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Utilization of oleoresin and bark extractives from *Pinus halepensis* Mill. in wood products

by **Costas N. PASSIALIS***, **Athanassios H. GRIGORIOU***
and **Elias V. VOULGARIDIS***

I - Introduction

Aleppo pine (*Pinus halepensis* Mill.) is a forest species grown mainly in Mediterranean countries and, in Greece, it covers 13.4% of the total forest area (2 470 000 ha) (Tsoumis 1980). Aleppo pine can be considered as an important Mediterranean forest species for both production of wood and oleoresin, a naturally occurring exudate collected by tapping the trees. Round timber production amounts only to about 20-25 000 m³ per year and it is utilized mainly in shipping constructions and in mining. The yearly production of oleoresin is about 10,000 tons (NSSG 1988) and comes exclusively from Aleppo pine. By distillation of oleoresin, two primary products can be produced, i.e. the solid gum rosin and the liquid turpentine in proportion about 3:1. Rosin is the most common material used in paper making and to some extent in fiber board industry during the sizing process for the purpose of controlling the

penetration of liquids into the final dry paper of board (Britt 1970; Suchsland, Woodson 1986).

The bark of Aleppo pine trees contains significant quantities of phenolic compounds (Tisler et al. 1983) that can be utilized as bonding and wood protecting agents. Bark extractives from various European *Pinus* species have been recently investigated as wood adhesives (Roffael 1976; Weissmann, Ayla 1980; Ayla, Weissmann 1981, Dix, Marutzky 1983, Tisler et al. 1983). Traditionally, such extractives have been used in protection of fishing nets.

In this paper, some experimental results concerning the utilization potentials of oleoresin, gum rosin and bark extracts from Aleppo pine as bonding and protecting agents in wood products are presented. More specifically, they include:

- Oleoresin and gum rosin as water repellent formulations applied to solid wood
- Gum rosin as water-repellent additive for particleboards.
- Bark extractives as water protective substances in solid wood.
- Bark extractives as bonding agents for plywood and particleboards.

II - Oleoresin and gum rosin as water repellent formulations applied to solid wood

Oleoresin water repellent solutions (10% oleoresin plus varying amounts of paraffin wax) were applied by immersion techniques to short-length, cross-sectional sapwood specimens (2cm x 2cm x 0.6cm) of broadleaved oak (*Quercus conferta* Kit.) and the water repellent effectiveness (WRE) was assessed by using tangential swell-

ing data.

The results showed that oleoresin solutions were equally effective when compared with common water repellents (see Fig. 1) and, hence, they can be successful substitutes for water repellent solutions based on synthetic resins.

Water repellent formulations

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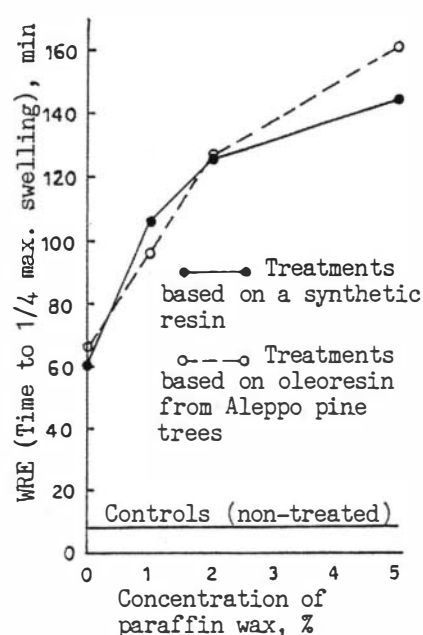


Fig. 1 : Water repellent effectiveness (WRE) in sapwood specimens of oak treated with formulations containing 10% resin and varying amount of paraffin wax (Voulgaridis 1988).

(WRFs) based on both oleoresin and gum rosin and on a commercial resin (straight chain hydrocarbon resin) were also applied to short and long specimens of various species by using immersion techniques or application of vacuum and atmospheric pressure. Water repellent solutions included 10% resin of a certain type, 1% paraffin wax and, in some cases, 0.1% or 0.2% tributyltin oxide (TBTO), whilst

water repellent effectiveness was based on tangential swelling (for short specimens) and water absorption (for long specimens) data. The sapwood specimens, 2cm x 2cm in cross section and 0.6 cm or 15 cm in length (short specimens and long specimens, respectively) were prepared from air-dried wood sticks of poplar (*Populus x euramericana* cv. "I-214"), beech (*Fagus silvatica* L.), fir (*Abies borisii regis* Mattf.) and Scots pine (*Pinus sylvestris* L.).

