emp. For. Rev. 35 : 420-436.

(18) Knowles, E. and White, T. (1954) - Tannin extracts as raw materials for the adhesives and resins industries. Adhes. Resins 2 : 226-230, 255-258.

(19) Kulvik, E. (1975) - Chestnut wood tannin extract in plywood adhesive (PCF adhesive). World Consultation on Wood-Based Panels, New Delhi, India 1975. Proc. Background paper No. 142. FAO.

(20) McCoy, J.P. (1918) - US Patent, 1,269,627 (June 18).

(21) MacLean, H. and Gardner, J.A.F. (1952) - Bark extracts in adhesives Pulp Pap. Mag. Can. 53 : 111-114.

(22) Markham, K.R. and Porter, L.J. (1973) - Extractives of *Pinus radiata* bark. I. Phenolic components. N.Z. Jl. Sci. 16 : 751-761.

(23) Mezoy, E. (1947) - El quebracho colorado y su extracto tanico. Editorial Labor, S.A. Argentina.

(24) Okuma, M. (1976) - Plywood properties influenced by the glue line. Wood Sci. Technol. 10 : 57-68.

(24a) Parrish, J.R. (1958) - Particle board from wattle wood and wattle tannin. Jl. S. Afr. For. Ass. No. 32 : 26-31.

(25) Plomley, K.F., Gottstein, J.W. and Hillis, W.E. (1957) - Tannin-formaldehyde adhesives. CSIRO Aust. For. Prod. Newsletter No. 234 : 6-8.

(26) Plomley, K.F. (1959) - The effect of soluble salts on the gelation of tannin-formaldehyde. Aust. J. Appl. Sci. 10 : 494-497.

(27) Plomley, K.F., Gottstein, J.W. and Hillis, W.E. (1964) - Tannin-formaldehyde adhesives for wood. I. Mangrove tannin adhesives. Aust. J. Appl. Sci. 15 : 171-182.

(28) Plomley, K.F. (1966) - Tannin-formaldehyde adhesives for wood. II. Wattle tannin adhesives. CSIRO, Div. For. Prod. Technol. Pap. No. 39.

(29) Plomley, K.F. (1969) - Report on quebracho tannin adhesive investigations for the Forestal Land, Timber and Railway Co. Ltd.

(30) Plomley, K.F. and Stashevski, A. (1969) - Waterproof particle board. CSIRO Aust. For. Prod. Newslett. No. 363 : 1.

(31) Plomley, K.F. (1975) - The development of wattle tannin-formaldehyde adhesives for wood by CSIRO. World Consultation on Wood-based Panels, New Delhi. India 1975. Proc. Background Paper No. 13. FAO

(32) Plomley, K.F. and Collins, P.J. (1975) - Tannin adhesives for
(32a) glued laminated structural timber. Forest Products Research Conference, 17th, Highett. Topic 1/37.

(33) Plomley, K.F., Pankevicius, E.R. and Palmer, R.E. - unpublished data.

(34) Roy, D.C., Sarkar, A. and Rajak, B.N. (1973) - Tannin adhesives for plywood manufacture. IPIRI J. 3 : 81-84.

(35) Saayman, H.M. and Oatley, J.A. (1975) - Wood adhesives from wattle bark extract. IUFRO Conference on Wood Gluing, Proc., Madison. pp. 28-43.

(36) Scott, D.S. and Korach, P. (1956) - Recovery of tannin from western hemlock bark. II Extraction rates with dilute alkaline solvents. Pulp Pap. Mag. Can. 57 : 147-150.

(37) Society of Leather Trades Chemists (1951) - Official methods of analysis. 2nd Ed. (Society of Leather Trades Chemists : Croydon, England.)

(38) Standards Association of Australia (1963) - AS 087, Plywood for exterior use.

(39) Standards Association of Australia (1964) - AS 090 - Methods of testing plywood.

(40) Standards Association of Australia (1976) - AS 1859, Flat pressed particleboard.

(41) Stashevski, A.M. (1975) - Ageing of particle boards under simulated service conditions. Forest Products Research Conference, 17th, Highett. Topic 1/36.

(41) Stashevski, A.M. (1975) - Ageing of particle boards under simulated service conditions. Forest Products Research Conference, 17th, Highett. Topic 1/36.

(42) Stashevski, A.M. - unpublished data.

