Holz als Roh- und Werkstoff 40 (1982) 51–60

Holz als Roh- und Werkstoff

Bark Extractives from Spruce as Constituents of Plywood Bonding Agents

O. Liiri, H. Sairanen, H. Kilpeläinen, and **A. Kivistö**

Technical Research Centre of Finland, Forest Products Laboratory, Espoo, Finland

The principles of the use of tannins and resins extracted from wood bark have been known since the 1950's. But only in recent years research on tannins has become lively. The literature review at the beginning of this paper concentrates mainly on the latest investigations in this field. The experimental part investigates the amount and quality of spruce bark extracts and their suitability as extenders in plywood adhesives. The use of chemically treated bark (bark dispersion) in plywood gluing is studied in the last part. If spruce bark is extracted with distilled water, the extract yield is 11.2% at the most, but when 10% of NaOH is added the yield increases to 40.0%. The extract content of drum-debarked pulpwood bark was clearly lower than that of unfloated logs, debarked in the sawmill. The results obtained reinforce the earlier belief that spruce bark extract can substitute Quebracho as an extender for plywood adhesives. Bark dispersion can also be used for this purpose. Exterior-grade birch plywood can be manufactured, using glues which contain spruce bark extract and dispersion. The extract and dispersion can also substitute part of the phenolic resin in the glue mixture, up to 20% at best, without any deterioration in the quality of gluing.

Fichtenrinden-Extrakte als Bestandteile von Sperrholz-Bindemitteln

Die Prinzipien der Anwendung für aus Holzrinde gewonnene Extrakt- und Gerbstoffleime sind seit den fünfziger Jahren bekannt. Aber erst in den letzten Jahren ist die Forschung auf diesem Gebiet aktiver geworden. Die nachfolgend gegebene Literaturübersicht umfaßt deshalb in erster Linie neuere Untersuchungen. Im experimentellen Teil werden Menge, Qualität und Anwendbarkeit des aus Fichtenrinde gewonnenen Extraktes als Streckmittel für Sperrholzleime geschildert und die Anwendung von chemisch behandelter Rinde und Rindendispersion in der Sperrholzverleimung geklärt. Wird Fichtenrinde mit destilliertem Wasser behandelt, gewinnt man bestenfalls 11,2% Extrakt. Werden der Extraktlösung aber 10% NaOH zugesetzt, so steigt die Extraktmenge auf 40,0%. Der Extraktgehalt von mit Trommelentrindern entfernter Faserholzrinde ist deutlich geringer als der von im Sägewerk geschälter, nicht geflößeter Sägeblockrinde. Die Forschungsergebnisse bestätigen die frühere Ansicht, daß das Quebracho-Pulver, das als Streckmittel in den Sperrholzleimen verwendet wird, durch Fichterindenextrakt ersetzt werden kann; die Rindendispersion ist für denselben Zweck verwendbar. Mit Fichtenrindenextrakt und -dispersion enthaltenden Leimen läßt sich Birkensperrholz erzeugen, das die Anforderungen für Außenverwendung erfüllt. Mit Extrakt und Dispersion kann man günstigenfalls 20% des Phenolharzes der Leimmischung ersetzen, ohne daß die Verleimungsqualität sinkt.

1 Introduction

The first part (Liiri et al. 1978) of the research on the applications of bark for gluing discussed the use of the bark of six Finnish wood species as an extender for adhesives. The best results were obtained by spruce bark extract when used in the gluing of plywood.

Owing to the continuously rising prices of synthetic raw materials, research on adhesives made from wood bark has markedly increased in the late 1970's. In these investigations efforts have been made to replace synthetic glue raw materials totally or partly by bark products. South-Africa, Australia and Brazil have been most successful in this field. Since the principles of the use of extract glues are known already on the basis of research made in the 1950's, the current research concentrates especially on the improvement of the applicability of the adhesives. Some of the most recent investigations on glues are discussed in more detail in the following literature survey.

The experimental part of the research tries to investigate the influence of the origin, treatment and conditions on the amount and quality of the bark extract and on its suitability as an additive in plywood glues. The possibilities of using chemically treated bark (bark dispersion) in plywood adhesive were also studied. The investigation was carried out in the Forest Products Laboratory of the Technical Research Centre of Finland (VTT).

2 Literature Survey

2.1 Tannin-Formaldehyde Adhesives

2.1.1 Catalyzing of Tannin-Formaldehyde Adhesives

The reaction accelerating effect between tannin and formaldehyde of bivalent metallic salts was observed already in the late 1950's (Plauley 1959). A. Pizzi, extensively investigated the effect of metal-ions in the 1970's. These investigations showed that the reaction is accelerated most by bivalent lead and zinc ions, which reduced the gelation time of resorcinol and formaldehyde used as phenolic reference material to one third of that of un-catalyzed reaction. Trivalent metal ions, such as Fe^{III}, Al^{III} and Cr^{III}, delayed the jellying of the reference materials. But the Cr^{III} ions can form stabile complexes both with phenolic reference materials and with tannins extracted from bark (Pizzi 1979 a, b, c). A small quantity of Cr^{III} salt does, however, not delay the reaction between tannin and formaldehyde. If the salt addition is high enough, the strength of tannin-formaldehyde adhesive increases. But such large additions are not economical (Pizzi 1979 c).

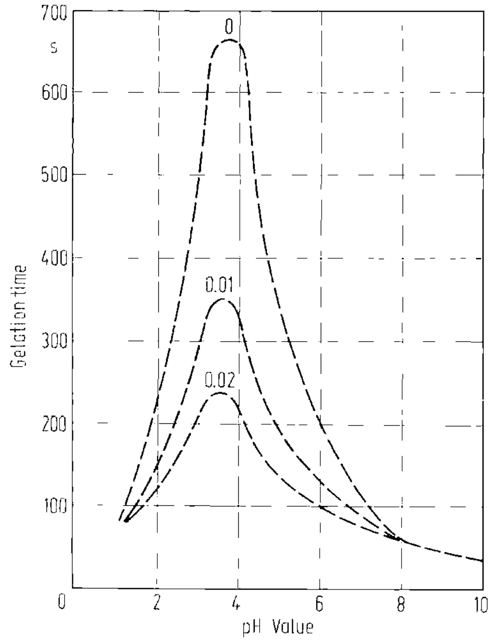

Fig. 1. Dependency of tannin-formaldehyde mixture's gelation time on pH and number of Zn^{2+} ions (mole percentage 0.0; 0.01; 0.02) (Pizzi 1979c)

Bild 1. Abhängigkeit der Gelierzeit der Tannin-Formaldehydharzmischung vom pH-Wert und der Zn^{2+}-Ionen-Konzentration (Pizzi 1979c)

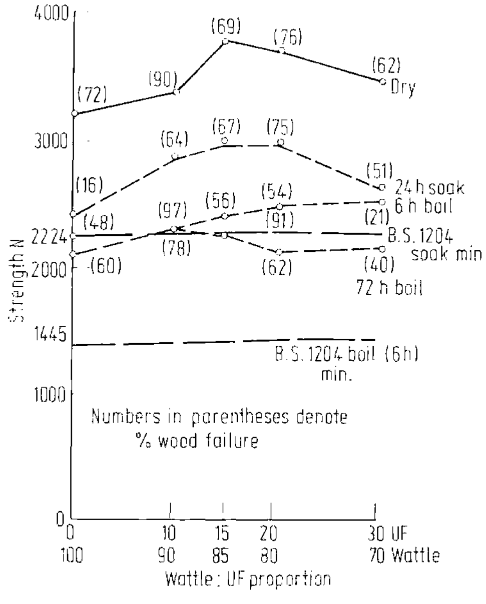

Fig. 2. Effect of tannin/urea resin ratio on gluing strength and wood failure for beech specimens (Pizzi 1977)

Bild 2. Einfluß des Verhältnisses von Tannin zu Harnstoffharz auf die Bindefestigkeit und den Holzbruchanteil von Buchenholzproben (Pizzi 1977)

The magnitude of the catalyzing effect of bivalent metal ions is strongly dependent on the pH of the tannin-formaldehyde mixture (Fig. 1). The changes in pH have a rather small effect when low or high pH is used, but they increase the reaction rate rather strongly within the range of minimum reactivity (about 3...5 pH) (Pizzi 1979c). This observation is of considerable practical significance in glue applications, because a reduced dependency between reaction rate and pH decreases the need for pH-control accuracy in the glue mixture.

