

EFFECT OF VARIOUS FIRE RETARDANTS ON BRINELL HARDNESS OF SOME WOOD

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This study was performed to determine the impact of impregnation materials on the Brinell hardness of varnished wood materials. For this purpose, test specimens prepared from Scotch pine (*Pinus sylvestris* L.) and Oriental beech (*Fagus orientalis* Lipsky), which met the requirements of ASTM D 358, were impregnated according to ASTM D 1413-07 with borax, boric acid, zinc chloride, and di-ammonium phosphate by a vacuum technique. After impregnation, the surfaces were coated by cellulosic, synthetic, and polyurethane varnishes in accordance with ASTM D 3023. The Brinell hardness of the specimens after the varnishing process was determined in accordance with ASTM D 4366. According to the result of the tests, the highest Brinell hardness (135.40 kpm/m²) was determined in oriental beech samples, cut tangentially, impregnated with di- ammonium phosphate, and varnished with polyurethane. The lowest Brinell hardness (23.20 kpm/m²) was determined in Scotch pine control samples, cut radially and synthetically varnished.

Keywords: Wood materials, Brinell hardness, Varnishes

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INTRODUCTION

Wood has many good properties from the point of view of processing, physical and mechanical properties, aesthetic, environmental, and health aspects. In many countries wood is widely used as a building material, in some areas as a main construction and decoration material.

Among the various surface processes applied to wood, varnishes are used to show its beauty, colour, and the wood pattern resulting from its nature, while at the same time protected it with a film layer. After the application of surface treatments performed according to industry standards the technical, aesthetic, and economic value of wood increases.

Impregnation of wood with chemicals is absolutely necessary to protect against insects, fungus, and other such agents in many applications. Painting and varnishing preserves unimpregnated wood surfaces for only about 2 years (Evans et al.1992).

Hardness is used to represent the resistance to indentation and/or marring. Hardness is measured by the load required to embed a 1.128- cm steel ball one-half its diameter into the wood (Winandy and Rowell 1984).

For paint and varnish layers, hardness is an important indicator of resistance to physical and mechanical effects. A pendulum damping test apparatus can be used for measuring the hardness of paints and varnishes (Kaygın 1997).

Uysal *et al.* studied the effects of chemicals used for the bleaching of the wood surfaces on the layer hardness of varnishes. They indicated that in the natural varnishing process the effects of the wood species on the layer hardness of varnish are unimportant, but the effects of varnish types are important. In the varnishing process, after bleaching the different wood types, bleaching chemicals and their concentration and varnish kinds affected the hardness of the varnish layer (Uysal *et al.* 1999).

Ors and Atar reported that the hardness of varnish layers was not affected by impregnation and bleaching materials, but the hardness of wooden materials was increased by impregnation materials. Solvent groups however, decreased the hardness. It was concluded that synthetic varnishes were found suitable for use after bleaching and impregnation processes (Ors and Atar 2001).

The aim of this experimental study was to determine the effect of impregnation materials on the Brinell Hardness of Scotch pine and Oriental beech, which are widely used in the furniture industry, treated with cellulosic, synthetic, and polyurethane varnishes.

EXPERIMENTAL

Materials

Scotch pine (*pinus sylvestris* L.), and oriental beech (*Fagus orientalis* Lipsky.) were chosen randomly from a timber supplier of Istanbul, Turkey. A blending process was carried out in order to ensure that there were representative control samples to compare with other groups. A special emphasis was put on the selection of the wood material. Accordingly, non-deficient, whole, knotless, normally grown (without zone line, reaction wood, decay, insect or fungal infection) wood materials were selected.

As impregnation chemicals, borax, boric acid, zinc chloride, and di-ammonium phosphate were used.

Preparation of Test Samples

Wood samples were randomly selected from the materials described above. The rough panels for the preparation of test and control specimens (massive panels) were cut from the sapwood parts of massive woods with dimensions of 190 X 140 X 15 mm³ and conditioned at 20 ± 2°C and 65 ± 3% relative humidity until a 12% humidity distribution was reached, in accordance with ASTM D 358(1983).

