

Impact of Impregnation with Boron Compounds on the Surface Hardness of Varnished Wood

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ABSTRACT: This study was performed to determine the impact of impregnation with boron compounds on the surface hardness of varnished wood materials. For this purpose, test specimens prepared from Oriental beech (*Fagus orientalis* Lipsky) and oak (*Quercus petraea* Lipsky), which met the requirements of ASTM D 358, were impregnated according to ASTM D 1413 with boric acid and borax by a vacuum technique. After impregnation, the surfaces were coated by cellulosic, synthetic, polyurethane, waterborne, acrylic, and acid hardening varnishes in accordance with ASTM D 3023. The surface hardness of the specimens after

the varnishing process was determined in accordance with ASTM D 4366. According to the wood type, impregnation material, and varnish type, the surface hardness was highest for the oak impregnated with borax and acrylic varnish and lowest for the oak impregnated with borax and synthetic varnish. Therefore, impregnation with boron compounds showed an increasing impact on the surface hardness of the varnished wood. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2327–2331, 2007

Key words: coatings; hardness; surfaces; swelling

INTRODUCTION

Preserving wood materials from environmental effects and providing long usage periods are economically important. Preserving and beautifying covering materials such as paints, polishes, and varnishes are used for this reason. Technical surface processes also increase the technical, esthetic, and economic value of wood.

The surfaces of wood materials are damaged by water and UV light under environmental conditions. Paints and varnishes are used to preserve surfaces from the negative effects of the environment, in addition to their decorative purposes.¹ Furniture coated only with paint and varnishes (surface applications) have surface protection for only 2 years.² After impregnation with materials having appropriate water repellency, varnishing and painting applications are important for long-term utilization against biotic and abiotic effects, photochemical degradation, dimensional changes, biological factors, and fire.³ For painting and varnishing applications with water-repellent materials, wood materials impregnated with boron are more resistant to environmental conditions.⁴

Treating the surfaces of wood materials with solutions of copper, chrome, and salt after impregnation with copper, chrome, and boron makes wood materials more resistant to environmental effects.⁵

Processes such as bleaching and impregnation affect the wood structure and specifications such as the surface hardness, color, and brightness to some extent. The hardness of the varnished layer is the most important parameter for the protection of wood against external factors.⁶ Impregnated and varnished wood specimens of Scotch pine and chestnut were exposed to open air, and the changes in the color surface, hardness, brightness, and surface bonding strength were measured. For Scotch pine, the highest surface hardness was obtained with Tanalith-CBC and a polyurethane varnish in autumn; the highest brightness value was obtained in winter.⁷ After the impregnation of Scotch pine wood with Tanalith-CBC and bleaching with a 18% solution group, the surfaces were varnished with a synthetic varnish. For the hardness of the varnish layer of the Scotch pine, the effects of the solution groups were unimportant, but the effects of the Tanalith-CBC and varnish were important.⁸ After exposure to outdoor conditions for 12 months, the hardness of the unvarnished and unimpregnated Scotch pine wood decreased.⁹

The aim of this study was to determine the impact of impregnation materials with boric acid and borax on the surface hardness of varnished Oriental beech and oak.

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TABLE I
Some Properties of Varnishes

| Type of varnish | pH | Density (g/cm ³) | Viscosity (snDIN Cup/ 4 mm) | Amount applied (g/m ²) | Nozzle gap (mm) | Air pressure (bar) |
|-----------------------------------|------|------------------------------|-----------------------------|------------------------------------|-----------------|--------------------|
| Polyurethane (filler) | 5.94 | 0.98 | 18 | 125 | 1.8 | 2 |
| Polyurethane (finishing) | 4.01 | 0.99 | 18 | 125 | 1.8 | 2 |
| Synthetic | — | 0.94 | 18 | 100 | — | — |
| Water-based ASTM D 17 (primer) | 9.17 | 1.014 | 18 | 100 | 1.3 | 1 |
| Water-based ASTM D 65 (filler) | 9.30 | 1.015 | 18 | 67 | 1.3 | 1 |
| Water-based ASTM D 45 (finishing) | 8.71 | 1.031 | 18 | 67 | 1.3 | 1 |
| Cellulosic (filler) | 2.9 | 0.955 | 20 | 125 | 1.8 | 3 |
| Cellulosic (finishing) | 3.4 | 0.99 | 20 | 125 | 1.8 | 3 |
| Acrylic (filler) | 4.3 | 0.95 | 18 | 125 | 1.8 | 2 |
| Acrylic (finishing) | 4.6 | 0.97 | 18 | 125 | 1.8 | 2 |
| Acid hardening (finishing) | 8.0 | 0.99 | 18 | 100 | 1.8 | 3 |

