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Investigations on bark extractives of Pinus halepensis Mill.

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Extractives were taken from the bark of Pinus halepensis, using water, 1% NaOH and 5% NaOH (with and without sulfonation), with resultant extract yields higher for the NaOH extracts than for those with water only. The NaOH extracts, however, showed lower reactivity. 30 days' storage in liquid or solid form had little influence on their viscosity, pH value and reactivity. At 33% concentration and pH's of 4 to 12 extracts done with water (with and without sulfonation) and with 1% NaOH solution (with sulfonation) showed high reactivity to formaldehyde. Extracts at pH 7 to 8 had short gelation times and longer ones at pH 4 (water extraction) and pH 10 (extraction with 1% NaOH solution, with sulfonation). The remaining three extracts proved unsuitable for further use as bonding agents, either due to their high viscosity or to their inability to cure. With the use of paraformaldehyde as hardener gelation times tended to become longer.

Untersuchung der Rindenextrakte von Pinus halepensis Mill.

Die Rinde von Pinus halepensis wurde mit Wasser, 1% NaOH und 5% NaOH (mit und ohne Sulfitierung) extrahiert, was zu höherer Extraktstoffausbeute führt als die reine Wasserextraktion. Die mit NaOH gewonnenen Extrakte zeigen jedoch niedrigere Reaktivitäten. Nach 30 Tagen Lagerung waren ihre Viskosität, pH-Wert und Reaktivität nur wenig verändert. Bei 33% Konzentration und pH 4 bis 12 zeigten die mit Wasser (mit und ohne Sulfitierung) und die mit 1% NaOH-Lösung (mit Sulfitierung) gewonnenen Extrakte hohe Reaktivität gegenüber Formaldehyd. Extrakte bei pH 7 bis 8 zeigten kurze, bei pH 4 (Extraktion mit Wasser) und bei pH 10 (Extraktion mit 1% NaOH-Lösung mit Sulfitierung) längere Gelierzeiten. Die übrigen drei Extrakte sind für eine weitere Verwertung als Bindemittel ungeeignet, entweder wegen ihrer hohen Viskosität oder ihrer Unfähigkeit, zu härten. Bei Verwendung von Paraformaldehyd als Härter werden die Gelierzeiten länger.

1 Introduction

During the last decade, the oil crisis has led to the continuously rising prices for synthetic wood adhesives (mainly phenolic type) which caused cost problems in their industrial application. As a consequence, increasing efforts have been made to replace, totally or partially, raw materials of synthetic glues by other new, cheaper and renewable sources of phenolic compounds such as bark and agricultural residues.

The use of phenolic materials (i.e. tannins) extracted from renewable sources (forest and agricultural residues) as bonding agents has been suggested since the 1950's (Dalton 1950, 1953; Plomley, Gottstein and Hillis 1957; Herrick, Conca 1960; Hall, Leonard and Nicholls 1960; Anderson, Breuer and Nicholls 1961). The bark of a number of forest trees (Pinus, Abies, Picea, Tsuga, Pseudotsuga, Acacia, Rhizophora, Quercus, Lithocarpus) and the wood of the genus Shinopsis have often been investigated as raw materials for production of phenolic type extractives and as bonding agents on a worldwide level. The use of certain barks or woods is associated with their availability, the extract yield and the quality of extractives. A matter of special importance is the content of hydrolizable and condensed tannins in the extractives. Condensed tannins are characterized by low solubility but high reactivity with formaldehyde when related to hydrolizable tannins (Houwink, Salomon 1965).