(43) Steiner, P.R. and Chow, S. (1975) - Some factors influencing the use of western hemlock bark extracts as adhesives. IUFRO Conference on Wood Gluing, Proc., Madison. pp. 61-70.

(44) Wissing, A. (1955) - The utilisation of bark. II. Investigation of the Stiasny reaction for the precipitation of polyphenols in pine bark extractives. Svensk Papp. - Tidn. 58 : 745-750.

(45) World Consultation on Wood-Based Panels, New Delhi, India, 1975. Proc. p. 166. Brussels, Miller Freeman, 1976.

(46) Soolagud, S.S., Mohandas, K.K., Rangaraju, T.S., Prasad, T.R. Narayana and George, Joseph (1975) - Tannin extended phenol-formaldehyde resin adhesives for BWP grade plywood. IPIRI, J. 5 : 59-63.

## TABLE 1

## BOND STRENGTH OF MANGROVE, WATTLE AND WANDOO TANNIN ADHESIVE FORMULATIONS WITH KLINKI PINE VENEERS

| Tannin | Amount of fortifying resin (%) | Failing load ($lb/in.^2$) and wood failure (%) | |
|---|---|---|---|
| | | Tested dry | Tested wet after 6 h or 72 h in boiling water |
| Mangrove | 0 | 221-0 | 123-0 |
| | 10 | 256-0 | 203-6 |
| | 20 | 330-76 | 283-85 |
| | 30 | 356-99 | 312-95 |
| Wattle | 0 | 290-47 | 236-100 |
| | 10 | 390-97 | 290-100 |
| | 20 | 481-100 | 296-100 |
| | 30 | 423-100 | 300-100 |
| Wandoo | 0 | 165-5 | 0-0 |
| | 10 | 301-52 | 150-21 |
| | 20 | 369-96 | 248-83 |
| | 30 | 382-82 | 266-93 |

**Note:** In this early work the fortifying resins used were commercial resorcinol-formaldehyde for mangrove tannin and phenol-resorcinol-formaldehyde for wattle and wandoo tannins.

## TABLE 2

## EFFECT OF ASSEMBLY TIME ON THE BONDING OF COACHWOOD VENEERS AT 5% MOISTURE CONTENT WITH WATTLE TANNIN AND FORTIFIED WATTLE TANNIN ADHESIVES

| Adhesive formulation | Assembly time (h) | Failing load (MPa and wood failure (%) | | |
|---|---|---|---|---|
| | | Tested dry | Tested wet after VPS | Tested wet after 72 h in boiling water |
| Wattle tannin | 1/2 | 2.000-44 | 1.990-74 | 1.733-90 |
| | 1 | 1.988-19 | 1.782-34 | 1.594-56 |
| | 2 | 1.723-6 | 1.695-24 | 1.365-33 |
| | Mean | 1.904-23 | 1.822-44 | 1.564-60 |
| Fortified wattle tannin | 1/2 | 2.535-68 | 1.865-98 | 1.733-98 |
| | 1 | 2.165-74 | 2.024-88 | 1.910-99 |
| | 2 | 2.202-69 | 1.792-79 | 1.424-89 |
| | Mean | 2.301-70 | 1.894-88 | 1.689-95 |

## TABLE 3

**PHYSICAL AND MECHANICAL PROPERTIES OF SOME COMMERCIAL FLOORING GRADE PARTICLEBOARDS BONDED WITH TANNIN- AND PHENOL-FORMALDEHYDE RESINS**

| Bond type | Tannin-formaldehyde | | Phenol-formaldehyde | AS 1859 Flooring Class 1 | |
|---|---|---|---|---|---|
| | | | | Lowest value | Highest value |
| Manufacturer | D | F | A | | |
| Board thickness, mm | 19 | 20 | 19 | | |
| Moisture content, % | 11.7 | 12.1 | 8.7 | 6 | 14 |
| Density, kg/m$^3$ | 699 | 676 | 710 | 640 | |
| Modulus of rupture: | | | | | |
| (a) Dry, MPa | 21.3 | 22.1 | 21.3 | 16 | |
| (b) Wet after 72 h boil, % | 43.7 | 40.1 | 51.1 | 36 | |
| (c) Wet after 24 h VPS, % | 63.7 | 50.6 | 84.5 | 46 | |
| Internal bond, kPa | 750 | 600 | 706 | 300 | |
| Thickness increase: | | | | | |
| (a) After 72 h boil, % | 17.8 | 17.2 | 13.5 | | |
| (b) After 24 h VPS, % | 8.5 | 10.3 | 10.0 | | 12% or 3 mm |
| Surface absorption, g/m$^2$ | - | - | - | | 300 |