The impregnation process was carried out according to the principles of ASTM D 1413-07. A vacuum, which was equal to 760 mmHg⁻¹, was applied to the samples. They were then dipped for 60 min in a solution subject to open air pressure. Before the impregnation process all samples were weighed and then kiln dried at the temperature of 103 ± 2°C until they reached constant weight. Then, the samples were weighed in an analytic balance with 0.01-g sensitivity. After impregnation, all impregnated samples were held for 15 days in circulating air for evaporation of the solvent.

After this period the impregnated samples were kiln-dried at $103 \pm 2^\circ\text{C}$ until they reached constant weight. After cooling, all dried samples in the desicator were weighed on the scale. The dry weight of the samples was determined and recorded. The amount of retention ($R, \text{kg/ m}^3$) and ratio of retention ($R, \%$) were calculated as follows,

$$R = \frac{G \times C}{V} 10^3 \quad (\text{kg/m}^3) \quad (1)$$

$$R(\%) = \frac{M_{di} - M_d}{M_d} 100 \quad (2)$$

$$G = T_2 - T_1 \quad (3)$$

where G is the mass of the sample after impregnation (M_2 , kg) minus the mass of the sample before impregnation (M_1 , kg), M_{di} is the dry mass after impregnation (kg), M_d is the dry mass before impregnation (kg), V is the volume of the sample (m^3), and C is the concentration of the solution (%).

The characteristic features of the impregnation chemicals were determined before and after the impregnation processes. All processes were carried out at the temperature of $20 \pm 2^\circ\text{C}$. Impregnated test samples were kept at the temperature of $20 \pm 2^\circ\text{C}$ and $65 \pm 3\%$ relative humidity until they reached constant weight.

Impregnation Process

The impregnation process was carried out according to the principles of ASTM D 1413-07 (2007). A vacuum, which was equal to 760 mmHg^{-1} , was applied to the samples. They were then dipped for 60 min in a solution subject to open air pressure.

Varnish

Cellulosic, synthetic, and polyurethane varnishes were used according to the producer's instructions. The type, selection, preparation, and surface application system of the varnish to be used and the post-application processes as recommended by the manufacturers and the techniques used are very important to make varnish layers durable against various effects and to ensure the desired properties. Therefore, materials used in the experiments (tests) were stored appropriately until their usage to prevent loss of properties. Varnishes were checked to confirm they had the properties specified in their descriptions and they were used after seeing that they were appropriate for the tests (viscosity control). The technical specifications of the conventional varnishes are given in Table 1.

Table 1. Some Technical Properties of the Conventional Varnishes

Technical Properties	Varnish Type		
	Synthetic	Cellulosic	Polyurethane
Density (g/cm ³)	0.94-0.95	0.94-0.96	0.95-0.96
Viscosity (second/DIN CUP 4 mm/20°)	18	20	16
Amount applied (gram/m ²) 100	100	125	120
Nozzle gap (mm)	-	1.8	1.8-2
Air pressure (bar)	-	3	2
Drying type	Physical	Physical	Chemical
Drying time (20°)	6-8 hour	20-30 minute	2-3 hour

Varnish Process

Approximately 120 g/m² varnish was applied to the surfaces of samples, based on ASTM 3023 (1988).

Brinell Hardness

Brinell hardness was determined using Hardness Tester FV-700, which measures the changes of successive profile according to ASTM-D-4366 standards (1984).

Statistical Procedure

By using four impregnation chemicals and one control sample, three varnish types and control, two wood types, directions (tangentially and radially), a total of 800 samples (5 x 4 x 2 x 2 x 10) were prepared using 10 samples for each parameter. Multiple analyses of variance were used to determine the differences between impregnated materials and varnishes on the Brinell hardness of the material surfaces of the prepared samples. The Duncan test was used to determine whether there was a significant difference between the groups.

RESULTS AND DISCUSSION

Properties of the solution used in the impregnation process are given in Table 2.

Table 2. Characteristics of Impregnation Chemicals

Impregnation Chemicals	Viscosity (20 °C) 4mm /Din cup/ sn	Solution concent. (%)	Temp. (°C)	pH		Density (g/ml)	
				BI	AI	BI	AI
Borax	10-11	5	23	9.12	9.15	1.08	1.10
Boric Acid	10	5	23	5.23	5.30	1.02	0.02
Zinc Chloride	10	5	23	6.00	6.09	1.07	1.07
Di-ammonium Phosphate	11	5	23	6.89	9.98	1.11	1.13

BI: Before impregnation AI: After impregnation

As a result of using fresh solution in every impregnation process, there was no important change in the acidity and density of the solutions before and after the impregnation, and the pH values due to Boric acid 5% solution's being in acidic zone

may be expected to affect the polysaccharide components of the wood. The retention proportion of impregnation chemicals is given in Table 3. In Scotch pine the highest retention proportion was observed with di-ammonium phosphate and the lowest with borax. In oriental beech the highest retention proportion was observed with borax and the lowest with di ammonium phosphate.

