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Tannin-based adhesives for bonding high-moisture Eucalyptus veneers: Influence of tannin extraction and press conditions

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The alkaline extraction of tannins from *Pinus pinaster* bark was studied as regards the influence of solid/liquid ratio, extraction time and NaOH concentration on the yield and Stiasny number of the extracts precipitated at pH 2. The extract with the highest Stiasny number(97) was copolymerized with a previously prepared resol to afford a resin with a 1:1 phenol/tannins ratio. Plywood boards of *Eucalyptus globulus* bonded with this resin at board humidities of 10 or 16%, temperatures of 130 or 185 °C and press times of 5 or 8 min all passed the WBP knife test (with one exception for the longer press time). We conclude that this resin is superior to commercial phenol-formaldehyde resins as regards its tolerance to moisture in plies and adhesive, its press time requirement, and its ability to bond veneers of woods known for their high levels of adhesive-repellent substances.

Tanninkleber zum Verleimen sehr feuchter Furnierblätter: Einfluß der Tanninextraktion und der Preßbedingungen

Die Alkaliextraktion von Tanninen aus *Pinus pinaster* wurde untersucht im Hinblick auf den Einfluß des Flottenverhältnisses, der Extraktionszeit und der NaOH-Konzentration auf die Ausbeute und die Stiasnyzahl der Extrakte nach Ausfällen bei pH 2. Der Extrakt mit der höchsten Stiasnyzahl (97) wurde mit Resol copolymerisiert, so daß sich ein Phenol-Tannin-Verhältnis von 1:1 ergab. Alle Sperrhölzer, die aus *Eukalytus-globulus*-Furnieren mit Feuchten von 10 oder 16% mit diesem Harz verleimt waren (Preßtemperaturen 130 oder 185 °C, Preßzeiten 5 oder 8 Minuten), bestanden entsprechende Qualitätstests. Eine Ausnahme bildeten Sperrhölzer, die bei längerer Preßzeit hergestellt waren). Dieses Tanninharz erscheint uns kommerziellen PF-Harzen überlegen in Hinsicht auf seine Feuchtetoleranz in Furnier und Harz, die Preßzeit und das Bindevermögen auch für Hölzer, die als schwerverleimbar gelten.

1 Introduction

Although phenol-formaldehyde (PF) adhesives have dominated the board industry for many years because they bond many woods satisfactorily at reasonable cost, their limitations are now well known. In particular, plywood boards made of certain woods of relatively high density, such as *Eucalyptus pilularis* and *Eucalyptus globulus*, fail to reach WBP standard when bonded with PF adhesives (apparently because of their high levels of adhesive-repellent substances; Yazaki et al. 1993); and commercial PF adhesives require that the moisture content of the wood to be bonded be no higher than about 5%.

It has also been known for some years that the above limitations can to a considerable extent be overcome by replacing part of the phenol content of the adhesive with tannins extracted from waste fractions of certain timber species. Unfortunately, this solution is only economically viable in countries growing appropriate species, hitherto mainly wattle and *quebracho*. Until recently, it was not possible to use the tannins of other softwoods (notably pine) because of their greater viscosity and variability and lower Stiasny numbers (Yazaki and Collins 1994b; Vázquez et al. 1992), and because their greater reactivity with formaldehyde meant that adhesives based on these tannins had inviably short pot-lives. However, the problems with these more reactive tannins now appear largely to have been overcome. It has been found that stable pine tannins can be prepared by concentration of the initial extracts, precipitation in acid medium and centrifugal filtration (Vázquez et al. 1992), and that mixing these tannins at room temperature with a suitable high-methylol resol (Vázquez et al. 1993) yields a resin which has a long enough pot life for industrial use while retaining the advantages of high reactivity (the possibility of using shorter press times and wood with higher moisture content). Exterior grade particleboards have been satisfactorily prepared with adhesives based on tannins from pine and other species (Pizzi and Stephanou 1994; Pizzi et al. 1994), and plywood boards have been manufactured from veneers with a 12% moisture content using tannins from *Pinus radiata* bark (Yazaki and Collins 1994a).