Table I summarises the results concerning the effectiveness of WRFs tested.

From this Table it is concluded that:

- All WRFs were found to afford a significant degree of protection against liquid water uptake in sapwood specimens of poplar, beech, fir and Scots pine tested.

- Differences in effectiveness between treatments existed and were related to wood species, group of wood specimens, specimen size, treatment method, assessment method of water repellency, retention differences and WRF.

- No particular WRF tested showed a superiority in all cases. WRFs based on oleoresin were found to be slightly more effective than those based on synthetic resin in poplar and fir wood but not in beech and Scots pine wood.

- WRFs based on gum rosin appeared, in some cases, to be more or equally effective and in other cases less effective than WRFs based on synthetic resin.

- A general comparison between performance results of WRFs for each wood species and group of specimens showed that the natural products oleoresin and gum rosin may be successful substitutes for the synthetic resin tested when incorporated as basic constituents in WRFs. This substitution is of great interest for Mediterranean countries which are producers of oleoresin and relevant derivatives.

III - Gum rosin as water-repellent additive for particleboards

Various series of one-layer hand-felted homogeneous particleboards were produced on laboratory scale. Commercial E3 grade urea-formaldehyde (UF) resin binder (45% resin solids) was applied by air spray to wood particles at a solid level 8%. As hardener 1.5% NH_4Cl , based on dry resin, was used.

Duplicate panels were made with each of the hydrophobic mixtures tried. For panel fabrication the following processing factors were used: plate temperature 180°C and pressure 3 N/mm². After pressing the panels were trimmed on each side and then cut into standard specimens. Standard test methods (DIN 52361, 52365 and 52364) were used to evaluate the density, internal bond and water swelling properties. Formaldehyde release was determined according to WKI 24h-Flask method (Roffael 1975).

The hydrophobic glue formulations used and the physical and mechanical properties of particleboards tested are shown in Tables II and III.

The results of Table II are summarised as

Wood		Effectiveness based on:					
Treatment	Cont-Immersion I rols Vacuum V)	Time to half max. swelling, min			Water absorption, %*		
		WRFs based on:			WRFs based on:		
		Oleoresin	Gum rosin	Synthetic resin	Oleoresin	Gum rosin	Synthetic resin
Poplar/I	0.9	74.5	-	59.1	93.6	-	94.5
Fir/I	8.3	62.5	-	60.7	91.6	-	91.1
Poplar/V	8.8	71.5	-	65.2	84.7	-	89.4
Poplar/V	19.9	84.9	57.5-104.0	65.0-78.8	81.5	79.8-81.3	80.1-80.9
Beech/V	32.3	185.7	175.5-220.2	197.2-251.4	73.3	73.1-76.0	82.9-83.4
S. pine/V	1.0	130.6	100.5-119.4	150.2-179.8	15.4	39.2-58.7	23.7-55.5

* Effectiveness for non-treated wood specimens : 0

Table I : Effectiveness of WRFs applied to wood (mean values or range of mean values in case of two or more WRFs based on the same resin) (Voulgaridis 1991)

Treatment Code	Treatment		Particleboard properties*				
	Glue formulation**	Method of application	Density (g/cm ³)	Internal Bond (N/mm ²)	Thickness Swelling (%)		Formaldehyde release (mg HCHO/100g particleboard)
					2h	24h	
A	Paraffin wax (40 % emulsion in water w/w basis)	Paraffin wax emulsion or rosin solutions were sprayed in mixture with UF-resin directly on wood particles	0.67	1.01	12.5	18.4	29.1
	UF + 1.0 % Paraffin		0.66	0.97	11.5	17.1	28.9
B	Gum rosin in furfuryl alcohol (20 % solution w/w basis)						
	UF + 1.0 % Rosin		0.67	0.95	14.5	19.6	27.4
	UF + 1.5 % Rosin		0.67	1.03	13.8	18.1	27.7
	UF + 3.0 % Rosin		0.67	1.07	13.1	17.8	27.7