2.1.2 Pure Tannin-Formaldehyde Adhesives

According to Brazilian investigations, exterior-grade plywood can be made with wattle-based bark extract-formaldehyde adhesive. The adhesive was also used to glue particle board that met the requirements of DIN 68761 in other respects than for tensile strength perpendicular to surface, when tested after 24 h water soaking. In plywood tests the pressing times were relatively close to those of synthetic adhesives, but in particle board tests the pressing time was longer (1 min/mm) (Coppens et al. 1980).

When pulverized tannin adhesive was used in the manufacture of particle board the mat moisture content was lower and the pressing times decreased to 11...17 s/mm. When the particles had a 15% dosage of the glue, the finished board met the requirements of DIN 68761 (Pizzi 1978). The advantages of pulverized glue are, besides faster process:

Large charges of adhesive can be prepared in the factory, and thus special manufacturing equipment in each factory for liquid adhesive is not necessary;

The quality of the adhesive is more uniform when prepared in large charges;

The storage life of the dry glue is good.

The disadvantage of this method is the expensive drying method (spray drying).

2.1.3 Reinforced Tannin-Formaldehyde Adhesives

The cohesion of pure tannin-formaldehyde adhesives is generally lower than that of synthetic adhesives. The glue strength can be considerably improved by adding a small quantity of synthetic adhesive resin to the tannin-formaldehyde adhesive. Either phenolic or resorcinol-formaldehyde resins have been used for this purpose (Plomley 1964, 1966).

The quantities of resin varied from 10% to 30%. Only special resins manufactured for the purpose are suitable as fortifying resins.

In seeking cheaper alternatives for fortifying resin, commercial urea adhesives were found the most suitable (Pizzi 1977, 1979c). The use of urea resin is based on the fact that its methylol groups can react with the aromatic structural components in the tannin units. According to the gluing tests, the best results are obtained when the percent of urea resin is about 10% of the quantity of tannin (Fig. 2). The advantage gained is evident particularly in improved wood failure test results.

When the addition of urea resin to the tannin-formaldehyde adhesive was 11%, the plywood manufactured met the requirements of BS 1088–1957 (marine plywood). The fact that tannin-formaldehyde adhesive reinforced with urea resin also withstands boiling water exceptionally well may be due to the protection given by the tannin molecules (Pizzi 1977).

In addition to wood gluing, the tannin-formaldehyde adhesive has given good results also in gluing moisture-resistant corrugated board. Normal starch adhesive becomes moisture-resistant already by addition of about 8% tannin-urea-formaldehyde adhesive (Clusters et al. 1979).

2.1.4 Tannin Extracts as Additives to Synthetic Adhesives

Polyphenols extracted from different sources have already long been used as hardeners and extenders in plywood adhesives. The Finish plywood industry has used Quebracho extract as hardener for phenolic resin already since the 1960's.

The use of tannin extracted from chestnut wood has given very positive results, because in factory tests the pressing times of plywood could be decreased by 33% on the average, without any deterioration in the quality of gluing (Kulvik 1977).

The quantitative use of the extract from conifer bark is restricted because large quantities of extract raise the viscosity of the resin too much. However, the viscosity of such extracts could be decreased by treating the extract at high temperatures under alkaline conditions. When the extract was precipitated with acid after heat treatment, the soluble compounds hampering gluing could also be eliminated. Almost 60% of the phenolic resin in the resin mixture could be replaced by treated extract (Hemingway 1978).

Another method to decrease extract viscosity and increase its viscosity stability is to treat it with sodium sulphide.

2.2 Summarized Literature Survey

Suitable adhesives for the wood industry can be made from polyphenols (tannins) extracted from wood and bark. The application of these adhesives is most advanced in South-Africa, where tannin-formaldehyde adhesives are used in the manufacture of plywood and particle board. Efforts have been made to improve the properties of these adhesives with various metal compounds. The exploitation of complex forming trivalent metal compounds (particularly Cr^{III}) has been studied in addition to already known bivalent metal salts. Essential improvement has been gained regarding the properties of tannin-formaldehyde adhesives by adding synthetic resins. The improvement of the gluing properties by commercial urea resins is a step in the right direction. Previously, only specially manufactured phenolic and resorcinol-formaldehyde resins were used for this purpose.

The high viscosity hampering the use of polyphenols extracted from wood species of the Northern Hemisphere has been reduced with chemical treatment of the extract. The synthetic resins used nowadays with these extracts do not form sufficiently strong crosslinks. Further studies should concentrate on the use of cheaper resins.

3 Experimental Research

3.1 Research Procedure

3.1.1 Background and Goals

In the first part of the research on the adaptation of bark in gluing, the best results were obtained using spruce bark. Therefore the second part of the research concentrated on this. Experiments were made to determine the influence of the type, origin, and method of treatment of the bark on the suitability of bark extract for gluing plywood. The possibilities of using chemically treated bark in plywood adhesives were also investigated.

3.1.2 Test Material

3.1.2.1 Origin and Pretreatment of Bark. Timber bark from both green timber (logs were felled two weeks before debarking) and from the barking plant of a sawmill was used in this research. The bark from the sawmill had been in a bark pile for 2 to 3 months. The logs had not been stored in water before barking, but they had been moistened during storage. Bark from green timber was taken both from the forest (barked about one week after felling) and from the barking plant of a pulp mill. At the mill the logs were debarked in a drum barker. The bark was delivered in two batches, one of which was from logs felld about two months earlier. The other batch was from logs that had been stored in water for about four months before barking. This batch had been felled about six months before water storage.

The main part of the bark was dried in a timber drying kiln at a temperature of 40 °C to an approximate moisture content of 10.6%. A small part was dried in an oven at 70 °C to 130 °C. Thereafter the bark was refined first with a ring flaker, screen size 2.5 mm, and then with a disk refiner, the distance of disks being 0.2 to 0.3 mm. Each bark batch was refined twice. A small part of the bark was ground with a hammer mill. Fractions of 2 to 0.063 mm (100 to 240 mesh) were screened for extraction tests, and fractions of 0.08 mm (185 mesh) for bark dispersion tests. The bark ground with the hammer mill was used as such, the grain size being 2.0 to 0.25 mm.

3.1.2.2 Preparation of Extract and Determination of its Properties. In one extraction 130 g ground bark and 1,300 ml solvent were used. After extraction the bark was filtered and washed with 2 × 700 ml distilled water. The extraction solvent consisted of distilled water and added sodium hydroxide. The amount of sodium hydroxide varied from 0% to 15% in dry substance. Extraction temperatures were 80 °C and 100 °C and the time spans varied from 1 to 18 h. In general the extraction was carried out under the following conditions: Extraction time 60 min, temperature 80 °C, amount of NaOH 5%.