In European research, there has recently been an increasing interest in the potential use of bark extractives from the species Pinus silvestris, P. radiata, P. nigra, P. brutia, P. halepensis and Picea abies in wood adhesive formulations. (Weissmann, Ayla 1980; Ayla, Weissmann 1981; Weissmann 1981; Liiri et al. 1982; Dix, Marutzky 1983; Tišler, Ayla and Weissmann 1983). The above mentioned research indicates that the highest extract yield and the best extract reactivity with formaldehyde are provided by the bark of Pinus halepensis and P. brutia. These two species are grown mainly in Mediterranean countries, and in Greece they cover 13,4% and 5,1% respectively of the total forest area (2,470,000 ha) (Tsoumis 1980). For countries like Greece, which import significant quantities of glues from abroad, the investigation of bark extractives from local species and their suitability for wood adhesives is of particular importance.

The objectives of this work are to investigate the properties of bark extracts from Pinus halepensis and to evaluate their suitability as bonding agents. The present research is the first stage of a series of studies aimed at investigating the utilization potential and applicability of bark and other renewable raw materials for the wood adhesive industry.

2 Materials and methods

Bark (inner and outer) was collected from the base logs (3 m long) of three haleppo pine trees (Pinus halepensis). The trees were 45 to 50 years old with barked diameter 30 to 35 cm and bark thickness 2 to 2.5 cm (at 50 cms height from the ground). The bark was dried at room condition at about 20% moisture content and practically all the bark was converted into small particles of less than 1.5 mm by successive hammer milling. This fraction was used for extraction. It is worth noting that the particle size of the bark did not appear to influence the extract reactivity with formaldehyde and that smaller particles merely increase the extract yield (Liiri et al. 1982).

Table 1. Extraction liquids of Pinus halepensis bark

a/a	Extraction liquid
1	Water + sulfonation[a]
2	Water
3	1% NaOH + Sulfonation[a]
4	1% NaOH
5	5% NaOH + Sulfonation[a]
6	5% NaOH

[a] 0.25% sodium sulphite + 0.25% sodium bisulphite based on dry weight of the bark powder

For each extraction, 110 g bark powder of moisture content 16.1% was used (94.75 g dry weight). The proportion dried bark: extraction liquid during the extraction process was 1:8 (g/ml). Table 1 shows the six extraction liquids used in this experiment. The addition of NaOH to the extraction liquid influences the yield and the properties of the extract. As far as the role of sulfonation is concerned, it has been reported that, in small quantities, it affords stability to the extract and reduces its viscosity (Hall, Leonard and Nicholls 1960). Extraction was carried out in 1,000 ml beakers placed in a waterbath at temperature 80 °C for 2 hours. Temperatures above 80 °C increase the extract yield but may adversely affect the quality of the extract by increasing its viscosity (Chen 1982a; Liiri et al. 1982; Steiner and Chow 1975) or by decreasing the reactivity with formaldehyde (Liiri et al. 1982; Chen 1982b). Weissmann and Ayla (1980) have found that by increasing the extraction temperature from 40 °C to 100 °C the extract yield increases but the reactivity remains more or less constant. Extraction time longer than 1 to 2 hours did not influence the extract yield (Liiri et al. 1982).

After extraction, the extract solutions were filtrated and stored at room condition (23 ± 2 °C). The extract yield was determined as a percentage of the dry weight of bark powder before the extraction. Samples of the extract solutions, each 50 ml in volume, were used for the determination of the extract concentrations. The properties of the extract solutions (pH, viscosity, reactivity) were determined within 2 days after the extraction and after 30-day's storage at room condition. Storage may change the extract properties (Hall, Leonard and Nicholls 1960) and, therefore, the study of storage effects is of practical significance. Acidity and viscosity of the extracts were measured at 21 °C by using a Chemtrix electric digital pH-meter and a Brookfield RVF-100 rotational viscometer respectively. The reactivity of the extracts with formaldehyde was determined by using the Stiasny method (Gnamm 1949) as follows: 10 ml of a 37% formaldehyde solution (formalin) and 5 ml of a 38% hydrochloric acid were added to 50 ml extract solution of concentration 0.4% and the final solution was heated for 30 minutes at boiling temperature. Then, the solution was filtrated through filter No. 3 by suction and the solid residue was washed and dried at 105 °C and weighed. The reactivity was calculated by the formula:

$$S(\%) = \frac{A}{B} \times 100\,,$$

where, S = reactivity (Stiasny-Number)[1]; A = dry weight of the solid, g; B = dry weight of the extract that is contained in 50 ml of the extract solution of concentration 0.4%.