* Mean values of 40 samples for density, internal bond, thickness swelling and 3 samples for formaldehyde release measurements ** Paraffin and rosin added in glue formations were based on the dry-mass of UF-resin

Table II : Methods of application of glue formulations and particleboard properties (Grigoriou, Passialis 1991)

Treatment Code	Treatment		Particleboard properties*					
	Glue formulation**	Method of application	Density (g/cm ³)	Internal Bond (N/mm ²)	Thickness Swelling (%)		Water absorption	
					2h	24h	2h	24h
	UF-resin	Spraying on dry chips	0.64	0.57	11.5	27.3	43.8	69.3
A	Gum rosin in acetone (31 % solution w/w basis)	Spraying of rosin solution in wet chips (30 % m.c.) followed by drying to 7.0 % m.c. and then mixing with UF glue						
	UF + 1.0 % Rosin		0.64	0.52	10.8	17.0	47.0	70.0
	UF + 3.0 % Rosin		0.64	0.31	7.9	14.5	39.5	69.4
B	UF + 1.0 % Rosin	Spraying of rosin solution on dry chips (6.0 % m.c.) followed by mixing of chips with UF glue	0.64	0.38	9.0	14.8	46.2	71.9
	UF + 3.0 % Rosin		0.63	0.25	8.3	14.1	42.3	73.7
C	Gum rosin as dry powder (fraction < 0.5 mm)	Spraying of rosin powder on wet chips (30 % m.c.) followed by drying to 7.0 % m.c. and then mixing with UF glue						
	UF + 1.0 % Rosin		0.64	0.55	9.6	14.7	48.7	73.7
	UF + 3.0 % Rosin		0.64	0.49	7.9	13.5	41.6	69.4
	UF + 5.0 % Rosin		0.64	0.47	6.5	12.1	34.0	64.5
D	UF + 1.0 % Rosin	Spraying of UF glue on dry chips (6.0 % m.c.) followed by mixing with rosin powder	0.64	0.56	8.5	13.3	46.1	70.4
	UF + 3.0 % Rosin		0.64	0.43	6.8	13.4	41.1	67.4

* Mean values of 20 specimens for density and internal bond, and 30 specimens for thickness swelling and water absorptio measurements ** Rosin added in glue formulations was based on the dry-mass of wood chips

Table III : Methods of application of glue formulations and particleboard properties (Passialis, Grigoriou 1992)

follows:

- The internal bond and thickness swelling between the treatments A and B were practically not different.

- The internal bond and thickness swelling seem to be reduced as the amount of paraffin increases from 1% to 1.5% while in UF + rosin formulations both these properties were slightly improved with increase of the rosin concentration from 1% to 3%.

- Formaldehyde release in particleboards glued with UF + rosin formulations (treatment B) was found to be slightly lower than in UF + paraffin bonded boards (treatment A).

Summarising the results of Table III it can be concluded that :

- The values of all properties were reduced as the rosin content was increased from 1% to 3% and 5%.

- Comparison between UF and UF + rosin bonded boards showed that the internal bond was reduced in all UF + rosin treatments except the UF + 1% rosin treatments C and D.

- Thickness swelling was reduced in all UF + rosin bonded boards, especially in treatment D.

- Treatment D (UF + 1% rosin powder) showed the best performance. More specifically, the addition of 1% rosin did not affect the internal bond, whilst it improved the hydrophobicity of the particleboards that resulted to 23% reduction of 24-hour thickness swelling.

IV - Bark extractives as water protective substances in solid wood

Water soluble bark extractives were taken from Aleppo pine trees and applied to sapwood specimens of poplar (*Populus x euramericana* cv. "I-214"), beech (*Fagus silvatica* L.) and Scots pine (*Pinus silvestris* L.), 2cm x 2cm in cross section and 0.6 cm or 15 cm in length. Aqueous solutions including 10% dry bark extractives (mass/volume basis) were used in the