Deviations from these basic conditions are mentioned in the results.

The extraction liquid was concentrated to dry solid content of 95.6% with a freeze dryer. The extract yield, the reactivity of the extract with formaldehyde, and the NaOH content of the extract were determined in each case. The reactivity of the extract with phenolic resin was investigated in gelation time tests. For the measurement of viscosity liquids of different concentrations were made from a part of the extract.

The pH of the extractive liquids and the dry solid material contents were measured by Forest Product Laboratory analysis methods (Valtion teknillinen tutkimuskeskus 1974).

The reactivity of the extracts with formaldehyde was determined by measuring the amount of formaldehyde bound by the extract (Hillis, Urbach 1969). The sodium hydroxide content was determined with atomic absorption spectrometer. Gelation times were measured by a method described in the first part of the research (Liiri et al. 1978). The viscosities of the extract liquids were measured with a Ferranti viscosity meter according to the instructions of the Finnish Pulp and Paper Research Institute.

3.1.2.3 The Production of Bark Dispersion and the Measurement of its Properties. To make a bark dispersion, 195 to 250 g of <0.08 mm bark powder was used for each treatment. 1,500 ml hot water and 0% to 2% NaOH and $Ca(OH)_2$ (of the amount of bark) were then added. Thereafter, the mixture was stirred for 20 to 30 min at a temperature of 100 °C. The conditions during the treatment are given in detail in Table 1. After the treatment the mixture was left to cool at room temperature whereafter its pH and viscosity were measured (VTT 1974).

3.1.3 Gluing Tests

In the investigations a three-ply birch plywood consisting of 600 mm × 600 mm × 1.5 mm birch veneers with 3.7% average moisture content was used.

The plywood was glued under the following conditions: quantity of glue 160 g/m^2; pre-stacking time 10 min; prepressing time, pressure 6 min, 0.6 N/mm^2; time between prepressing and hot pressing 1 h; hot pressing temperature 130 °C; hot pressing time 6 min (2 panels at a time); pressure in hot pressing 1.7 N/mm^2.

Table 1. Preparation of bark dispersion mixtures

Mixture	NaOH content %	Ca(OH)$_2$ content %	Time of treatment min	Bark content of mixture %
N1	0	–	20	11.5
N2	2		20	11.5
N3	5	-	21	11.5
N4	10	-	20	11.5
N5	20	–	20	11.5
N6	5	–	20	14.7
M1	5	–	11	14.7
M2	5		60	14.7
M3	5	–	300	14.7
O1	5	3.7	20	11.5
O2	5	9.2	20	11.5
O3	10	9.2	20	11.5
O4	10	18.5	20	11.5

Table 2. Composition of glues containing bark extract

Constituent	Mixture									
	U1	U2	U3	U4	U5	U6	U7	U8	U9	U10
Exter A[a]	100	100	100	100	100	100	100	100	100	100
Quebracho	5									
Extract[b] 1		2.5	5	1.3						
2					2.5	5.0	1.3			
3								2.5	5.0	1.3
Chalk	10	10	10	10	10	10	10	10	10	10
Wood flour	2.5	2.5	2.5		2.5	2.5		2.5	2.5	
Bark flour				2.5			2.5			2.5
Paraformaldehyde	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Wheat flour	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2	2.0
Water	7.5	2.5	23.5	3.8	4.0	8.0	0	20	35.8	4.0

[a] Commercial phenolic resin

[b] 1 green pulpwood bark, in extraction 10% NaOH of quantity of bark
2 green pulpwood bark, in extraction 15% NaOH of quantity of bark
3 green timber bark, in extraction 10% NaOH of quantity of bark

Table 3. Composition of glues containing bark dispersion

Constituent	Mixture									
	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10
Exter A	100	100	100	100	100	100	100	100	100	100
Quebracho	5									
Bark dispersion M2		38								
N2			38							
N3				38						
N4					38					
N5						38				
N6							25			
O1								25		
O3									25	
O4										25
Chalk	10	10	10	10	10	10	10	10	10	10
Wood flour	2.5	6.0	7.5	6.0	6.0	6.0	5.9	5.5	5.5	5.9
Paraformaldehyde	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Wheat flour	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Water	5	–	–	–	–	–	–	1.5	12.2	3.0

Table 4. Conditions during extraction, extract yield, the pH of the extract, and formaldehyde reactivity

Extract	Bark[a]	Fraction	Drying temperature	NaOH dosage	Extraction conditions		pH of extraction solution	Yield		Bound HCHO	Moisture content of bark
					Temp.	Time		Total	NaOH		
		mm	°C	%	°C	h		%	%	%	%
A 1	k/m	~1.0	40	5	80	1	9.8	36.5	32.7	3.5	9.8
A 2	k/m	0.15	40	5	80	3	9.9	31.6	28.1	3.0	9.8
A 3	k/m	0.15	40	5	80	6	9.4	35.8	32.1	3.1	9.8
A 4	k/m	0.15	40	5	80	18	9.4	33.3	29.6	3.3	9.8
A 5	k/m	0.15	40	5	100	1	9.4	34.7	30.8	2.8	9.8
A 6	k/m	0.15	40	5	100	3	9.0	35.6	31.5	2.6	9.8
A 7	k/m	0.15	40	5	100	6	8.3	36.7	33.2	3.2	9.8
A 8	k/m	0.15	40	5	100	18	8.3	37.9	33.5	2.7	9.8
B 1	k/m	> 1.0	40	5	80	1	10.6	29.3	25.6	2.7	9.8
B 2	k/m	#0.49	40	5	80	1	10.4	33.1	28.9	3.2	9.8
B 3	k/m	#0.29	40	5	80	1	10.3	31.3	27.4	3.2	9.8
B 4	k/m	#0.15	40	5	80	1	10.2	35.2	31.2	3.0	9.8
B 5	k/m	#0.09	40	5	80	1	10.0	38.2	34.0	2.8	9.8
B 6	k/m	< 0.09	40	5	80	1	9.6	40.9	36.5	2.8	9.8
C 1	k/m	~1.0	40	0	80	1	4.3	11.2		1.4	9.8
C 2	k/m	0.15	40	1	80	1	6.9	16.6	15.9	1.8	9.8
C 3	k/m	0.15	40	2	80	1	8.0	20.3	19.1	2.6	9.8
C 4	k/m	0.15	40	5	80	1	10.5	33.2	29.1	2.9	9.8
C 5	k/m	0.15	40	10	80	1	12.5	48.5	40.0	3.3	9.8
C 6	k/m	0.15	40	0	80	6	4.0	11.9	11.8	1.9	9.8
C 7	k/m	0.15	40	1	80	6	6.1	20.4	19.6	2.3	9.8
C 8	k/m	0.15	40	2	80	6	7.1	23.9	22.2	2.3	9.8
C 9	k/m	0.15	40	0	80	18	3.5	12.9		1.4	9.8
D 1	s/m	0.15	40	5	80	1	10.2	35.4	31.6	3.0	10.7
D 3	s/t	0.15	40	5	80	1	10.2	36.4	32.5	2.9	9.3
D 5	k/t	0.15	40	5	80	1	9.8	26.1	22.5	2.6	8.2
D 7	k/tv	0.15	40	5	80	1	10.0	25.4	21.6	2.9	12.7
K 1	k/m	~1.0	70	5	80	1	9.8	35.5	31.6	2.8	9.8
K 2	k/m	0.15	100	5	80	1	9.9	37.4	33.4	2.9	9.8
K 3	k/m	0.15	130	5	80	1	9.8	37.7	33.8	2.8	9.8
L 1	s/t	J1	20	10	100	1	11.1	41.5			23.5
L 2	s/t	J1	20	10	100	3	10.3	47.7			23.5
L 3	s/t	J1	20	10	100	6	10.3	43.1			23.5
L 4	s/t	J1	20	10	100	24	10.2	39.5			23.5
L 5	s/t	J2	20	10	100	1	11.3	39.7			17.0
L 6	s/t	J2	20	10	100	6	11.1	42.3			17.0
V	s/t	1… 0.15	40	10	100	1	11.4	44.7			11.0