TABLE 4

SURFACE WATER ABSORPTION BY COMMERCIAL PARTICLEBOARDS

| Adhesive | Urea-formaldehyde | | | Tannin-formaldehyde | | Phenol-formaldehyde | |
|---|---|---|---|---|---|---|---|
| Manufacturer | A | H | J | D | F | A | K |
| Board thickness (mm) | 20 | 19 | 20 | 19 | 20 | 20 | 19 |
| Water absorbed in 2 h, g/m² | 54 | 59 | 32 | 74 | 70 | 136 | 308 |

These commercial boards were tested for compliance with the draft of AS 1859, which requires thickness increase after immersion in water but not water absorption.

Surface water absorption has been incorporated in AS 1859 as a measure of a board's tendency to absorb moisture when exposed to the weather in platform construction for up to 3 months and in service as the result of water spillage. The method of determining surface absorption is given in Appendix F of AS 1859.

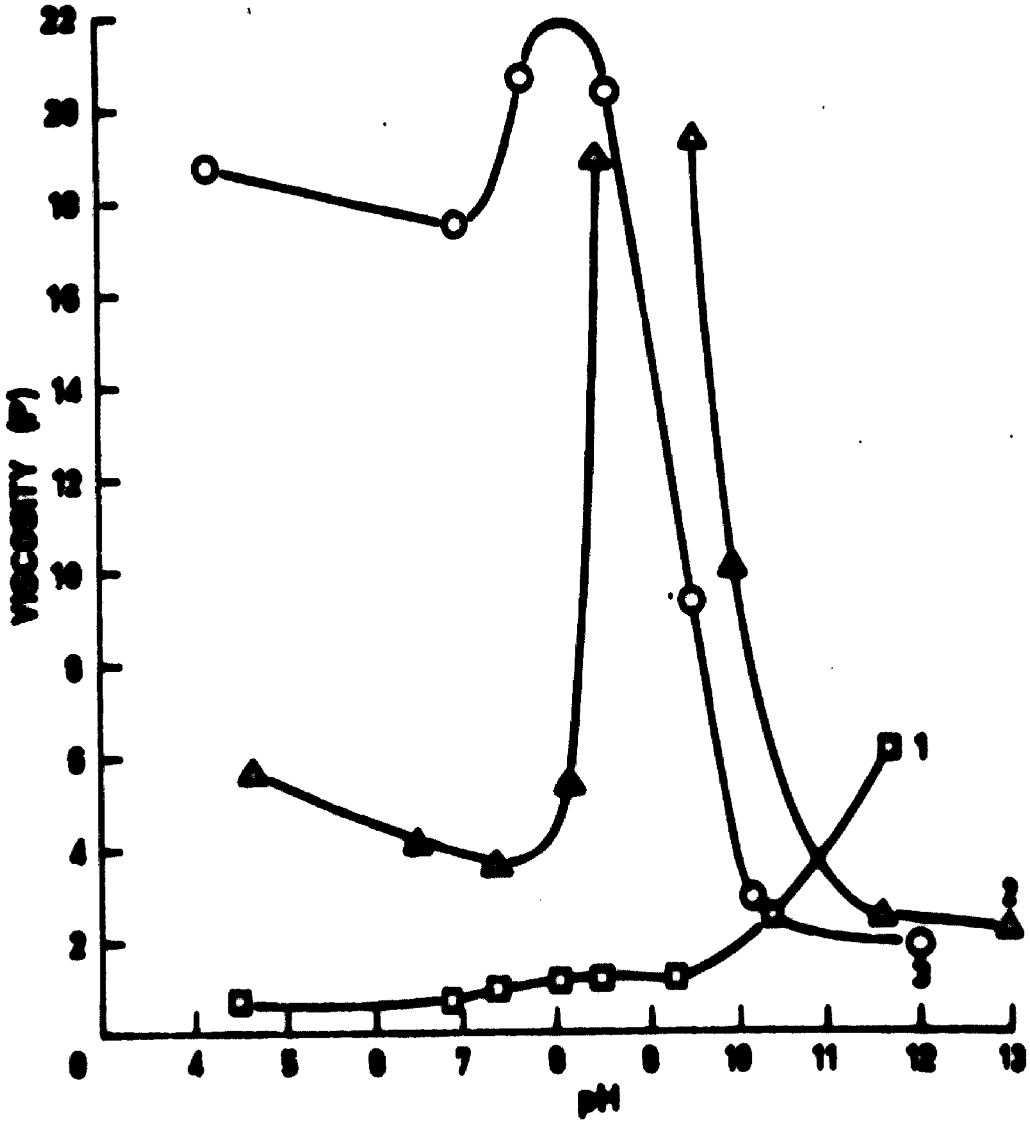


Fig. 1. Effect of pH on the viscosity of
1, Wattle; 2, Mangrove; 3, Quebracho (non-sulphited)
tannin solutions

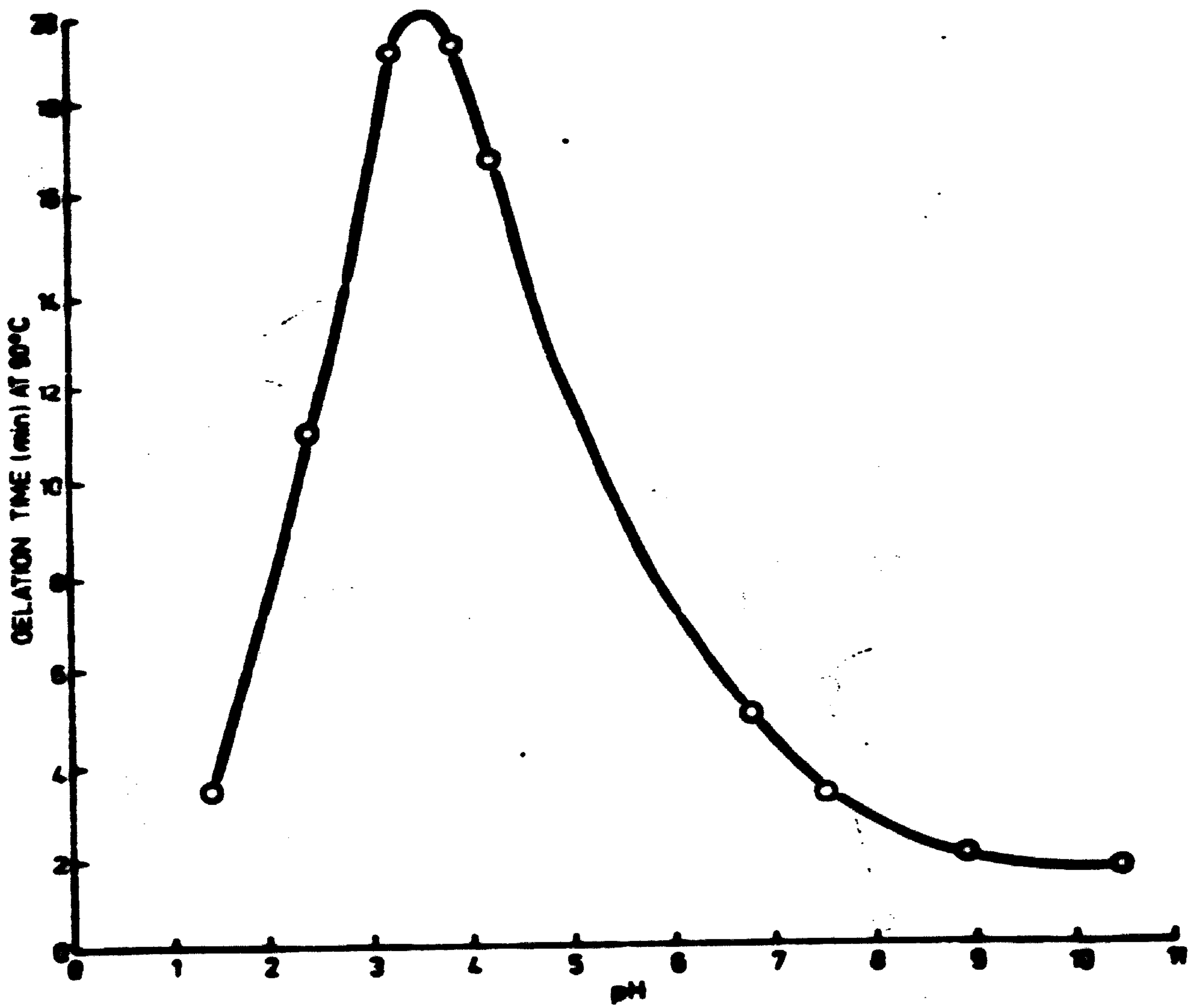


Fig. 2. The influence of pH on the gelation time at 90°C of an aqueous solution of 35% wattle tannin and 3% formaldehyde