EXPERIMENTAL

Materials

Wood materials

Oriental beech (*Fagus orientalis* Lipsky) and oak (*Quercus petraea* Lipsky) were chosen randomly from timber merchants of Ankara, Turkey. Special emphasis was given to the selection of the wood material. Accordingly, non-deficient, proper, knotless, normally grown wood materials (without zone lines, without reaction wood, and without decay, insect, or mushroom damage) were selected according to the TS 1476 standard.¹⁰

Varnishes

Cellulosic, synthetic, polyurethane, waterborne, acrylic, and acid hardening varnishes were used according to the producer's definition. The technical specifications of the varnishes are given in Table I.¹¹

Impregnation materials

Boric acid (H₃BO₃; composition = 56.30% ½B₂O₃ and 43.70% H₂O; molecular weight = 61.84; density = 1.435 g/cm³; molten weight = 780–815 kg/m³; mp = 171°C) and borax (Na₂B₄O₇·5H₂O; composition = 21.28% Na₂O, 47.80% B₂O₃, and 30.92% H₂O; density = 1.815 g/cm³; molecular weight = 291.35; molten weight = 980 kg/m³; mp = 741°C) were used as impregnation materials in this study and were supplied by Etibank Bandirma Borax and Acid Factories.¹²

Preparation of the test specimens

Wood samples were randomly selected from timber manufacturers of Ankara, Turkey. The rough drafts

for the preparation of test and control specimens were cut from the sapwood parts of massive woods with dimensions of 190 × 140 × 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 358.¹³ The air-dry specimens with dimensions of 150 × 100 × 10 mm³ were cut from the drafts for impregnation and varnishing. The test specimens were impregnated with 5.5% boric acid and 5% borax according to ASTM D 1413.¹⁴ Accordingly, the samples were exposed to a 700 mm/Hg⁻¹ prevacuum for 60 min and then were held in a solution under normal atmospheric pressure for 60 min for the diffusion of the impregnation material. The processes were carried out at 20 ± 2°C. The retention of the impregnation material (*R*) was calculated with the following formula:

$$R = \frac{G \cdot C}{V} 10 \quad (1)$$

where $G = T_2 - T_1$ is the amount of the impregnation solution absorbed by the specimen, T_2 is the specimen weight after the impregnation, T_1 is the specimen weight before the impregnation, C is the concentration (%) of the impregnation solution, and V is the volume of the specimen. The impregnated test specimens were kept at 20 ± 2°C and 65 ± 3% relative humidity until reaching a stable weight.¹⁵

Varnishing

Test specimens were varnished according to ASTM D 3023.¹⁶ The surfaces of the impregnated specimens were sanded with abrasive paper to remove the fiber swelling, and dust was cleaned before varnishing.

TABLE II
Surface Hardness Average Values (Swing)

| Impregnation Material | <i>x</i> | HG ^a |
|------------------------|----------|-----------------|
| Control | 81.45 | C |
| Boric acid | 91.33 | A |
| Borax | 89.48 | B |
| Varnish | <i>x</i> | HG ^b |
| Cellulose varnish | 79.77 | C |
| Synthetic varnish | 42.83 | E |
| Polyurethane varnish | 120.6 | A |
| Water-borne varnish | 70.83 | D |
| Acrylic varnish | 119.7 | A |
| Acid hardening varnish | 90.83 | B |

^a Least significant difference (LSD) = 1.132.
^b LSD = 1.602.
HG, homogeneity groups; *x*, arithmetic mean.