In our work on the stabilization of *Pinus pinaster* tannins by concentration and on the use of these concentrates in adhesives for plywoods (Vázquez et al. 1992, 1993), the crude extracts that were concentrated were obtained under conditions that had been optimized for maximum total extract yield (Vázquez et al. 1987): bark particles sizes < 1 mm were treated for 15 min with 1% NaOH. We have now re-examined extraction conditions from the point of view of the yield and formaldehyde-condensable polyphenol content of the concentrated tannins obtained from the crude extracts. In this paper we report our results in this respect, together with the influence of press time, press temperature and veneer moisture content on the quality of plywood boards made of *Eucalyptus globulus* veneers bonded with an adhesive prepared from a tannin concentrate with a Stiasny number of 97.

2 Experimental

Figure 1 shows the scheme of the whole procedure followed, from bark to board.

2.1 Bark preparation

Pinus pinaster bark was obtained from the debarking drums of a local chipboard factory. Woody material was removed, the

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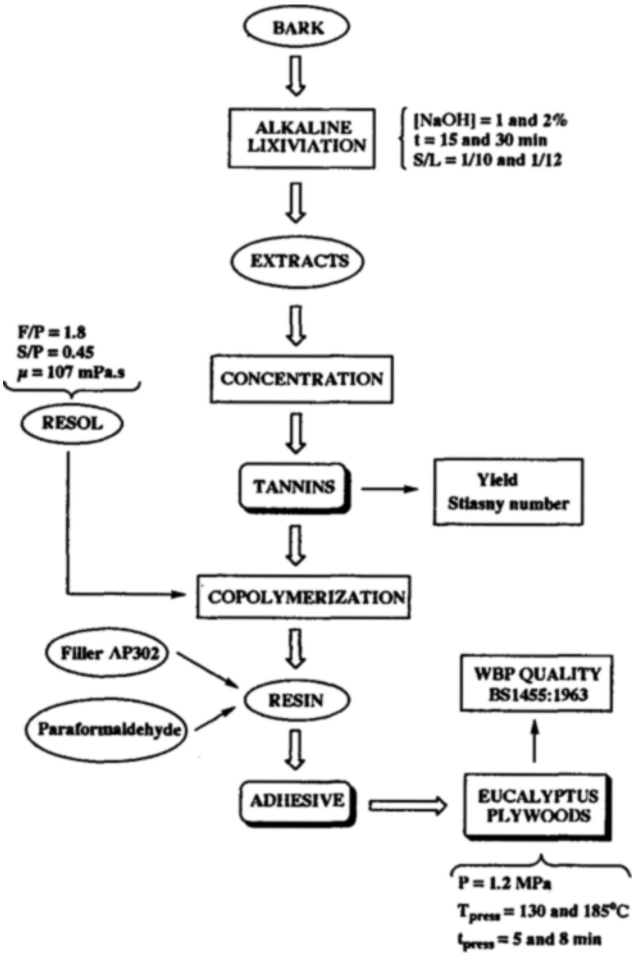

Fig. 1. Diagram of the process from bark extraction to plywood preparation and testing
Bild 1. Schema der Sperrholzherstellung von der Rindenextraktion bis zum Testen der fertigen Platten

bark was air-dried to a moisture content of about 20% and ground in a crushing mill, and the fraction sized > 1 mm was discarded.

2.2
Extraction of tannins

Experiments conforming to a replicated 2 × 2 × 2 factorial design were carried out to determine the influence of extraction conditions on tannin concentrate yield and quality. The ground bark was boiled with NaOH for 15 or 30 min in a 250 ml reactor at solid/liquid ratios S/L of 1/10 and 1/12 and NaOH concentrations of 1% and 2%. For preparation of adhesives, extraction was performed in a 10 l reactor under the conditions affording the tannin concentrate chosen as most suitable (S/L = 1/10, 1% NaOH, extraction time 15 min).

2.3
Concentration of tannins

Bark extracts were separated from the extraction mixture by filtration, and tannins were precipitated at pH 2 as per Vázquez et al. (1993). The precipitate was separated by vacuum filtration in the experiments to determine the influence of extraction conditions, and by centrifugal filtration for the preparation of adhesive for board manufacture. In the former case, the yield of tannin concentrate was determined as a percentage of dry bark weight, and the formaldehyde-condensable polyphenols content of the concentrate was evaluated as its Stiasny number (Voulgaridis et al. 1985). In the latter, the moisture content of the concentrated tannins was reduced from 80% to about 50% prior to their storage in a refrigerator.