Material	Retention, Kg/m ³	Time to 1/2 max swelling, min	Water absorption after 30 min immersion, %*	Effectiveness** $\frac{I}{C} = X$ %
Poplar				
a. Short specimens	87	10.0		2.4
b. Controls	-	4.2		1.0
c. Long specimens	28		12.4	38.3
d. Controls	-		20.1	0
Beech				
a. Short specimens	65	125.1		3.9
b. Controls	-	32.2		1.0
c. Long specimens	26		4.5	38.3
d. Controls	-		7.3	0
Scots pine				
a. Short specimens	72	5.4		5.3
b. Controls	-	1.0		1.0
c. Long specimens	4		4.3	14
d. Controls	-		5.0	0

* % of the weight of air-dry wood specimens

** $\frac{I}{C} = X$: Time of impregnated specimens (I) / Time of controls (C) = X times

** %: Absorption from controls / Absorption from impregnated specimens x 100

Table IV : Retention of dry bark extractives by wood specimens and effectiveness protection from liquid water entry) of the treatments based on 10% extractive aqueous solutions (Voulgaridis 1991)

experiment and applied to wood specimens by using vacuum and atmospheric pressure at temperature 60°C. After treatment, the impregnated wood specimens were air-dried in room conditions and the effectiveness of the treatments was determined by using swelling (short specimens) or absorption (long specimens) data.

The results are shown in Table IV.

From Table IV it can be concluded that:

- A relatively low degree of protection against liquid water entry for poplar, beech and Scots pine wood specimens is achieved after treatment with 10% Aleppo pine bark extractive aqueous solutions.

- The rate of tangential swelling in short wood specimens is retarded after treatment 2.4-5.3 times for the three wood species tested. It means that treatment of wood specimens makes more difficult the entry of liquid water in cell walls although this retardancy is not satisfactory for high degree of protection.

- The effectiveness of the treatments

based on absorption data was found to be only 38% for poplar and beech and 14% for Scots pine wood. Hence, capillary penetration of water in wood is not strongly retarded.

V - Bark extractives as bonding agents for plywood and particleboards

Bark (inner and outer) was collected from mature Aleppo pine trees. The bark was dried at room conditions at about 20% m.c. 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. Extraction was carried out in beakers placed in a waterbath at temperature 80°C for 2 hours. The proportion "dried bark:

extraction liquid" during the extraction process was 1: 8 (g/ml). After extraction, the extract solutions were filtrated and stored at room conditions (~ 23 °C).

The properties of the extract solutions (pH, viscosity, reactivity) were determined within 2 days after extraction. Acidity and viscosity were measured at 21°C and at the concentrations of the extract solutions achieved. For viscosity measurements a rotational viscometer was used. The reactivity of the extracts with formaldehyde was determined by using the Stiasny method (Gnamm 1949).

Table V shows the six extraction liquids used, the extract yield, the concentration of each extract solution and the corresponding properties of extract solutions (i.e. acidity, viscosity, and reactivity).

From Table V it can be concluded that:

- Sulfonation of the extraction liquid did not appear to influence the extract yield and does not seem to influence the viscosity, acidity and reactivity of bark extract solutions at the concentrations achieved.

- 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.

- The extraction liquids containing 1% and 5% NaOH significantly increase the pH value of the extracts (2 to 3 times).

- The viscosity of all extract solutions at their initial concentrations (after extraction) appeared to be small

a/a	Extraction liquid	Extract yield, %**	Concentration of extract solution, %***	Acidity, pH	Viscosity, mPa.s	Reactivity, Stiasny-Number
1-	Water + sulfonation*	27.6	3.7	4.32	9.4	81.45
2-	Water	29.7	3.6	4.27	8.6	30.30
3-	1% NaOH + sulfonation*	40.2	5.8	10.07	11.0	67.85
4-	1% NaOH	39.9	5.8	10.04	10.6	69.35
5-	5% NaOH + sulfonation*	47.2	10.1	12.27	11.0	38.45
6-	5% NaOH	47.2	10.7	12.28	11.0	37.30

* 0.25 sodium sulphite +0.25% sodium bisulphite based on dry weight of the bark.

** Based on dry weight of bark powder (w/w) before extraction

*** Based on the volume of extract solution after filtration (w/v)

Table V : Extraction liquids, extract yield, concentration of extract solutions and their propertie (Voulgaridis et al. 1985)

and without differences.

- The reactivity of water extracts is high, but it is reduced by adding NaOH to the extraction liquid.