[a] k pulpwood bark
s saw timber bark
m bark from forest
t bark from sawmill or pulp mill
v wood water stored before barking

Tables 2 and 3 give the compositions of the test glues. After pressing the panels were allowed to cool and then the necessary specimens were sawn. The shear strength of the glue joint and wood failure percentage were determined from the test panels after a two-phase boiling according to standard SFS 2416.

3.2 Test Results

The results pertaining to the properties and preparation of bark extracts are shown in Table 4 and Figs. 3…13. Table 5 and Fig. 14 show the results pertaining to bark dispersion. The results of the gluing tests for bark extract are given in Table 6 and Fig. 15. Table 7 and Fig. 16 show the results obtained with resins containing bark dispersion.

3.3 Examination of the Results

3.3.1 Properties of the Extract

If the bark is taken from freshly felled trees, the type of bark (pulpwood↔saw timber) has no significant effect on extract yield or formaldehyde reactivity (Table 4 and Fig. 3). The extract content of bark from the pulp mill barking plant is about 30% lower than the extract yield of bark from the sawmill. The reason is probably due to the fact that the part of bark containing the highest amount of extract is leached with the waste water from the drum barking plant. The origin of the bark is of little significance to the formaldehyde reactivity of the extract.

Within the temperature range tested (40…130 °C) the drying temperature of bark does not seem to be of any practical significance for extract yield or extract reactivity (Fig. 4).

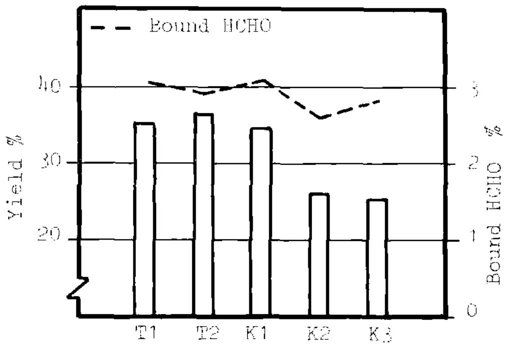

Fig. 3. Dependency of yield and formaldehyde reactivity of extract on spruce bark quality and origin. *T1* Fresh pulpwood bark; *T2* Timber bark from sawmill, stored in pile for 2...3 months, road transport; *K1* Fresh pulpwood bark; *K2* Drum-debarked pulpwood bark, open-air storage; *K3* Drum-debarked pulpwood bark, water storage
Bild 3. Abhängigkeit der Ausbeute und Formaldehyd-Reaktivität der Extrakte von Qualität und Herkunft der Fichtenrinde. *T1* frische Faserholzrinde; *T2* Rinde von Sägerundholz, 2...3 Monate gestapelt, Lkw-Transport; *K1* frische Faserholzrinde; *K2* Trommel-entrindete Faserholzrinde, freiluftgelagert; *K3* Trommel-entrindete Faserholzrinde, wassergelagert

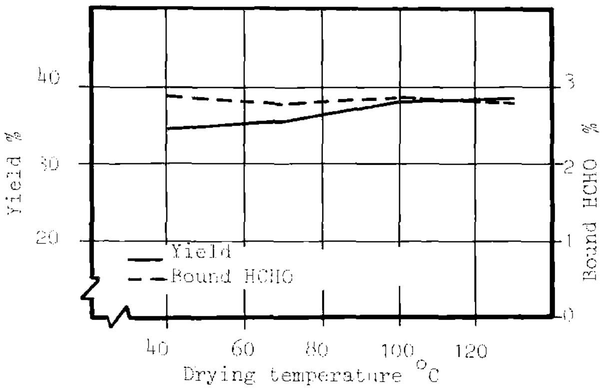

Fig. 4. Influence of drying temperature on extract yield and extract reactivity
Bild 4. Einfluß der Trocknungstemperatur auf Extrakt-Ausbeute und -Reaktivität

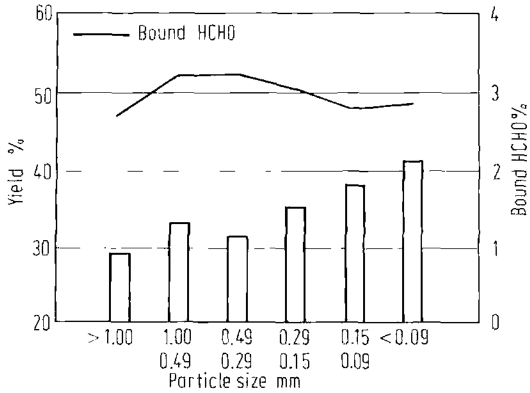

Fig. 5. Influence of the particle size of the bark on extract yield and extract reactivity
Bild 5. Einfluß der Rinden-Partikelgröße auf Extrakt-Ausbeute und -Reaktivität

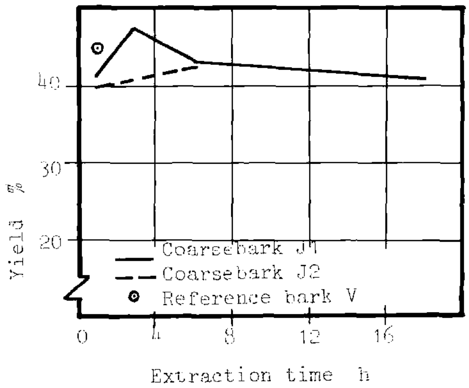

Fig. 6. Extraction of coarse bark. Influence of extraction time on yield. Temperature 80 °C, NaOH-content 10%
Bild 6. Extraktion von Roh-Rinde. Einfluß der Extraktionszeit auf die Ausbeute. Temperatur 80 °C; 10% NaOH-Gehalt

The extract yield is significantly dependent on the particle size of the bark to be extracted, because the finest bark fraction gives about 30% more extract than the coarsest (Fig. 5). The explanation may be that during grinding the inner bark layer that contains the highest amount of extract is ground finest. This assumption is supported both by a previously published investigation (Hegert 1969) and an observation made in this investigation, namely that the particle size has relatively little influence on extract yield when the bark is used unfractioned (Figs. 6 and 7). The particle size has no significant influence on the extract reactivity (Fig. 5).

Figure 8 shows that the extraction time has no significant influence on the extract yield and formaldehyde reactivity within 1...18 h. When long extraction times are used the yield at 100 °C is about 5%-units higher than at 80 °C. The reactivity of extract prepared at higher temperature is lower than that extracted at lower temperature.