The producer’s definition was taken into account for the composition of the solvent and hardener ratio. One or two finishing layers were applied after the filling layer. The spray nozzle distance and pressure were adjusted according to the producer’s definition and moved in parallel to the specimen surface at a distance of 20 cm. Varnishing was performed at 20 ± 2°C and 65 ± 3% humidity.

Hardness measurements

The measurements were performed after the varnish coating; the test samples were conditioned at 23 ± 2°C and 50 ± 5% relative humidity for 16 h. The hardness measurements of the varnished surfaces were taken according to ASTM D 4366 with a pendulum damping test.¹⁷ The test device determined the layer hardness by means of the swing of a pendulum. The pendulum had marbles 5 ± 0.0005 mm in diameter with a Rockwell conventional hardness value of 63 ± 3.3. The amount of the swing was directly proportional to the surface hardness.

Data analysis

Through the use of 2 different types of wood, 2 types of impregnation specimens, 1 control specimen, and 6 types of varnishes, a total of 180 specimens (2 × 3 × 6 × 5) were prepared, with 5 specimens for each parameter. Multiple variance analysis was used to determine the differences in the surface hardness values of the specimens. A Duncan test was used to determine the significant difference between the groups.

RESULTS AND DISCUSSION

Retention

The retention of the impregnation materials according to the types of wood and impregnation materials is highest in oriental beech and boric acid (40.99 kg/

m³) and lowest in oak and borax (1.79 kg/m³). Accordingly, the types of wood and impregnation materials are important for retention.

Hardness

The average surface hardness values according to the types of varnishes and impregnation materials are given in Table II.

The impregnation materials had an increasing effect on the varnish layer hardness. According to the varnishing materials, the hardness was highest in the polyurethane varnish and lowest in the synthetic varnish. According to the impregnation materials, the hardness was highest in boric acid. The varnish layer hardness was higher in impregnated samples. Average values according to the wood material/impregnation material and impregnation material/varnishing material combinations are given in Table III.

The hardness value for the wood/impregnation material combination was highest in the oak and bo-

TABLE III
Surface Hardness Average Values According to the Wood Material Type, Impregnation Material, and Varnish Type (Swing)

| Type of material | <i>x</i> | HG |
|---|----------|----|
| Impregnation and wood materials ^a | | |
| I | 82.53 | c |
| I + Ba | 89.77 | b |
| I + Bx | 88.67 | b |
| II | 80.37 | d |
| II + Ba | 92.90 | a |
| II + Bx | 90.30 | b |
| Impregnation materials and varnishes ^b | | |
| Sv | 73.00 | j |
| Ba + Sv | 86.30 | g |
| Bx + Sv | 80.00 | h |
| Sn | 39.60 | m |
| Ba + Sn | 48.20 | l |
| Bx + Sn | 40.70 | m |
| Pu | 114.2 | c |
| Ba + Pu | 121.1 | b |
| Bx + Pu | 126.5 | a |
| Wb | 61.00 | k |
| Ba + Wb | 74.40 | ij |
| Bx + Wb | 77.10 | i |
| Ac | 110.5 | d |
| Ba + Ac | 121.0 | b |
| Bx + Ac | 127.5 | a |
| As | 90.40 | f |
| Ba + As | 97.00 | e |
| Bx + As | 85.10 | g |

Ac = acrylic varnish; As = acid hardening varnish; Ba = boric acid; Bx = borax; Pu = polyurethane varnish; Sn = synthetic varnish; Sv = cellulose varnish; Wb = water-borne varnish.

^a Least significant difference (LSD) = 1.602.
^b LSD = 2.74.
HG, homogeneity groups; *x*, arithmetic mean.