The viscosity and gelation time of the bark extracts after 30-day's storage (Measurements of extract properties after 30 day's storage of extracts in liquid or solid form were found to be not substantially different) at 33% concentration are shown in Table VI.

The conclusions of Table VI are summarised below:

- 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 solution tested. This increase was very great in extract solutions 3 and 4 (1% NaOH), especially in solution 4. 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 extract solutions 5 and 6 results to low values of viscosity.

- Gelation time of the extracts when using 2.5% formalin was found to be considerably lower than that determined when using paraformaldehyde.

- The non-curing of extract solutions 5 and 6 (5% NaOH) within 30 min may be attributed to low reactivity (see Table V).

- From the three extract solutions (numbered, 1, 2 and 3) which appeared

a/a	Extraction liquid	Viscosity mPa.s	Gelation time, S				
			5 % paraformaldehyde at initial pH*	2.5 % formaldehyde (37 %) at initial pH*			
				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	Not measured due to very high viscosity				
5	5% NaOH + sulfonation	34	No curing achieved within 30 min				
6	5% NaOH	29	No curing achieved within 30 min				

* The initial pH (after 3 day's storage) for the extract solutions No. 1, 2 and 3 was : 4.14, 3.8 and 8.45 respectively

Table VI : Viscosity and gelation of bark extracts at concentration 33 % (Voulgaridis et al. 1985)

red 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 only in extract yield.

From all extracts tested (see Table V), the aqueous extract solutions were considered as most suitable for gluing experimental plywood and particle-boards.

1 - Plywood

For the evaluation of bark extracts as plywood adhesives, four formulations were prepared in combination with commercial phenolic resin (see Table VII). These formulations were used for gluing three-ply Okoumé plywood, 2.5 mm in thickness. The gluing conditions were as follows: quantity of glue 293-364 g/m², dependent on concentration; quantity of dry phenolic resin or extractives 128 g/m²; application of glue on one of the two bonded surfaces; hot pressing time 7 min for the glues A, B and 15 min for the less concentrated glues C and D; pressure in hot pressing 1.4 N/mm²; hot pressing temperature 135°C.

The dependency of viscosity from time is shown in Fig. 2 for various glue formulations. It appears that the viscosity of a glue mixture remains at normal level only by replacing small amounts of bark extractives with phenolic resin (up to 5%) or of phenolic

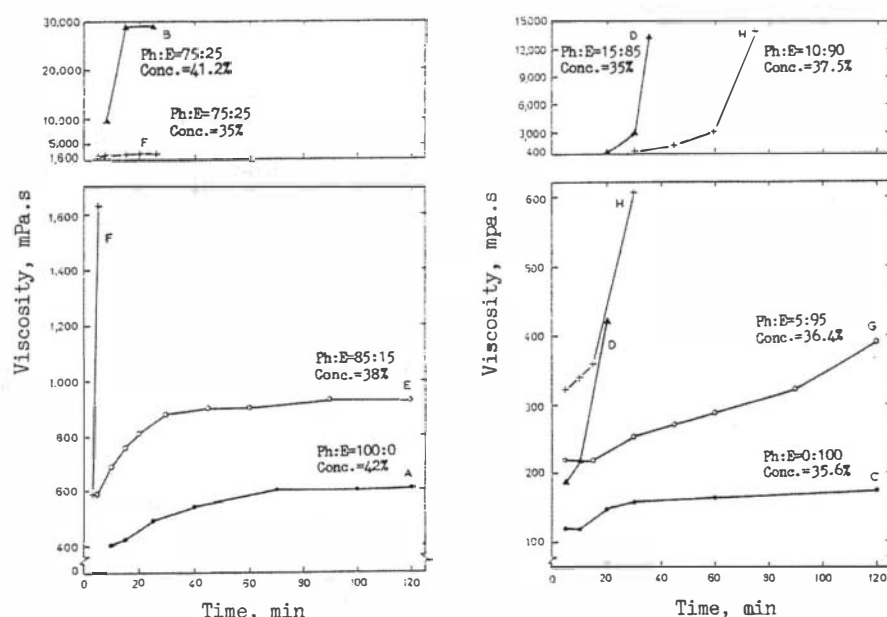


Fig. 2 : Dependency of viscosity from time for various phenolic resin/bark extractives formulations, Ph:E = Phenolic resin: Bark extractives, Conc. = Glue concentration (Grigoriou et al. 1987).

resin with bark extractives (up to 15%). Two other formulations with phenolic resin: bark extractive ratio 50: 50 and 25: 75 were prepared for use but gluing was not feasible due to fast curing.