The quantity of sodium hydroxide used during extraction has a very strong influence on the yield. When extraction was carried out with hot water the yield was 11.2%. If 10% NaOH (related to bark quantity) were added, the yield rose to 48.5%. If the NaOH in the extract is not considered, the yield is 40.0% (Fig. 9). When 5% NaOH were used, the average yield was 35.6% and 31.5%, if NaOH was not used (Fig. 9, Table 4). The yield is clearly higher than the values, 20...25% presented in the literature (Norin, Fremer 1977). The difference between the results may be due to the fact that the alkaline extraction liquids used in this investigation can partly dissolve the acidic phenolic compounds in bark lignin, the so-called phenolic acids. The reactivity of the extract increases slightly with increasing alkalinity of extract solution.

The formaldehyde reactivity of the extract is strongly dependent on pH (Fig. 10). The reactivity is lowest when the pH is 2...6, and the quantity of formaldehyde bound by the extract increases fast when the alkalinity of the reaction mixture grows. The dependency of spruce bark extract reactivity on the pH is almost similar to that of Quebracho extract (Fig. 10) and wattle-based extract (Pizzi 1979c).

The viscosity of the extract solutions is strongly dependent on the concentration of the solutions (Figs. 11, 12, 13). The increase in viscosity is markedly higher than in wattle-based extracts (Plomley 1966). Such increase in viscosity is generally unfavourable to glue applications because it limits the quantity of the extract used.

Figure 11 shows clearly that an extract prepared at higher temperature increases viscosity more than an extract prepared at lower temperature.

Addition of NaOH to the extract solution reduces its viscosity (Fig. 12). Similar observations have also been presented in the literature (Hemingway 1978).

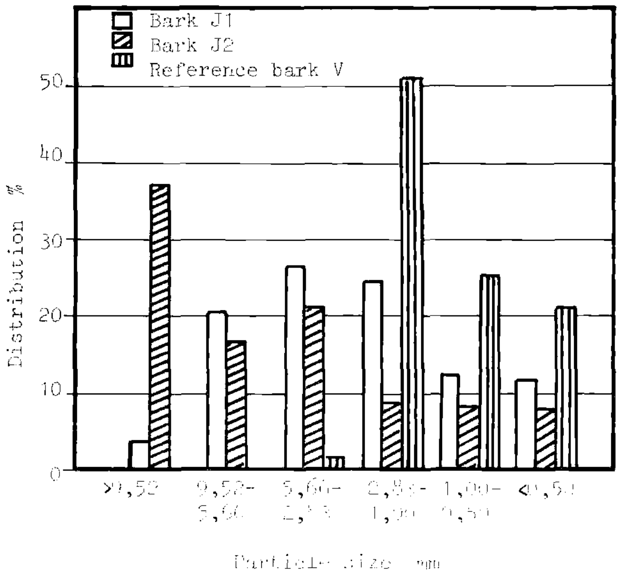

Fig. 7. Extraction of coarse bark. Distribution of particle sizes
Bild 7. Extraktion von Roh-Rinde. Verteilung der Partikelgrößen

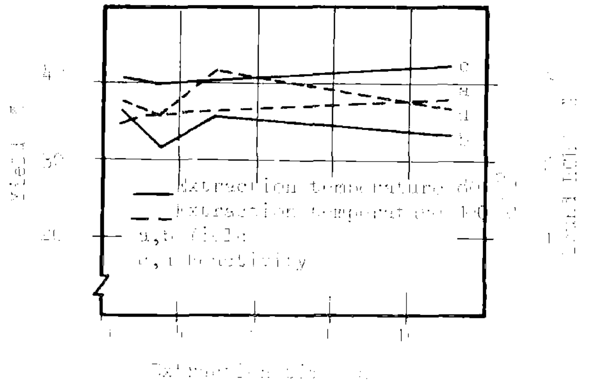

Fig. 8. Influence of extraction time and temperature on extract yield and reactivity
Bild 8. Einfluß von Extraktionszeit und -temperatur auf Extrakt-Ausbeute und -Reaktivität

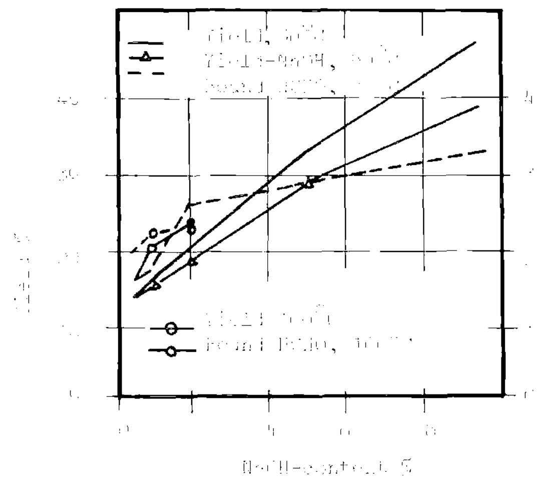

Fig. 9. Dependency of extract yield and formaldehyde reactivity on the NaOH-content (in percentage of bark quantity) of extraction liquid and on extract temperatures
Bild 9. Abhängigkeit von Extrakt-Ausbeute und Formaldehyd-Reaktivität vom NaOH-Gehalt (in % der Rindenmenge) der Extraktionsflüssigkeit und von der Extraktionstemperatur

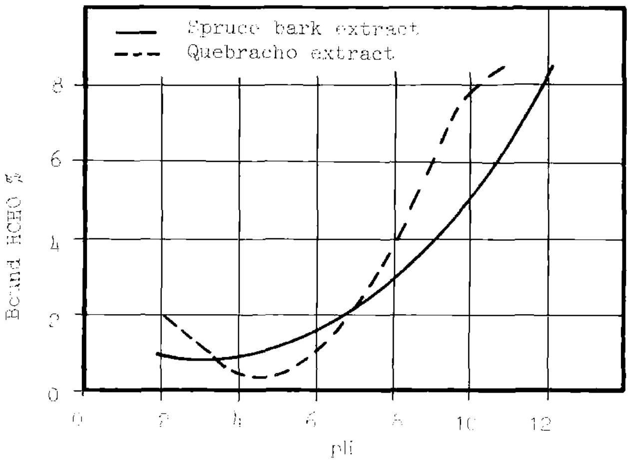

Fig. 10. Dependency of formaldehyde reactivity of extract on pH
Bild 10. Abhängigkeit der Formaldehyd-Reaktivität der Extrakte vom pH-Wert

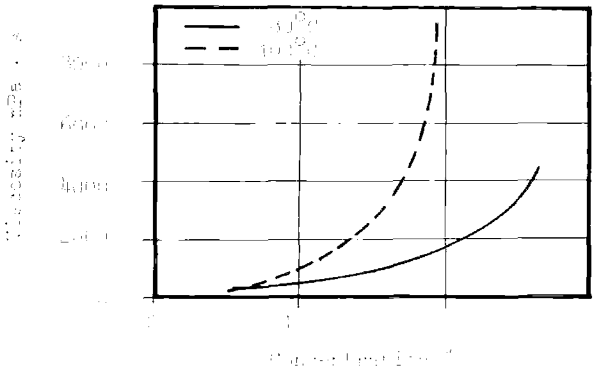

Fig. 11. Dependency of extract solution viscosity on concentration and extraction temperature
Bild 11. Abhängigkeit der Viskosität der Extraktionslösung von der Konzentration und der Extraktionstemperatur

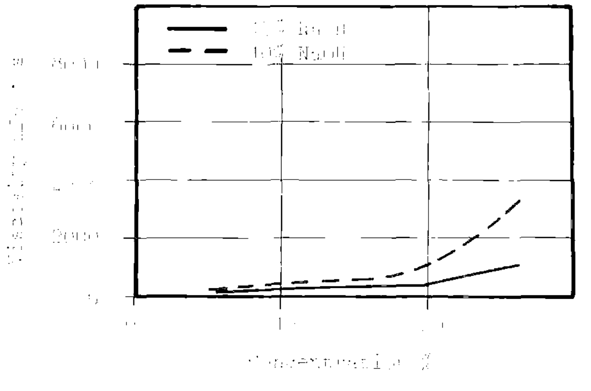

Fig. 12. Dependency of extract solution viscosity on concentration and NaOH-content
Bild 12. Abhängigkeit der Viskosität der Extraktionslösung von der Konzentration und dem NaOH-Gehalt

The age of the wood seems to have a distinct influence on the viscosity of the extract solution. It is possible that the observed large difference in viscosity between timber and pulpwood is due to the different bark grinding results (Fig. 13).