In Scotch pine the highest retention proportion was observed with di-ammonium phosphate and the lowest with borax. In oriental beech the highest retention proportion was observed with borax and the lowest with di-ammonium phosphate.

The results of the multiple variance analyses connected with these values are shown in Table 3.

Table 3. Proportion of Retention

Wood Species	Impregnated Materials	Retention (%)	
		X	H.G.
Oriental Beech	Borax	9.85	AB
	Boric Acid	9.47	AB
	Zinc Chloride	9.46	AB
	Di- Ammonium Phosphate	9.12	B
Scotch Pine	Borax	7.78	C
	Boric Acid	8.17	BC
	Zinc Chloride	10.13	A
	Di- Ammonium Phosphate	10.26	A

The average of Brinell hardness values is given in Table 4. When the wood species were compared according to their Brinell hardness, the Brinell hardness of Oriental beech was higher than that of Scotch pine. With respect to their directions, the samples cut tangentially gave higher Brinell hardness than the ones cut radially. It is said that impregnation chemicals have decreased the Brinell hardness, and control samples gave higher Brinell hardness value. Among the varnish types, cellulosic varnish gave the highest value. Concerning the variance analysis, the effects of wood type, grain orientation, impregnation type, and varnish type were statistically significant. The interaction between the factors was statistically identical ($p < 0.05$).

Table 4. Average Values of Brinell Hardness

Wood Species	Direction	Brinell Hardness	Impregnated Materials	Brinell Hardness	Varnish	Brinell Hardness
Oriental Beech	Radial	70.59	Borax	62.05	Cellulosic	86.14
	Tangential	54.91	Boric Acid	58.18	Synthetic	34.60
Scotch Pine	Radial	61.56	Zinc Chloride	62.87	Polyurethane	85.75
	Tangential	63.94	Di- Ammonium Phosphate	64.68	Control	44.52
			Control	65.98		

The mean values of the variation sources that were found to be significant were compared using Duncan's test, and the results are summarized in Table 5 (see Appendix). According to the Duncan test results, the highest Brinell hardness value (135.40 kpm/m²) was determined in oriental beech samples, cut tangentially, impregnated with di-ammonium phosphate and polyurethane varnished. The lowest Brinell hardness value (23.20 kpm/m²) was determined in Scotch pine samples, cut radially, unprocessed impregnated and synthetic varnished. According to Table 5, in the Brinell hardness values that were impregnated with di-ammonium phosphate and polyurethane varnished in wood materials: oriental beech samples gave higher than values when compared to Scotch pine samples.

The Brinell hardness value of Scotch pine is given in Table 5. For tangentially cut samples, the highest Brinell hardness of 114.20 kpm/m² was obtained in Scotch pine control samples, finished with polyurethane varnish and the lowest Brinell hardness of 24.40 kpm/m² was obtained with synthetic varnish and in impregnated with Borax. For radially cut samples, the highest Brinell hardness of 103.20 kpm/m² was obtained in Scotch pine control samples, finished with cellulosic varnish and the lowest Brinell hardness of 23.20 kpm/m² was obtained in Scotch pine control samples with synthetic varnish.

The Brinell hardness value of oriental beech is given in Table 5. For tangentially cut samples, the highest Brinell hardness of 135.40 kpm/m² was obtained in samples with polyurethane varnish and in impregnated with di-ammonium phosphate and the lowest Brinell hardness of 33.60 kpm/m² was obtained with synthetic varnish and in impregnated with di-ammonium phosphate. For radially cut samples, the highest Brinell hardness of 105.60 kpm/m² was obtained in oriental beech control samples, finished with polyurethane varnish and the lowest Brinell hardness of 32.80 kpm/m² was obtained in oriental beech control samples with synthetic varnish.