Gelation time was measured after 30-days' storage of the extracts at 95 °C by adding 2.5% formaldehyde solution of 37% formaldehyde content or 5% paraformaldehyde (both based on dry weight of the extract) to extract solution of concentration ~33%. This concentration was achieved by condensation of the extracts in a waterbath at 80 °C.

3 Results and discussion

The results are presented in Tables 2–5. Table 2 shows the extract yield and the concentration of each extract solution. The bark extract yield taken with water from domestic haleppo pine was found to be similar to that of Algerian (28.6%), but higher than that of Jugoslavian origin (16.1%) (Tišler et al. 1983). Sulfonation of the extraction liquid did not appear to influence the extract yield. However, Dix and Marutzky (1983) have found that the addition of Na_2SO_3 (up to 0.25%) in the extraction liquid (water) resulted in an increased extract yield from the bark of Pinus silvestris, Pinus radiata and Picea abies. Addition of 1% NaOH to the extraction liquid increased the extract yield. Further increase of extract yield was achieved by increasing the amount of NaOH (from 1% to 5%) added to the water (Table 2). Such effects of NaOH on extract yield have also been found by other investigators (Dietrichs et al. 1978; Weissmann, Ayla 1980; Chen 1982a; Liiri et al. 1982; Dix, Marutzky 1983).

Table 3 presents some properties of the extract solutions (acidity, viscosity, reactivity) before and after storage. The extraction liquids containing 1% and 5% NaOH significantly increase the pH value of the extracts (2 to 3 times). Storage of the extract solutions for 30 days at room condition did not appear to have any practical effect on pH. A decrease of pH up to 1.5 units was measured only in 1% NaOH solutions. The viscosity of all extract solutions at their initial concentrations (after extraction) appeared to be small and without differences. Storage did not change the viscosity of the extract solutions (Table 3). The reactivity of bark extracts of Pinus halepensis achieved with hot water was found to be similar to that found by other researchers on Pinus halepensis and Pinus brutia but greater when compared with other species of the genus Pinus and with Picea abies (Table 4). The reactivity of bark extracts is reduced by adding NaOH to the extraction liquid (Table 3). Such reduction was observed by Weissmann and Ayla (1980) in Pinus brutia and by Dix and Marutzky (1983) in Pinus silvestris, Pinus radiata and Picea abies by using more than 1% NaOH solutions as extraction liquids. Opposite results have been attained, however, by

Table 2. Yield and concentration of bark extracts from Pinus halepensis

a/a	Extraction liquid	Extract yield[a] %	Concentration of extract solution[b] %
1	Water + Sulfonation	27.56	3.72
2	Water	29.69	3.56
3	1% NaOH + Sulfonation	40.17	5.76
4	1% NaOH	39.85	5.82
5	5% NaOH + Sulfonation	47.23	10.10
6	5% NaOH	47.21	10.72

[a] Based on dry weight of bark powder (w/w)

[b] Based on the volume of extract solution after filtration (w/v). Extract solutions include the corresponding amounts of NaOH, sodium sulphite and sodium bisulphite

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[1] Stiasny-Number is considered an index of the amount of reactive phenolic compounds included in the extracts

Table 3. Acidity, viscosity and reactivity of bark extracts before and after storage

a/a	Extraction liquid	Acidity[a] pH		Viscosity[a] mPa. s		Reactivity[a] Stiasny-Number		
		A	B	A	B	A	B	C
1	Water + Sulfonation	4.32	4.14	9.4	10.6	81.45	83.10	81.35
2	Water	4.27	3.83	8.6	9.0	80.30	82.20	84.45
3	1% NaOH + Sulfonation	10.07	8.45	11.0	14.0	67.85	68.50	70.35
4	1% NaOH	10.04	8.78	10.6	11.0	69.35	68.65	71.95
5	5% NaOH + Sulfonation	12.27	12.27	11.0	11.6	38.45	28.45	28.75
6	5% NaOH	12.28	12.28	11.0	11.2	37.30	32.05	28.90