2.4
Preparation of the adhesive

The adhesive resin was prepared at room temperature by copolymerization of a solution of the concentrated tannin extracts in NaOH with a resol prepared under previously optimized conditions (the formaldehyde/phenol mole ratio (F/P) was 1.8, the soda/phenol mole ratio (S/P) 0.45 and the viscosity (μ) 107 mPa . s, Vázquez et al. 1993) with a phenol/tannins ratio 1:1 (w/w). Immediately prior to use, the resin was supplemented with paraformaldehyde catalyst (1 g per 100 g of resin), AP302 filler (15 g per 100 g of resin; from FORESA) and wheat flour (2 g per 100 g of resin).

2.5
Plywood board manufacture

250 × 250 mm 5-ply boards were manufactured from *Eucalyptus globulus* veneers with thickness of 1.5 mm (the face plies) and 2.2 mm (the core plies). Adhesive was applied in a double glue line at a surface density of 300 g/m². The assembly time was 10 min and the press pressure 1.2 MPa. The influence of press time, press temperature and veneer moisture content on board quality (as evaluated following BS 1455:1963 norms for WBP quality boards) was determined by means of experiments conforming to a replicated 2 × 2 × 2 factorial design with press times of 5 and 8 min, press temperatures of 130 and 185 °C and veneer moisture contents of 10 and 16%.

3
Results and discussion

3.1
Yield and quality of the tannin concentrate

Table 1 lists the yields (13.8–22.4%) and Stiasny numbers (76–97) of the concentrates obtained from extracts prepared under the various experimental conditions employed, and Fig. 2 shows the response surfaces calculated for the influence of NaOH concentration and extraction time on yield (Fig. 2a) and

Table 1. Yields and Stiasny numbers of the tannin concentrates obtained from extracts prepared under various conditions

S/L	t (min)	[NaOH]	Yield (% o.d. bark)	Stiasny Number
1/10	15	1	16.47	89.82
1/10	15	1	16.72	97.26
1/12	15	1	13.80	95.59
1/12	15	1	16.14	91.19
1/10	30	1	17.09	87.46
1/10	30	1	16.52	96.63
1/12	30	1	17.42	83.61
1/12	30	1	17.18	94.81
1/10	15	2	20.38	78.09
1/10	15	2	16.06	91.76
1/12	15	2	19.28	81.20
1/12	15	2	17.89	86.30
1/10	30	2	19.94	84.60
1/10	30	2	22.39	76.59
1/12	30	2	19.35	83.64
1/12	30	2	19.65	86.05