As the gelation of the glues containing bark extract could not be reliable measured with the equipment available, the

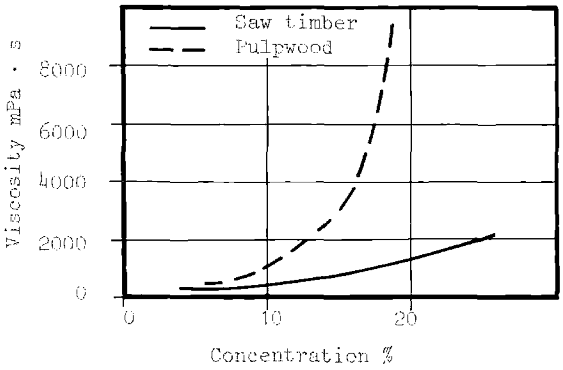

Fig. 13. Dependency of extract solution viscosity on concentration and origin of bark
Bild 13. Abhängigkeit der Viskosität der Extraktionslösung von der Konzentration und der Herkunft der Rinden

Table 5. Viscosity and dry solids content of the bark dispersions

Mixture	NaOH %	$Ca(OH)_2$ %	Dry solid content %	Viscosity mPa × s
N 1	0		7.4	38
N 2	2	–	10.3	175
N 3	5	–	9.7	805
N 4	10		9.6	295
N 5	20	–	10.4	60
N 6	5	–	11.9	2.820
M 1	5	–	9.8	1.040
M 2	5	–	9.9	1.360
M 3	5	–	9.2	855
O 1	5	3.7	13.1	440
O 2	5	9.2	13.5	1.020
O 3	10	9.2	14.7	770
O 4	10	18.5	15.1	1.960

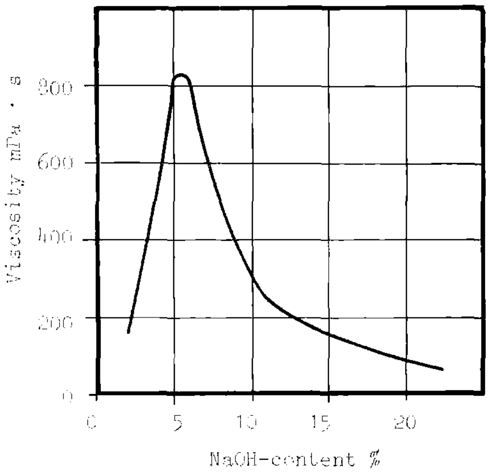

Fig. 14. Dependency of bark dispersion viscosity on NaOH-content used in treatment (in percentage of bark quantity)
Bild 14. Abhängigkeit der Viskosität der Rindendispersion vom NaOH-Gehalt während der Behandlung (in % der Rindenmenge)

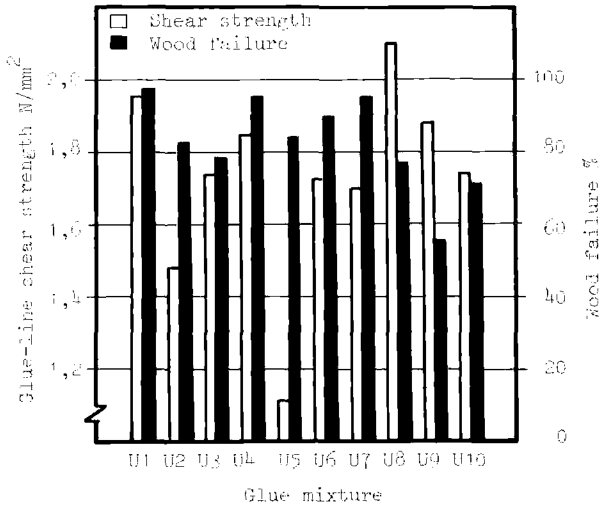

Fig. 15. Glue-line shear strength and wood failure after two-phase boiling of plywood test panels glued with phenolic resin containing spruce bark extract
Bild 15. Scherfestigkeit der Leimfuge und Holzbruchanteil nach einer 2-Phasen-Kochung von Sperrholzproben, die mit Phenolharzleim verleimt waren, welcher Fichtenrinden-Extrakt enthielt

extracts were selected for the gluing tests primarily on the basis of the extract yield. In the final selection the formaldehyde reactivity of the extract was also taken into account. The extracts for the tests were prepared as follows: pulpwood bark: temperature 80 °C, NaOH-content 10% and 15%; timber bark: temperature 80 °C, NaOH-content 10%.

3.3.2 The Properties of the Bark Dispersion

The quantity of NaOH used for bark treatment affects strongly the viscosity of the finished dispersion (Table 5, Fig. 14). Maximum viscosity is reached with ~6% NaOH-content, with lower or higher NaOH-contents the viscosity drops considerably. The bark treatment time has no significant influence on dispersion viscosity (Table 5, mixtures M1 ... M3).

The use of $Ca(OH)_2$ increases bark dispersion viscosity considerably (Table 5). The explanation may be that $Ca(OH)_2$ decreases the number of soluble components in the dispersion (U.S. Patent 1957).

As the reactivity of bark dispersion cannot be measured reliably with the available equipment, as many „different" dispersion types as possible were selected for the gluing tests.

3.4 Gluing Tests

3.4.1 Glues Containing Extract

The results of the gluing tests meet the requirements for exterior-grade birch plywood in Standard SFS 2415 and in FINPLY-quality control. With the extract the proportion of phenolic resin can be reduced by 11 ... 18% (glue mixtures U3, U5 and U9), compared with the quantity of phenolic resin in the reference glue. Regarding the pot-life the properties of the glues in use do not deviate from phenolic resin (Table 6) except mixture U8, but the prepressing adhesion of the glues containing extract is somewhat poorer than of the reference glue.