CONCLUSION

As shown in Table 4, the Brinell hardness of oriental beech was higher than that of Scotch pine. The reason of this is that the density of oriental beech is quite high, depending on its structure. The Brinell hardness of tangential direction was higher than radial direction. It can be said that impregnation chemicals decreased the Brinell hardness, and control samples gave higher Brinell hardness value. It has been observed that while di-ammonium phosphate decreased Brinell hardness values 1.9% on average, zinc chloride decreased them by 4.7% on average, borax decreased them 5.6% on average, and boric acid decreased them 11.8% on average.

At the same time, the mechanical properties of woods treated with fire retardant were reduced compared to those observed in untreated wood (Rowell 1984).

According to Table 4, varnish types increased the Brinell hardness, except for synthetic varnish. While cellulosic varnish increased Brinell hardness values by 93% on average, polyurethane varnish increased it by 92% on average, and synthetics decreased it by 22% on average.

Oil-borne materials used in synthetic varnish production may cause the varnish layout to have a more flexible structure by making a more flexible layout. Based on this,

it is possible to say that, after the varnishing process, the effect of solution groups on varnish layout hardness is not very important, and the real effect is caused by varnish (Özen and Sönmez 1999).

Polyurethane-based varnish showed more resistance to the scratch and abrasion than cellulosic varnish. This supports previous findings that polyurethane-based varnish penetrates in to the wood easily, makes a sufficient quantity of linkages with wood, and shows a tighter structure on the surface (Ozdemir 2003).

The highest Brinell hardness values were determined with the polyurethane varnish and the lowest with synthetic varnish. Surface treatment provides protection against ultraviolet and water, and will be affected by the weather resistance of the bonding agents of the finish (drying oils, synthetic resins, latexes, etc.) (Feist and Hon 1984).

Consequently, for each of the hardness values of the varnishes used in the experiments, a decrease has been determined in synthetic varnish compared to the control sample. Varnishes being produced from artificial resins and the use of oiled materials in synthetic varnish production may be effective. Moreover, it is possible to say that oriental beech's having a regular texture structure may form a better surface by increasing the adhesion strength with polyurethane varnish. Oriental beech samples, cut tangentially, impregnated with di- ammonium phosphate and polyurethane varnish were found to be the most successful relative to Brinell hardness.

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APPENDIX

Table 4A. Duncan Test Results (first part)

Wood	Direct.	Impregnated materials	Varnish Type	Mean/ Homogeneity
O.Beech	Tang.	DAP	Polyurethane	135.40/a
O.Beech	Tang.	ZC	Polyurethane	118.80/ b
O.Beech	Tang.	DAP	Polyurethane	117.40/ b
S. Pine	Tang.	Control	Polyurethane	114.20/b
O.Beech	Radial	Control	Polyurethane	105.60/c
O.Beech	Tang.	Control	Cellulosic	104.80/c
O.Beech	Tang.	DAP	Cellulosic	104.40/c
O.Beech	Tang.	Boric Acid	Polyurethane	104.20/c
O.Beech	Tang.	Borax	Cellulosic	104.00/c
S. Pine	Radial	Control	Cellulosic	103.20/c
O.Beech	Radial	ZC	Cellulosic	100.20/cd
O.Beech	Radial	ZC	Polyurethane	98.00/cde
O.Beech	Radial	Boric Acid	Cellulosic	94.60/de
S. Pine	Tang.	Borax	Cellulosic	93.60/def
O.Beech	Tang.	Borax	Polyurethane	92.80/defg
S. Pine	Tang.	Borax	Polyurethane	92.20/defg
O.Beech	Tang.	Boric Acid	Cellulosic	91.40/defg
O.Beech	Radial	Borax	Polyurethane	90.60/efg
O.Beech	Radial	DAP	Cellulosic	89.00/e-h
S. Pine	Radial	DAP	Cellulosic	84.80/f-i
S. Pine	Radial	Borax	Cellulosic	83.80/g-i
S. Pine	Radial	ZC	Cellulosic	82.00/h-j
O.Beech	Radial	Control	Cellulosic	81.40/i-k
O.Beech	Tang.	Control	Polyurethane	81.40/i-k
O.Beech	Tang.	ZC	Cellulosic	79.00/j-l
S. Pine	Tang.	DAP	Cellulosic	78.80/j-m
S. Pine	Radial	ZC	Polyurethane	73.20/j-m
O.Beech	Radial	Borax	Cellulosic	72.80/k-n
S. Pine	Tang.	Control	Cellulosic	72.80/k-n
S. Pine	Radial	Control	Polyurethane	71.80/lm
S. Pine	Tang.	Boric Acid	Polyurethane	70.20/lm
S. Pine	Tang.	Boric Acid	Cellulosic	70.20/lm
S. Pine	Tang.	DAP	Polyurethane	69.40/m-o
S. Pine	Tang.	ZC	Cellulosic	66.60/m-ö
S. Pine	Radial	Boric Acid	Cellulosic	65.40/m-ö
O.Beech	Radial	Boric Acid	Polyurethane	65.13/m-ö
O.Beech	Tang.	Control	Control	63.67/n-ö
O.Beech	Radial	ZC	Control	60.87/o-p
S. Pine	Radial	Borax	Polyurethane	59.80/öp
S. Pine	Radial	DAP	Polyurethane	55.00/pt