The results of shear tests according to DIN 53255 are shown in Table VII.

From Table VII it is concluded that:

- The shear strength values of plywood test specimens bonded with aqueous bark extractives (glue formulation C) are lower than those achieved with the other three glue formulations (A, B, D) for both dry and wet

tests. The addition of 15% phenolic resin to bark extractives (glue formulation D) leads to an improvement of plywood bond.

- In comparison with pure phenolic resin (glue formulation A), an improvement of glue bonds in the dry test occurs when 25% of phenolic resin is replaced by bark extractives (glue formulation B).

- In plywood bonded with aqueous bark extracts (glue C) the low percentage of wood failure observed is consistent with the low shear strength values. In wet test, where shear streng-

Shear tests**

Glue formulation	Phenolic resin : extractives ratio	Content of dry glue mass, %*	After equilibration (23°C, 50 % RH)		After 6 hour-boiling and 2-hour immersion in water	
			Glue line shear strength, N/mm ²	Wood failure, %	Glue line shear strength, N/mm ²	Wood failure, %
A	100 : 0	42.0	2.81	40	1.64	15
B	75 : 25	41.2	3.14	50	1.62	45
C	0 : 100	35.6	2.31	15	1.16	5
D	15 : 85	35.0	2.64	55	1.55	10

* In each formulation, 10 % paraformaldehyde as hardener and about 10 % wheat flour based on dry glue mass were added

** Mean values. The number of specimens used ranged between 6 and 18

Table VII : Glue formulations for bonding Okoume plywood and shear strength properties (Grigoriou et al. 1987)

th was reduced in all glued plywood, wood failure was also reduced except for one glue mixture (B) for which it remained, unexpectedly, relatively high.

2 - Particleboards

For the evaluation of bark extracts as particleboard adhesives, five glue formulations (A-E) were prepared in combination with commercial UF resin (see Table VIII). These formulations were used for gluing 1-layer experimental particleboards, 16 mm in thickness.

Various series of hand-felted homogeneous particleboards were produced. Commercial E3 grade urea - formaldehyde (UF) resin binder (45% resin solids) was applied by air spray to wood particles at a solid level 8%. As hardener 1.5 NH_4Cl , based on dry resin, was used. For panel fabrication the following processing factors were used; plate temperature 180°C, pressing time 3 min and pressure 3 N/mm^2 . After pressing, the panels were trimmed on each side and then cut into standard specimens. Standard test methods (DIN 52361, 52362, 52365 and 52364) were used to evaluate the density, static bending, internal bond and water swelling proper-

ties. Formaldehyde release was determined according to WKI 24h-Flask method (Roffael 1975). For viscosity measurements a rotational viscometer was used.

The relationship between the viscosity and time of the glue formulations tested is shown in Fig. 3. By increasing the proportion of extractives in UF resin from 2 to 10%, the viscosity of the glue mixture appeared to increase with the time rapidly. However, it is possible to reduce the rate of increase in viscosity by adjustment the pH of the glue formulation from 5 to 7 with NaOH (see formulations D and E).

The properties of particleboards glued with the above formulations are shown in Table VIII. It appears that:

- The addition of small amounts of extractives (2%, 5% and 10%) in UF resin improved slightly the mechanical properties of experimental particleboards (glue A, B, C, D).

- Hygroscopicity properties (swelling, water absorption) of the boards glued with UF resin incorporating 2% extractives (glue B) were also slightly improved but in the other glue mix formulations (glue C, D) tested (5% and 10% extractives) no substantial changes occurred.

- In case of glue E, when pH was adjusted to 7, with NaOH, no changes

of mechanical properties were observed, whilst thickness swelling and water absorption were increased.

- The incorporation of 2-10% pine bark tannins in UF resin reduced the formaldehyde emission from the particleboards up to 17%.