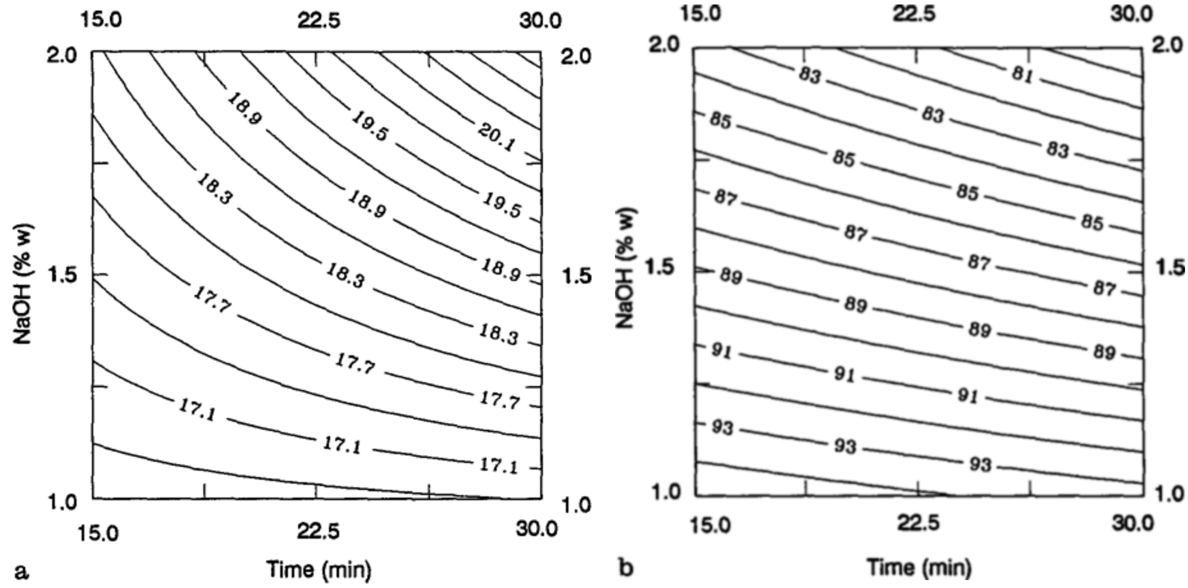

Fig. 2a, b. Dependence of yield (a) and Stiasny number (b) on time and NaOH concentration at a solid/liquid ratio of 1/10
Bild 2a, b. Abhängigkeit von Ausbeute (a) und Stiasny-Zahl (b) von der Zeit und von der NaOH-Konzentration bei einem Flottenverhältnis von 1/10 (fest/flüssig)

Stiasny number (Fig. 2b) for an S/L ratio of 1/10 (data for S/L = 1/12 are not shown because S/L proved to have relatively little influence on the dependent variables). Yield increased and Stiasny number decreased with increasing NaOH concentration and extraction time, although all Stiasny numbers were well above the figure of 65 stated by Yazaki and Collins (1994b) to be the lower limit for tannin concentrates that can be used in the formulation of adhesives. For both dependent variables, changing NaOH concentration had a greater effect than changing extraction time; the effect of latter was greater at the higher NaOH concentration than at the lower, and was greater for yield than for Stiasny number.

3.2 Characteristics of the adhesive

The tannin concentrate with the highest Stiasny number (97) was redissolved in a 45% NaOH solution and was copolymerized at room temperature, with a resol prepared as described elsewhere (Vázquez et al. 1993). The resultant resin had a gel time of 11 min, a viscosity of 414 mPa . s, a pH of 10.4, a solids content of 38% and no detectable formaldehyde.

The short gel time indicates a reactivity considerably higher than that of commercial phenolic adhesives, which typically have gel times of about 18 min. This high reactivity proved to allow shorter press times than usual (see below), but did not reduce pot life excessively.

As has been pointed out by Pizzi and Stephanou (1994), the tolerance of faster reacting tannin-based adhesives to high moisture contents allows better control of their viscosity. The adhesive prepared in this work, which performed well in plywood bonding tests (see below), compared favourably with PF adhesives in this respect, having a solids content of 38% as against the minimum solids content of 42% of PF adhesives used for plywood manufacture.

Finished boards must comply with legal limits on formaldehyde emission, which usually depends largely on the free formaldehyde content of the adhesive bonding the board. No free formaldehyde was detected in the adhesive prepared in this work, presumably because of the high reactivity of its tannin component.

3.3 Influence of press conditions and veneer moisture on board quality

Table 2 lists knife test results for the boards made under the conditions specified in Experimental. All except one of the boards met BS1455:1963 for WBP-quality boards, and the exception (manufactured by pressing veneers with a moisture content of 16% for 8 min at 130 °C) failed to make the standard by only 0.25.

Statistical analysis showed veneer moisture content to be the independent variable with the greatest influence on mean knife test rating, even though the response surfaces presented in Fig. 3 show that for the shorter press time the effects of veneer moisture content and press temperature were very similar. The least influential of the three independent variables was press time, doubtless because even the shorter press time is sufficient for good bonding by the fast-setting tannin-based adhesive used

Table 2. BS 1455 delamination test ratings for eucalyptus plywood boards

T_{press} (°C)	t_{press} (min)	Veneer moisture content	Knife test	
			Glue line	Mean
130	5	10	7-5-4-7	5.75
130	5	10	8-3-4-7	5.50
185	5	10	8-5-3-8	6.00
185	5	10	7-4-5-7	5.75
130	8	10	8-6-4-7	6.25
130	8	10	7-5-5-6	5.75
185	8	10	8-4-4-6	5.50
185	8	10	7-5-4-7	5.75
130	5	16	6-4-3-8	5.25
130	5	16	6-4-4-6	5.00
185	5	16	7-4-4-6	5.25
185	5	16	8-3-5-8	6.00
130	8	16	7-4-4-6	5.25
130	8	16	6-4-4-5	4.75
185	8	16	7-4-5-6	5.50
185	8	16	8-4-3-7	5.50