TABLE IV
Multiple Variance Analysis of the Hardness Values for the Interactions of the Wood Material Type, Varnish Type, and Impregnation Material

| Source | Degrees of freedom | Sum of squares | Mean square | F | Probability (% significance) |
|----------|--------------------|----------------|-------------|-----------|------------------------------|
| Factor A | 1 | 33.800 | 33.800 | 3.4209 | 0.0600 |
| Factor B | 5 | 134222.178 | 26844.436 | 2716.8954 | 0.0000 |
| AB | 5 | 5239.933 | 1047.987 | 106.0656 | 0.0000 |
| Factor C | 2 | 3312.744 | 1656.372 | 167.6396 | 0.0000 |
| AC | 2 | 223.900 | 111.950 | 11.3303 | 0.0000 |
| BC | 10 | 2440.189 | 244.019 | 24.6969 | 0.0000 |
| ABC | 10 | 572.367 | 57.237 | 5.7929 | 0.0000 |
| Error | 144 | 1422.800 | 9.881 | | |
| Total | 179 | 147467.911 | | | |

ric acid and lowest in the Oriental beech and borax. For the impregnation material/varnishing material combination, the hardness was highest in borax, polyurethane, and acrylic varnish and lowest in borax and synthetic varnish. The impregnation materials had an increasing impact on the varnish layer hardness in comparison with control specimens. This impact was the highest in the samples impregnated with borax.

The results of multiple variance analysis for the impact on the hardness of wood and varnishing and impregnation materials is given in Table IV.

The impact of wood, impregnation materials, and varnishing materials on the layer hardness is important for the effect of variance sources on the surface hardness ($\alpha = 0.05$). Duncan test results are given in Table V to indicate the importance of differences between the groups.

The hardness was highest in the Oriental beech and polyurethane varnish and lowest in the oak and synthetic varnish for the varnished wood materials without impregnation. For samples varnished after impregnation, the hardness was highest in the oak varnished with the acrylic varnish after impregnation with borax but lowest in the Oriental beech var-

nished with the synthetic varnish after impregnation with borax (Fig. 1).

CONCLUSIONS

The amount of retention of impregnation materials according to the wood and impregnation materials is highest in Oriental beech and boric acid and lowest in oak and borax. The higher amount of retention with boric acid may depend on the higher concentration of the solution. This provides advantages for applications requiring high retention values. On the other hand, higher retention values in oriental beech than in oak may depend on the tyloses formation in oak wood.

The layer thickness was 78 μm in the cellulose varnish, 92 μm in the synthetic varnish, 120 μm in the polyurethane varnish, 66 μm in the waterborne varnish, 128 μm in the acrylic varnish, and 100 μm in the acid hardening varnish. The differences between the varnish layers may have depended on the different solid materials.

The hardness value was highest in boric acid and polyurethane and acrylic varnishes and lowest in bo-

TABLE V
Duncan Test Results (Swing)

| Process type | x | HG ^a | Process type | x | HG ^a | Process type | x | HG ^a |
|--------------|-------|-----------------|--------------|-------|-----------------|--------------|------|-----------------|
| II + Bx + Ac | 131.4 | a | II + Pu | 108 | g | I + Bx + As | 74 | n |
| I + Bx + Pu | 128 | ab | II + As | 101.8 | h | II + Ba + Wb | 73.8 | n |
| II + Bx + Pu | 125 | bc | II + Bx + As | 96.2 | i | II + Sv | 69.8 | o |
| II + Ba + Ac | 124 | bcd | I + Ba + Sv | 90.60 | j | II + Bx + Wb | 69.6 | o |
| I + Ba + Pu | 123.8 | bcd | I + Ba + As | 85.20 | k | I + Wb | 64.4 | p |
| I + Bx + Ac | 123.6 | cd | I + Bx + Wb | 84.6 | k | II + Wb | 57.6 | q |
| I + Pu | 120.4 | de | I + Bx + Sv | 84.2 | k | II + Ba + Sn | 50.4 | r |
| II + Ba + Pu | 118.4 | e | II + Ba + Sv | 82 | kl | I + Ba + Sn | 46 | s |
| I + Ba + Ac | 118 | e | I + As | 79 | lm | II + Bx + Sn | 43.8 | s |
| I + Ac | 112.6 | f | I + Sv | 76.2 | mn | I + Sn | 42.6 | s |
| II + Ba + As | 108.8 | fg | II + Bx + Sv | 75.8 | mn | I + Bx + Sn | 37.6 | t |
| II + Ac | 108.4 | g | I + Ba + Wb | 75 | mn | II + Sn | 36.6 | t |

Ac = acrylic varnish; As = acid hardening varnish; Ba = boric acid; Bx = borax; Pu = polyurethane varnish; Sn = synthetic varnish; Sv = cellulose varnish; Wb = water-borne varnish.