3.4.2 Glues Containing Bark Dispersion

The plywoods bound with glues containing bark dispersion passed the requirements for exterior-grade birch plywood in

Table 6. Viscosities of glues containing bark extract

Glue mixture	Viscosity, mPa × s Age of glue 0 h	2 h	6 h	24 h
U 1	580	520	540	790
U 2	655	725	650	600
U 3	645	725	735	805
U 4	565		570	615
U 5	570	470	550	650
U 6	700	700	800	910
U 7	580	580	570	740
U 8	830	1.500	1.750	
U 9	490[a]	-		
U 10	605	610	785	825

[a] Other values could not be measured

Table 7. Viscosities of glues containing bark dispersion

Glue mixture	Viscosity, mPa × s Age of glue 0 h	2 h	6 h	24 h
D 1	520	580	655	800
D 2	595	780	890	855
D 3	495	650	770	770
D 4	485	540	560	640
D 5	560	540	595	705
D 6	550	610	640	730
D 7	570	705	825	980
D 8	590	665	645	790
D 9	640	675	810	800
D 10	510	680	730	805

Standard SFS 2415 and FINPLY-quality control, except for one glue mixture (D5) (Fig. 16). With regard to pot-life the properties of the glue mixtures in use do not deviate from normal phenolic resin. The prepressing adhesion of glues containing bark dispersion is poorer than that of the reference glues.

The glues with bark dispersion contained 13...20% less phenolic resin than the reference glue.

3.5 Summary of the Results

There is no difference between pulpwood and timber bark in the extract contents of forest barks. The extract content of pulpwood bark, drum debarked in the pulp mill is significantly lower than that from the sawmill. Drying temperature and extraction time were not found to have much significance on extract yield and reactivity. An increase in extraction temperature raises the yield to some extent when the extraction times are long. When the particles size of the bark flour to be extracted diminishes, the extract-yield increases. The quantity of NaOH used during extraction has a decisive effect on the extract-yield. When extraction is carried out with distilled water, the yield is 11.2%, but the yield increases to 40.0% (related to NaOH in the extract, the yield is 48.5%) when 10% NaOH are added to the extract solution.

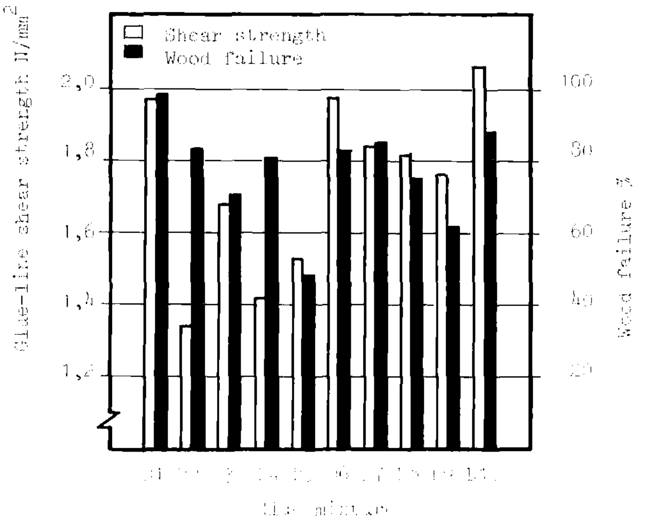

Fig. 16. Glue-line shear strength and wood failure after two-phase boiling of plywood test panels glued with phenolic resin containing spruce bark dispersion

Bild 16. Scherfestigkeit der Leimfuge und Holzbruchanteil nach einer 2-Phasen-Kochung von Sperrholzproben, die mit Phenolharzleim verleimt waren, welcher Rindendispersion enthielt

The formaldehyde reactivity of the extract is strongly dependent on the pH of the reaction mixture. The viscosities of the extract solutions greatly depend on the on concentration and also on the extraction temperature, the bark type and the alkalinity of the extraction solution.

The quantity of NaOH used in the preparation of bark dispersion affects significantly the dispersion viscosity. $Ca(OH)_2$ increases the viscosity of bark dispersion.

Birch plywood meeting the exterior-grade requirements could be manufactured with glues containing extract and dispersion. The amount of phenolic resins in the glue mixtures could be reduced at most by 18...20% in glues containing bark extract and dispersion.

4 Literature

Clusters, A. J. L. 1979: Industrial application of wattle tannin, urea-formaldehyde fortified adhesives for damp-proof corrugated cardboard. Holzforsch. Holzverwert. 31 (6):131–133

Coppens, H. A. 1980: Tannin formaldehyde adhesive for exterior grade plywood and particleboard manufacture. Forest Prod. J. 30 (4):38–41

Hegert, H. L. 1969: Chemical composition of tannins and polyphenols from conifer wood and bark. Forest Prod. J. 10 (10):610–617

Hemingway, R. W. 1978: Adhesives from southern pine bark. A review of past and current approaches to resin formulation problems. Complete Tree Utilization of Southern Pine. Edit. C. W. McMillin. Proceedings of a Symposium. New Orleans, Louisiana, April 1978

Hillis, W. E.; Urbach, G. 1969: Reaction of polyphenols from conifer wood and bark. Forest Prod. J. 6 (10):610–617

Kulvik, E. 1977: Chestnut wood tannin extract as cure accelerator for phenol-formaldehyde wood adhesive. Adhesives Age 3:33–34

Liiri, O.; Sairanen, H.; Kilpeläinen, H.; Kivistö, A. 1978: Puun kuoren käyttö liimojen raaka- ja jatkoaineina. (The use of bark as raw material and extender of adhesives.) Espoo 1978. Valtion teknillinen tutkimuskeskus, Materiaali- ja prosessitekniikka, Julkaisu 3 (VTT Publication M3)

Norin, T.; Fremer, K.-E. 1977: Kuoren rakenne ja kemiallinen koostumus. (Structure and chemical compound of bark). Puukemia. Edit. W. Jensen. Helsinki

Pizzi, A. 1977: Hot-setting tannin-urea-formaldehyde exterior wood adhesive. Adhesives Age 12:27–29

Pizzi, A. 1978: Utilizing wattle-based adhesive in making particleboard. Adhesive Age 9:33

Pizzi, A. 1979a: Wood waterproofing and lignin crosslinking by means of chromium trioxide/quajacylunit complexes. Holzforsch. Holzverwert. 31 (6):128–130

Pizzi, A. 1979b: Phenolic and tannin-based adhesive resins by reactions of coordinated metal ligands I. Phenolic Chelates. J. Appl. Polym. Sci. 24:1247–1255

Pizzi, A. 1979c: Phenolic and tannin-based adhesive resins by reactions of coordinated metal ligands II. Tannin adhesive preparation, characteristics and application. J. Appl. Polym. Sci. 24:1257–1268

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

Plomley, K. F.; Gottstein, I. W.; Hillis, W. E. 1964: Tannin-formaldehyde adhesives for wood I. Mangrove tannin adhesives. Austral. J. Appl. Sci. 15:171–182

Plomley, K. F. 1966: Tannin-formaldehyde adhesives. CSIRO Division of Forest Products. Technological Paper 1966:46

Plomley, K. F. 1966a: Tannin formaldehyde adhesives for wood II. Wattle tannin adhesives. CSIRO Division of Forest Products. Melbourne. Technological Paper 39

U.S. Patent 2781327: Phenolic resin glue compositions containing modified bark phloem flour. Ayers, J. W. & Bradley, J. J., 1957

Valtion teknillinen tutkimuskeskus Puulevylaboratorio 1974: Urea- ja fenoliliimojen analyysiohjeita (Analytical methods for testing of ures-formaldehyde and phenolic resins.) Tiedonanto 6 (VTT/PLE Report No. 6)

Zeitschriftenreferate

Ezell, A.W.: Variation of cellular properties in sweetgum and their relation to other wood properties (Schwankung der Zellartanteile im Holz von Sweetgum (Liquidambar styraciflua L.) im Verhältnis zu anderen Holzeigenschaften). Wood and Fiber 11 (1979) No. 2, S. 136–143; 3 Abb., 6 Tab.