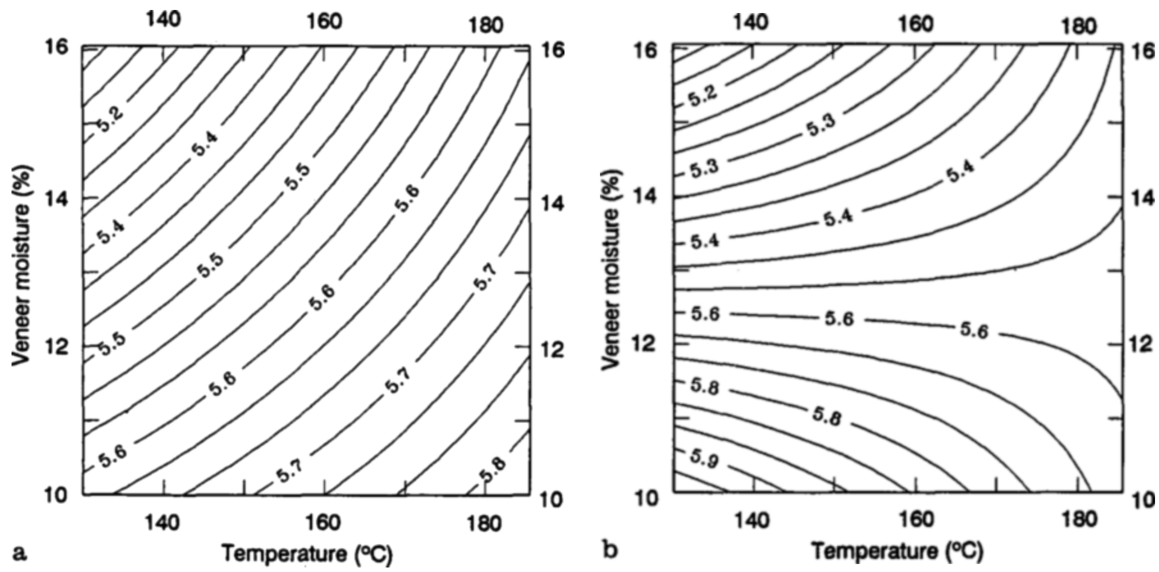

Fig. 3a, b. Dependence of delamination test mean ratings (BS 1455:1963 for WBP quality plywoods) on veneer moisture and press temperature for press times of 5 min (a) and 8 min (b)

Bild 3a, b. Ergebnisse der Qualitätstests (nach BSD 1455:1963) für verschiedene Feuchtegehalte und Preßtemperaturen. a Preßzeit 5 min; b Preßzeit 8 min

(although similar analyses for the individual glue lines show press time to have a greater effect than temperature for the inner lines).

As expected, for any given temperature and time, mean bond quality falls as veneer moisture content increases. More surprisingly, with a press time of 8 min bond quality is predicted to increase with temperature for veneer moisture contents $> 14\%$, to remain unaffected by temperature for veneer moisture contents between 12% and 14%, and to decrease with rising temperature for veneer moisture contents $< 12\%$; and the analogous response surfaces for the individual glue lines show that it is the inner glue lines that are responsible for this behaviour. With a press time of 5 min bond quality behaves more consistently, increasing with temperature for all values of veneer moisture content (though more rapidly for high moisture contents than for low).

The ability of tannin-based adhesives to bond high-moisture veneers satisfactorily can be attributed in part to their favourable rheology. PF resins require low veneer moisture contents because at higher moisture contents no satisfactory compromise can be reached between good spreading and the need to neutralize the tendency of the resin to migrate to the interior of high-moisture veneers, so leaving the glue line glueless; migration can be reduced by increasing the molecular weight of the resin, but PF resins must have relatively low molecular weights in order to spread well (Steiner et al. 1993). The fact that the molecular weight of a tannin-phenol-formaldehyde (TPF) resin has a higher mean but a broader distribution than those of PF resins seems partly to explain why TPF resins with viscosities in the usual range for industrial manufacture of plywoods show no marked tendency to migrate into the wood. Yazaki and Collins (1994a) have even reported that high veneer moisture content improves bonding by some resins based on *Pinus radiata* bark tannins.