In a second attempt aiming to utilize bark extractives in large proportions and to overcome viscosity problems, the two glue components (extracts, UF resin) were sprayed separately on wood chips. Five glue formulations (see Table IX) were used for gluing 1 - layer particleboards, 12 mm in thickness.

Various series of hand-felted homogeneous particleboard were produced. Commercial E₃ grade urea-formaldehyde (UF) resin binder (45% resin solids) was applied by air spray to wood particles at a solid level of 8% for E glue and 12% for A, B, C, D glue formulations. As hardener 15% paraformaldehyde, based on dry bark extracts was used for A, B, C, D glues. For B, C, D glues an additional amount of 1.7% NH_4Cl , based on dry resin was used. For panel fabrication the following processing factors were used; plate temperature 180°C, pressing time 7 min and pressure 3 N/mm^2 . After pressing, the panels were trimmed on each side and then

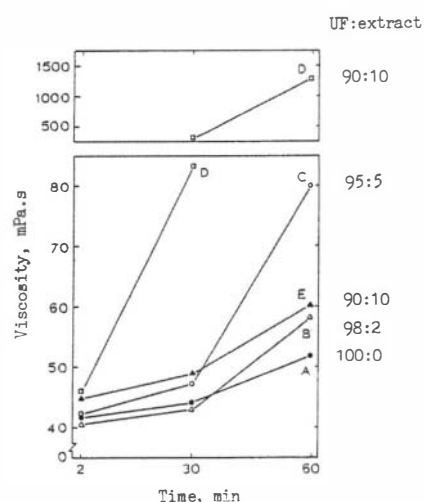


Fig. 3 : Dependency of viscosity from time for the experimental formulations.

For A, B, C and D: pH = 5,
for E : pH = 7
(Passialis et al. 1988).

Properties*	Glue formulations (UF resin: extractives, ratio)**				
	(A) 100 : 0	(B) 98 : 2	(C) 95 : 5	(D) 90 : 10	(E) 90 : 10
Density, g/cm ³	0,76	0,76	0,79	0,77	0,76
Bending, N/mm ²	18,4	20,9	21,1	20,6	18,5
Internal bond, N/mm ²	0,74	0,86	0,85	0,83	0,72
Thickness swelling, %					
2-hours	31,5	28,0	31,2	32,3	35,2
24-hours	39,4	35,5	38,7	40,3	43,4
Water absorption, %					
2-hours	70,5	65,8	67,0	71,9	74,3
24-hours	87,4	82,6	84,3	90,2	93,1
Formaldehyde release					
WKI 24h-method	76	73	70	63	63
(mg HCHO/100 g particle-board)					

* Mean values of 20 samples for density, bending, internal bond, thickness swelling, water absorption and 2 samples for formaldehyde release measurements

** For glue formulations A, B, C and D: pH = 5, for E: pH = 7

Table VIII : Glue formulations and particleboard properties (Passialis et al. 1988)

cut into standard specimens. Standard test methods (DIN 52361, 52362, 62365, and 68763) were used to evaluate the density, static bending and internal bond before and after 2 hours boiling.

Table IX presents certain physical and mechanical properties of the experimental particleboards.

From Table IX it is concluded that:

- The addition of 10% UF-resin in extracts (glue B) improved slightly the basic properties (bending and internal bond strength, thickness swelling and water absorption) as well as the wet bonding strength of the boards when compared with those glued with unmodified tannin resin.

- Glue formulations containing higher amounts of UF resin (glue C, D) reduced the mechanical properties of the boards while hygroscopic properties were slightly improved.

- Glue formulations with high amount of extracts (90-100%) appeared to be superior in wet bonding strength.

C.P., A.G., E.V.