[a] A = Within two days of extraction,
B = After 30 days' storage in liquid form,
C = After drying of extract solutions at 105 °C, and 30 days' storage in solid form and re-solution. Acidity and viscosity were measured at the concentrations of the extract solutions achieved (Table 2)

Table 4. Bark extract reactivity (Stiasny-Number) of various pine species and Picea abies

a/a	Species	Reactivity Stiasny-Number	Source
1	Pinus halepensis (Greece)	80.3	Present study
2	Pinus halepensis (Jugoslavia)	75.2	Tišler, Ayla, Weissmann (1983)
3	Pinus halepensis (Algeria)	78.5	Tišler, Ayla, Weissmann (1983)
4	Pinus brutia	77.9	Weissmann, Ayla (1980)
5	Pinus nigra	24.0	Tišler, Ayla, Weissmann (1983)
6	Pinus silvestris	24.8	Roffael (1976)
7	Pinus silvestris	43.4	Dix, Marutzky (1983)
8	Pinus radiata	65.9	Dix, Marutzky (1983)
9	Picea abies	50.2	Dix, Marutzky (1983)
10	Picea abies	64.8	Roffael (1976)
11	Picea abies	~50.0	Weissmann (1981)

Liiri et al. (1982) for Picea abies and by Chen (1982b) for southern pine.

Storage of bark extracts either in liquid or in solid form did not appear to affect their reactivities except for 5% NaOH solutions in which storage caused a reduction of reactivity (Table 3).

Sulfonation of the extraction liquids used in this study does not seem to influence the viscosity, acidity and reactivity of bark extract solutions at their initial low concentration (Table 3). Other investigators (Dix, Marutzky 1983) have observed a small increase of bark extract reactivity in Pinus silvestris and Picea abies and quite a large increase in Pinus radiata by adding up to 0.25% Na_2SO_3 to the extraction liquid. However, sulfonation of extraction liquid by the mixture Na_2SO_3 and $NaHSO_3$ (1:1) at relatively high concentrations (1 to 5%) reduced the bark extract reactivity of the above species. It has also been observed (Dix, Marutzky 1983) that sulfonation of extraction liquid up to 1% caused an increase in pH, but had no effect in greater amounts (1 to 5%).

The viscosity and gelation time of the bark extracts at 33% concentration are shown in Table 5. In general, the increase of extract concentration from the initial to 33% seems to cause an increase in viscosity but in varying degrees for the six extract solutions used in the experiment (Table 5). This increase in viscosity caused by increasing the extract concentration had to be expected, and has also been observed by other investigators (Hall et al. 1960; Ayla, Weissmann 1980; Liiri et al. 1982; Tišler, Ayla and Weissmann 1983). The viscosity (108 mPa.s) of the extract solution 2 (water without sulfonation) at 33% concentration was found to be greater than that for haleppo pine bark extract of both Jugoslavian (98 mPa.s) and Algerian (78 mPa.s) origin at 35% concentration in water. The increase in viscosity at 33% concentration was very great in extract solutions 3 and 4 (1% NaOH)

Table 5. Viscosity and gelation time of bark extracts of Pinus halepensis at concentration 33%

a/a	Extraction liquid	Gelation time's					
		Viscosity mPa · s	5% para-formaldehyde at initial pH[a]	2.5% formaldehyde (37%)			
				at initial pH[a]	pH = 4	pH = 7	pH = 10
1	Water + Sulfonation	76	180	105	–	46	48
2	Water	108	177	100	–	53	46
3	1% NaOH + Sulfonation	1,362	79	65	76	65	83
4	1% NaOH	30,139[b]	–	–	–	–	–
5	5% NaOH + Sulfonation	34	No curing achieved within 30 min				
6	5% NaOH	29	No curing achieved within 30 min				