Von 18 Sweetgum-Bäumen wurden Holzproben in axialer und radialer Richtung entnommen, um die Streuung der Zellartenanteile innerhalb der Stämme zu erfassen und sie miteinander und mit der Rohdichte und Faserlänge zu korrelieren. Die Messung der Zellartenanteile erfolgte nach dem Punktzählverfahren mit Hilfe eines Integrationsokulars und der indirekten Fluoreszenz-Mikroskopie. Die Gefäße nehmen rund 57%, die Fasern 25% und das Parenchym 18% des Holzes ein, wobei die Gefäß- und Faseranteile innerhalb der Bäume stark streuen und der Parenchymanteil nahezu konstant bleibt. Der Faseranteil ist in hohem Maße positiv, der Gefäßanteil negativ mit der Rohdichte korreliert, so daß beide Parameter zur Vorhersage der Rohdichte geeignet sind. D. Eckstein

Shelly, J.R.; Arganbright, D.G.; Birnbach, M.: Severe warp development in young-growth ponderosa pine studs (Schwere Verwerfungen bei Kanthölzern aus jungwüchsiger Ponderosa-Kiefer). Wood and Fiber 11 (1979) No. 1, S. 50–56; 2 Abb., 2 Tab.

In der Studie werden anatomische und physikalische Eigenschaften von stark verworfenen, jungwüchsigen Kiefernkanthölzern, welche teils freiluftgetrocknet, teils kammergetrocknet wurden, untersucht. Die statistische Analyse zur Bestimmung der Ursachen der Verwerfungen ergab folgendes: 1. Die Trocknungsmethode hat anscheinend keinen Einfluß auf den Zusammenhang zwischen Holzeigenschaften und Verwerfungen. 2. Der größte Teil der durch die Trocknung bedingten Verwerfungen konnte nicht statistisch gesichert auf einen der gemessenen Faktoren zurückgeführt werden. Als mögliche Einflußfaktoren für Verwerfungen wurden gemessen: Häufigkeit von Ästen, Feuchtigkeitsgehalt, Rohdichte, Druckholz, Kernholzanteil, Vorhandensein von Mark im Kantholz, sowie Faserabweichungen. Von den gemessenen Eigenschaften scheint das Vorhandensein von Mark den größten Einfluß auf das Auftreten von Verwerfungen zu haben. Kernholz an einer Seite in Kantholz führte zu starken Verwerfungen, jedoch konnte keine Beziehung zwischen prozentualem Anteil und Stärke der Verwerfung gefunden werden. Keiner der anderen Faktoren konnte eindeutig als Ursache von Verwerfungen ermittelt werden, vielmehr scheint das Zusammenspiel einer Vielzahl von Faktoren eine Rolle bei der Entstehung von Verwerfungen zu spielen. Vorhersagen für das Auftreten von Verwerfungen im Hinblick auf eine Aussortierung der gefährdeten Stücke vor der Trocknung zur Erhöhung der Wirtschaftlichkeit der Trocknung erscheinen vorerst nicht möglich. J. Welling

Warren, W.G.: The contribution of earlywood and latewood specific gravities to overall wood specific gravity (Anteil der Rohdichte von Früh- und Spätholz an der Gesamtrohdichte des Holzes). Wood and Fiber Bd. 11 (1979) No. 2, S. 127–135; 4 Tab.

Es ist bekannt, daß der Spätholzanteil einen dominanten Einfluß auf die Rohdichte von Nadelholz hat. Auf der anderen Seite zeigten einfache mathematische Analysen, daß die Gesamt-Rohdichte vornehmlich von der Frühholz-Rohdichte abhängt. Zur Klärung dieser Situation wurde ein neuer Rechenansatz gewählt und Methoden der mathematischen Statistik eingesetzt. Ausgehend von der Identitätsgleichung $z \equiv x(1-P)+yP$, wobei z Gesamt-Rohdichte, x Frühholz-Rohdichte, y Spätholz-Rohdichte und P Spätholzanteil bedeuten, wurde an einem beispielhaft aufgeführten Datenteil, der 24 verschiedene Gesamt-Rohdichten, Spätholz- und Frühholz-Rohdichten sowie Spätholzanteile enthielt, mit Hilfe der Statistik festgestellt, daß ein alleiniger Einfluß der Frühholz-Rohdichte auf die Gesamt-Rohdichte des Nadelholzes (Pseudotsuga menziesii) nicht vorhanden ist. Die Varianzanalyse zeigte vielmehr, daß der Spätholzanteil einen respektablen Anteil an der Variabilität der Gesamt-Rohdichte des Holzes hat und daß daneben entweder die Früh- oder die Spätholz-Rohdichte von Einfluß ist. F.-W. Bröker

Koran, Z.: Tensile properties of spruce under different conditions (Zugfestigkeitseigenschaften von Fichte bei wechselnden Temperaturen). Wood and Fiber. Bd. 11 (1979) No. 1, S. 38–49.

Das Verhalten des Holzes bei Zugbeanspruchung quer zum Faserverlauf wird am Beispiel der Holzart Picea mariana im Temperaturbereich von −190 °C bis +250 °C untersucht. Hierzu werden aus 8 sorgfältig ausgewählten frischen Stäben (Querschnitt 7,5 cm × 7,5 cm) jeweils 10 Querzugproben hergestellt. Die Hälfte der 80 Proben wird in frischem Zustand, die andere Hälfte nach Imprägnierung mit Glycerin geprüft. Die Zugprüfung erfolgt innerhalb einer in die Prüfmaschine eingesetzten, temperierten Kammer. Die verschiedenen Probenserien werden in folgenden Medien temperiert: flüssiger Stickstoff (−190 °C), Eis-Aceton-Gemisch (−60 °C), Eis-Wasser-Gemisch (0 °C), Wasser (25 °C und 100 °C) bzw. Glycerin (25 °C, 100 °C, 150 °C, 200 °C und 250 °C). Bei den Extremtemperaturen treten besondere experimentelle Schwierigkeiten auf. So führt die Abkühlung unter −60 °C bei vielen Proben zur Rißbildung. Bei Temperaturen über 150 °C gewinnt die thermische Zersetzung zunehmend an Bedeutung. Die Meßergebnisse des Elastizitätsmoduls, der Zugfestigkeit, der Bruchdehnung und der zum Bruch erforderlichen Zugarbeit sind als Funktion der Probentemperatur graphisch dargestellt. Diese Graphiken erlauben folgende Aussagen:
1. Elastizitätsmodul und Festigkeit nehmen mit zunehmender Temperatur ab. Dabei gilt für die Zugfestigkeit β_z im Temperaturbereich 83 °K $< T <$ 423 °K die Geradengleichung
$\beta_z = 56{,}4 - 1{,}24T$ (in kp/cm^2).
2. Die Bruchdehnung steigt mit zunehmender Temperatur, erreicht bei 125 °C ein Maximum und fällt dann wieder ab. 3. Die Brucharbeit erreicht bereits bei −40 °C ein Maximum und nimmt dann mit steigender Temperatur stark ab. Dabei fällt die stärkste Abnahme in den gleichen Temperaturbereich, in dem die Bruchdehnung ihr Maximum erreicht. Dies wird mit ausgeprägter Erweichung der Hemicellulosen und des Lignins bei Temperaturen um 125 °C erklärt. Auf die besondere Problematik des Phasenüberganges beim freien und gebundenen Wasser im Temperaturbereich zwischen 0 °C und −40 °C wird hingewiesen. E. Schwab