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Properties*	Glue formulations (Bark extractives : UF resin, ratio)				
	(A) 100 : 0	(B) 90 : 10	(C) 80 : 20	(D) 50 : 50	(E) 0 : 100
Density, g/cm ³	0,73	0,74	0,73	0,73	0,74
Bending, N/mm ²	19,0	20,5	18,6	18,0	20,9
Internal bond, N/mm ²					
V 20	0,92	1,05	0,70	0,40	1,12
V 100	0,11	0,14	Disintegrated during boiling		
Thickness swelling, %					
24-hours	23,9	23,5	23,1	22,0	22,3
48-hours	24,8	24,6	24,4	24,1	24,3
Water absorption, %					
24-hours	70,6	68,2	67,2	65,3	60,0
48-hours	77,7	74,8	74,5	73,1	71,1

* Mean values of 19-20 measurements

Table IX : Glue formulations and particleboard properties (Grigoriou 1990)

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Résumé

Utilisation de l'oléorésine et des produits d'extraction de l'écorce de *Pinus halepensis* Mill. dans les produits du bois

Le pin d'Alep (*Pinus halepensis* Mill.) est une essence de la forêt méditerranéenne. En Grèce, elle couvre environ 13,4 % de la surface forestière totale.

L'importance de cette espèce ne provient pas uniquement de son bois mais surtout de la production d'oléorésine (gomme de pin) qui est un composant naturel et la base de plusieurs produits.

En outre, le pin d'Alep peut fournir une importante quantité de composés phénoliques provenant de son écorce, induisant un intérêt accru dans l'utilisation de ce résidu forestier.

L'utilisation potentielle de ces matériaux naturels et renouvelables (oléorésine et écorce) est présentée dans ce travail en ce qui concerne le collage et l'amélioration des propriétés des produits composites, et la protection du bois en menuiserie.

Il a été montré que l'utilisation d'une petite quantité de colophane pour le collage des panneaux de particules améliore certaines propriétés des panneaux suivant la méthode d'application et la quantité de colophane incorporée.

Il a été montré que les produits hydrofuges basés sur l'oléorésine ou bien sur le colophane sont des substituts efficaces des résines synthétiques après incorporation comme constituants de base dans les solutions, application sur le bois et tests de comparaison pour un certain nombre d'espèces (bois de peuplier, sapin, hêtre, pin sylvestre, chêne).

D'importantes quantités d'extraits solubles dans l'eau peuvent être produits à partir de l'écorce de pin d'Alep et semblent avoir des propriétés de collage convenable (réactivité, viscosité, temps de prise en gel, acidité). Des extraits d'écorce en combinaison avec des résines phénoliques ou Urée Formol ont été testés en collage, respectivement sur un panneau de particules 1 couche et sur un contreplaqué d'Okoumé 3 plis.

Certaines de ces combinaisons améliorent les propriétés de base de ces 2 panneaux composites telles que les propriétés mécaniques et hygroscopiques, la résistance du collage humide et l'émission de formaldéhyde. Les extraits

d'écorce de pin d'Alep solubles dans l'eau utilisés sur des échantillons de bois de peuplier, de hêtre et de pin sylvestre montrent un certain degré de protection contre l'entrée d'eau.

Summary

Utilization of oleoresin and bark extractives from *Pinus halepensis* Mill. in wood products.

Aleppo pine (*Pinus halepensis* Mill.) is a Mediterranean forest species and, in Greece, covers about 13.4% of the total forest area. The importance of this species is associated not only with wood but mainly with the production of oleoresin (pine gum) that is a naturally occurring exudate and basis for many products. Furthermore, Aleppo pine may provide significant amounts of bark containing phenolic compounds, while there has been an increasing interest in utilizing this forest residue. Utilization potentials of both these natural and renewable materials (i.e. oleoresin, bark) are presented in this work either for gluing and improving the properties of composite products or protecting wood in joinery.

Participation of small amounts of gum rosin, in gluing UF-particleboards was found to improve certain properties of the boards dependent on the method of application and amount of incorporated gum rosin. Water repellent formulations based either on oleoresin or gum rosin were found to be successful substitutes for the synthetic resins after incorporation as basic constituents in the above solutions, application to wood and comparative testing for a number of wood species (poplar, fir, beech, Scots pine, oak).

Significant amounts of water soluble extracts can be produced from Aleppo pine bark and appear to have suitable gluing properties (reactivity, viscosity, gelation time, acidity). Bark extracts in combination with UF or phenolic resin were tested in gluing experimental one-layer particleboards and three-ply Okoumé plywood, respectively. Some of these combinations improved basic properties of both composite products such as mechanical and hygroscopic properties, wet bonding strength and formaldehyde emission. Water soluble bark extracts from Aleppo pine applied to wood specimens of poplar, beech and Scots pine exhibited a certain degree of protection against water entry.