DAP = Di-Ammonium phosphate; ZC = Zinc chloride

Table 4B. Duncan Test Results (second part)

Wood	Direct.	Impregnated Materials	Varnish Type	Mean/ Homogeneity
O.Beech	Tang.	ZC	Control	54.40/p-s
O.Beech	Radial	Borax	Control	53.33/p-s
O.Beech	Radial	DAP	Control	52.33/p-t
S.Pine	Tang.	ZC	Polyurethane	50.40/ r-t
S.Pine	Radial	Boric Acid	Polyurethane	49.60/ r-t
O.Beech	Radial	Control	Control	47.80/ r-u
S.Pine	Tang.	Control	Control	45.73/ s-u
S.Pine	Tang.	Boric Acid	Control	45.47/ s-ü
O.Beech	Tang.	DAP	Control	45.40/ s-ü
O.Beech	Tang.	Boric Acid	Control	45.20/ s-ü
O.Beech	Radial	ZC	Synthetic	45.00/ ş-v
O.Beech	Radial	DAP	Synthetic	44.40/ ş-y
O.Beech	Tang.	Borax	Control	43.80/ t-y
O.Beech	Radial	Boric Acid	Control	43.47/ t-y
S.Pine	Radial	DAP	Control	40.07/ u-z
S.Pine	Radial	Boric Acid	Control	39.93/ u-z
S.Pine	Radial	Borax	Control	39.80/ u-z
O.Beech	Radial	Boric Acid	Synthetic	39.80/ u-z
S.Pine	Radial	ZC	Control	39.73/ u-z
S.Pine	Tang.	Boric Acid	Synthetic	39.20/ u-z
O.Beech	Tang.	Boric Acid	Synthetic	38.60/ u-z
O.Beech	Radial	Borax	Synthetic	38.20/ u-z
S.Pine	Tang.	ZC	Control	37.40/ ü-A
O.Beech	Tang.	Control	Synthetic	37.40/ ü-A
S.Pine	Tang.	ZC	Synthetic	37.00/ ü-A
O.Beech	Tang.	ZC	Synthetic	36.60/ ü-A
O.Beech	Tang.	Borax	Synthetic	36.20/ ü-A
S.Pine	Radial	DAP	Synthetic	35.40/ v-B
S.Pine	Tang.	Control	Synthetic	35.00/ y-B
S.Pine	Radial	Control	Control	34.87/ y-B
S.Pine	Radial	Borax	Synthetic	34.80/ y-B
O.Beech	Tang.	DAP	Synthetic	33.60/ z-B
O.Beech	Radial	Control	Synthetic	32.80/ z-D
S.Pine	Tang.	Borax	Control	32.67/ z-D
S.Pine	Radial	Boric Acid	Synthetic	28.60/ B-E
S.Pine	Radial	ZC	Synthetic	26.80/ B-E
S.Pine	Tang.	DAP	Synthetic	25.00/ C-E
S.Pine	Tang.	DAP	Control	24.47/ DE
S.Pine	Tang.	Borax	Synthetic	24.40/ DE
S.Pine	Radial	Control	Synthetic	23.20/ E

DAP = Di-Ammonium phosphate; ZC = Zinc chloride