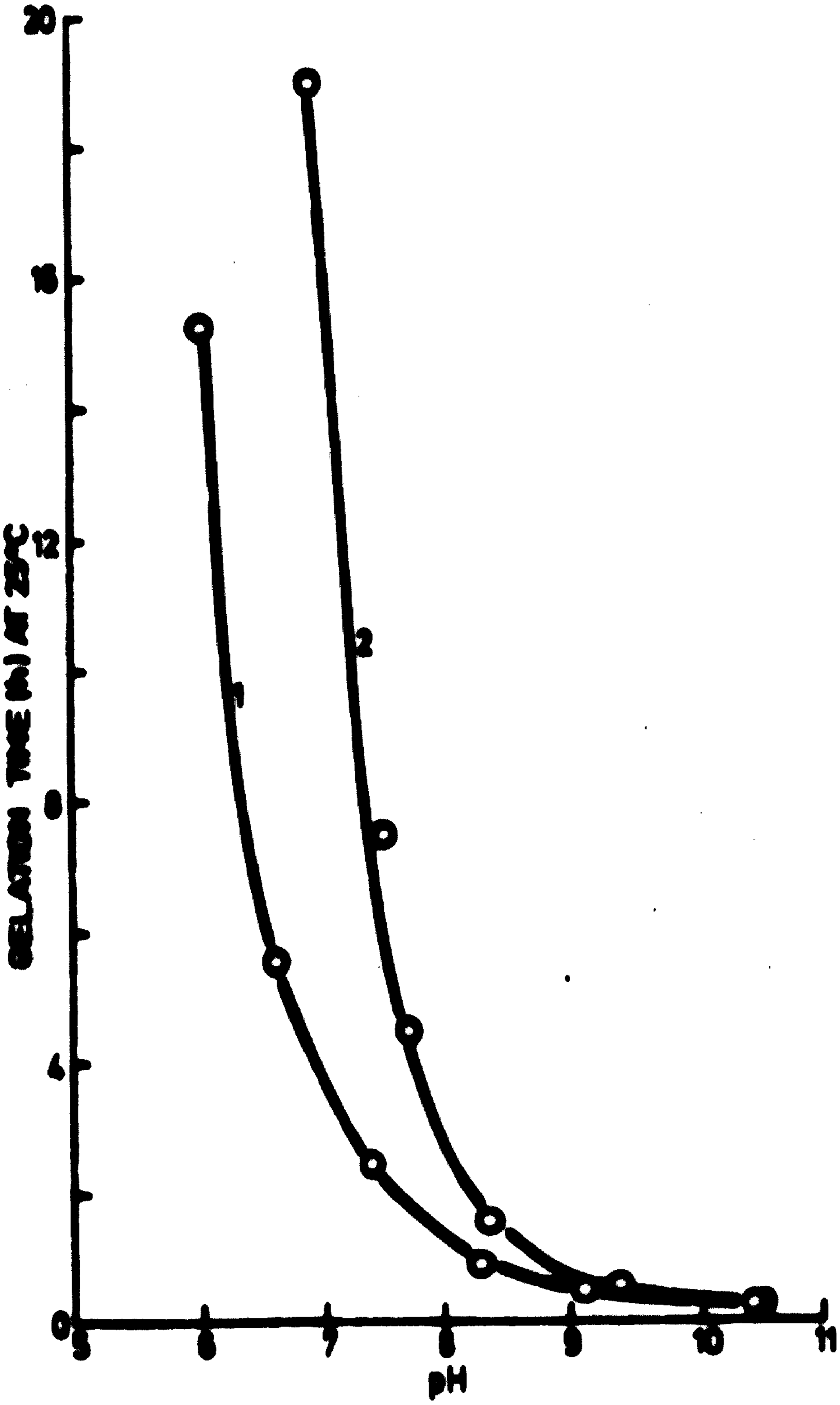


Fig. 3. The influence of pH on the gelation time at 25°C of a 40% solution of wattle tannin with 8% (on oven-dry extract) of 1, Formaldehyde; 2, Paraformaldehyde

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