Yazaki et al.'s (1993) finding that certain *Eucalyptus pilularis* extracts retard the gelling and deteriorate the rheology of PF resins suggests that the general inability of PF resins to bond eucalyptus well may be partly due to the effects of these substances at the veneer surface. Our results suggest that such substances do not significantly hinder the bonding of *Eucalyptus globulus* veneers by the tannin-based adhesive used in our work, which like similar adhesives tested previously (Vázquez et al. 1993) exhibited excellent spreading properties favouring high board quality and low cost.

Although no formaldehyde was detected in the resin used, the boards prepared with this resin had a mean formaldehyde content of 2.86 mg per 100 g of board due to the paraformaldehyde catalyst added prior to spreading. It may be pointed out that in previous work (Vázquez et al. 1992) a similar resin bonded eucalyptus boards satisfactorily even without addition of paraformaldehyde.

4
Conclusions

The alkaline extraction of tannins from *Pinus pinaster* bark was studied as regards the influence of solid/liquid ratio, extraction time and NaOH concentration on the yield and Stiasny number of the extracts precipitated at pH 2. Increasing NaOH concentration and extraction time increased yield but reduced the Stiasny number, a measure of reactivity with formaldehyde. The highest Stiasny number, 97, was obtained by extracting for 15 min with 1% NaOH at a solids/liquid ratio of 1/10, under which conditions the yield was 16.7% of dry bark weight.

The optimal tannin concentrate specified above was copolymerized with a previously prepared resol to afford a resin with a 1:1 phenol/tannins ratio whose gel time and viscosity allowed its use for the manufacture of exterior grade plywoods. With respect to commercial PF resols this resin had the advantages of a) zero free formaldehyde content, and b) satisfactory performance at a lower solids content.

A study of the influence of press time, press temperature and veneer moisture content on the quality of plywood boards of *Eucalyptus globulus* bonded with the above resin showed veneer moisture content to have the greatest influence. However, all the boards except one passed the WBP knife test. With respect to the phenol-formaldehyde resols currently used for plywood manufacture, the adhesive used in this work has the advantages of 1) allowing shorter press times; 2) allowing higher veneer moisture contents (up to at least 16%), and 3) affording good spreading and satisfactory bonding even with a wood (*Eucalyptus globulus*) with high levels of adhesive-repellent substances.

9
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Identification of Reaction Beech Wood by X-ray Computed Tomography

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Subject Reaction wood (RW) is a defect of wood-structure, which occurs very frequently in beech wood raw material. A non-destructive method that enables identification of reaction wood in beech logs is described.

Material and methods For identification of RW an X-ray computed tomography (CT) from Siemens Somatom DR was used. With the application of X-ray CT method we issued from the fact that the absorption of X-rays in wood depends on wood density. The intensity I of X-rays transmitted through a specimen is expressed by the relation

$$I = I_0 \exp(-\mu x) \qquad (1)$$

where I_0 is the intensity of incident X-ray, μ is the linear absorption coefficient and x is the thickness of the specimen. The linear absorption coefficient is dependent on the specimen density ρ and moisture content w

$$\mu = f(\rho, w). \qquad (2)$$

By X-ray CT we obtained tomograms of cross-sections in arbitrarily chosen places of logs. A microphotometer and image analysis were used for the evaluation of these tomograms. For identification of RW beech logs with the diameter from 30 to 350 mm and the length from 50 to 500 mm were used.

Results First of all, the reaction wood on the planed cross sections was identified visually as lighter areas contrasting with opposite wood (OW) (Fig. 1a). By X-ray CT we then obtained tomograms in the vicinity of these sections (Fig. 1b). The moisture content in specimens was 6%. After having immersed the specimens into water and after a certain period of watering we again obtained tomograms using X-ray CT in the same places (Fig. 2a). These tomograms were evaluated with the aid of image analysis (Fig. 2b). The analysis of the tomograms showed that the accuracy of the RW recognition is dependent on the difference between densities of RW and OW. In the most cases the density of oven-dried RW ρ_0 was significantly higher than that of the opposite one. But a high variability of RW density was observed not only between the different stems but also within one stem. As wood density is influenced by moisture content, the absorption of X-rays