^a Least significant difference (LSD) = 3.923.

HG, homogeneity groups; x , arithmetic mean.

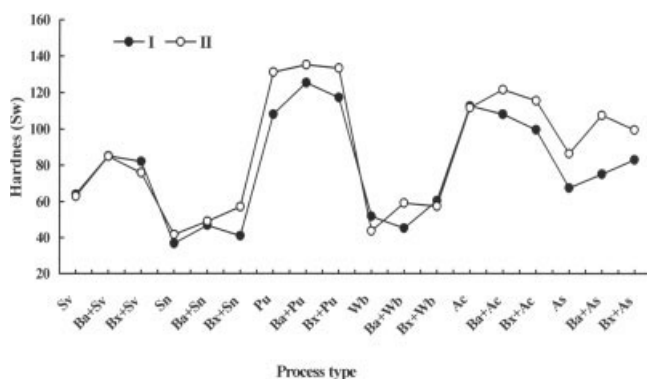


Figure 1 Hardness changes in varnished surfaces according to the type of wood and the treatment (Ac = acrylic varnish; As = acid hardening varnish; Ba = boric acid; Bx = borax; Pu = polyurethane varnish; Sn = synthetic varnish; Sv = cellulose varnish; Wb = water-borne varnish).

rax and the synthetic varnish in all types of wood. Accordingly, the wood material type is unimportant for the varnish layer hardness, but first the varnish type and second the impregnation material are important.

The hardness value in the impregnation treatment was 11% higher in boric acid and 9% higher in borax than in the control specimen. Accordingly, the impregnation materials had an increasing effect on the hardness values. This may depend on the increase in the density of the wood material because of the impregnation material. It was reported that after treatments with different impregnation materials, the density of Scotch pine increased.¹⁸ In this respect, impregnation with boron compounds provides advantages for applications for which mechanical impacts on the varnish layer occur.

The hardness value for wood and impregnation materials was highest in II and boric acid (93.27) but lowest in I and borax (80.70). The impregnation materials showed an increasing effect on the hardness values of the Oriental beech and oak at rates of 8 and 14% in boric acid and 7 and 11.5% in borax, respectively.

The hardness value according to the impregnation and varnishing material combination was highest in boric acid and the acrylic varnish (127.5) and lowest in borax and the synthetic varnish (40.70). The hardness values of varnished but unimpregnated samples were lower than those of impregnated and varnished samples. The impregnation materials showed an increasing effect in the hardness values of cellulosic, synthetic, polyurethane, waterborne, acrylic, and acid hardening varnishes at rates of 15, 8, 6, 8, and 9% in boric acid and 9, 3, 10, 11, and 14% in borax, respectively. With the acid hardening varnish, the hardness increased by 7% in boric acid but decreased by 6% in borax. The hardness value was

the lowest in the synthetic varnish. This may depend on the dried oils in the varnish compound. Accordingly, boron compounds have a positive impact on the varnish layer hardness.

The hardness value according to the wood, impregnation material, and varnishing material combination was highest in II, boric acid, and the polyurethane varnish (131.4) and lowest in I, boric acid, and the synthetic varnish (37.6). For the varnish layer hardness, the impregnation material and varnish type were effective in addition to the wood type, but the impregnation material and varnishing material were the main sources of this effect. In industry, boron compounds are being used as surface-hardening materials in metals.

As a result, boron compounds have a higher capacity for reactions, creating cross and chemical bonds with wood and varnishing materials. These chemical bonds somehow transfer the hardness of boron compounds to varnishing materials.

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