[a] The initial pH (after 30 days' storage) for the extract solutions No. 1, 2 and 3 was: 4.14, 3.83 and 8.45 respectively

[b] Gelation time not measured due to very high viscosity

especially in solution 4 (compare Tables 3 and 5). The great difference between the extract solutions 3 and 4 may be attributed to sulfonation of solution 3. A similar effect of sulfonation on viscosity was also observed in extract solutions 1 and 2 but to a much lesser degree. On the contrary, in extract solutions 5 and 6 (5% NaOH) low and approximately equal viscosities were determined and the effect of sulfonation is not clear. The addition of relatively large quantities of NaOH to the extraction liquid is likely to cause a reduction in bark extract viscosity and such indications were also found by Liiri et al. (1982) and Saayman, and Vatley (1976) when adding NaOH either to the extraction liquid (during extraction) or to the extract solution (after extraction).

Gelation time of the extracts when using 2.5% formalin was found to be considerably lower than that determined when using 5% paraformaldehyde (Table 5). Similar results are referred to by Ayla and Weissmann (1981) for Pinus brutia. Prolonged gelation time determined by using paraformaldehyde is of practical importance because prolongs pot life. When using formalin, the lowest gelation time of the extract solutions 1 and 2 was determined at pH = 7 to 10 (0.77 to 0.88 min) and of the solution 3 at pH = 7 to 8 (1.08 min). At pH = 7 the extract solutions 1 and 2 were cured earlier than solution 3. In the extract solutions 1 and 2 the largest gelation times were observed at pH = 4 (Table 5). This is in agreement with earlier results according to which the longest gelation times of bark extracts of Pinus halepensis (Tišler, Ayla and Weissmann 1983), Pinus brutia (Ayla, Weissmann 1981) and Tsuga heterophylla (Steiner and Chow 1975) were determined at pH = 3 to 5. The non-curing of extract solutions 5 and 6 (5% NaOH) within 30 min may be attributed to low reactivity (Tables 5 and 3).

4 Conclusions

The results may be summarised as follows:

1. From the bark of Pinus halepensis significant amounts of extracts can be extracted. By using hot water as extraction liquid the extract yield was 29.7% whilst the addition of 1% and 5% NaOH to the extraction liquid increased the yield to 40.2% and 47.2% respectively.
2. Bark extracts taken by using hot water showed the highest reactivity (81.45 Stiasny-Number). The addition of 1% and 5% NaOH in the extraction liquid led to a decrease in extract reactivity (Stiasny-Numbers 67.85 and 37.30 respectively). Storage of the extracts either in liquid or in solid form caused a reduction in extract reactivity only in the case of 5% NaOH.
3. Storage of extracts in liquid form did not appear to affect acidity and viscosity of the extract solutions. At 33% concentration the viscosity of the extract solutions appeared very variable. Significantly high values of viscosity were measured in 1% NaOH solutions whilst the reverse (very low values) applied for 5% NaOH solutions.
4. The lowest gelation time of extract solutions 1, 2 and 3 (water after sulfonation, water and 1% NaOH after sulfonation respectively) at concentration 33% was determined at pH = 7 to 8 and the highest at pH = 4 (solution 1 and 2) and at pH = 10 (solution 3). The use of paraformaldehyde resulted in gelation times higher than those determined when using formaldehyde. The other solutions (4, 5 and 6) were found unsuitable due to high viscosity (solution 4) or to curing inability (solutions 5, 6).
5. From the three extract solutions (numbered 1, 2 and 3) which appeared to be suitable for use as bonding agents, the aqueous extract solutions (numbered 1 and 2) are superior in extract reactivity, while solution 3 (1% NaOH after sulfonation) exceeds the other two solutions in extract yield.

5 Literature

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