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The Effects of Industrial-Scale Heat Treatment and Impregnation with Boron Compounds on Water Uptake and Tangential Swelling of Some Wood Species

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The Effects of Industrial-Scale Heat Treatment and Impregnation with Boron Compounds on Water Uptake and Tangential Swelling of Some Wood Species

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ABSTRACT

This study evaluated the effects of boron impregnation and heat treatment on water uptake and tangential swelling of spruce (*Picea orientalis*), pine (*Pinus nigra)*, beech (*Fagus orientalis*) and poplar (*Populus deltoides*) wood species. The samples (10 x 5 x 40 - tangential x radial x longitudinal cm) were impregnated with 4 % boric acid and 4 % borax according to the ASTM D-1413 standard method. After the impregnation, heat treatment was applied on the impregnated test samples in an industrial plant, at four different temperatures and two different durations under steam atmosphere. Soft wood and hard wood samples were subjected to the heat treatment at 212 °C - 220 °C, and at 180 °C - 190 °C, respectively, for 90 and 120 min. Heat treated and impregnated test samples were reduced smaller sizes (3 x 3 x 1.5 cm - tangential x radial x longitudinal) for water uptake and tangential swelling tests. The tests were carried out based on TS 2472.

Results indicated that the highest retension was 26.9 kg/m^3 in pine wood samples impregnated with BA (26.93 kg/m^3). Hardwood retention was lower than soft wood retention. In generally, water uptake and tangential swelling ratios of only heated samples was found lower than non-treated control samples.The combination of heat treatment and BX impregnation was negatively affected water uptake especially in spruce and poplar wood. Borax was more hygroscopic than boric acid. The tangential swelling rates of four wood species impregnated with boric acid and borax were found lower than the non-treated control samples. The tangential swelling rates of spruce and pine wood samples impregnated with boric acid decreased compared to the only heated samples. Heat treatment process significantly affected the remaining boron compounds in wood. Although the steam atmosphere in the oven during the heat treatment, the amount of boron leached from wood was low especially in BX treatment.

Key words: Boron compounds, heat treatment; impregnation, tangential swelling, water uptake

1. INTRODUCTION

Wood, which is originally a hydrophilic material, becomes hydrophobic after heat treatment. Heat treatment of wood at high temperatures is one of the wood modification methods to improve the dimensional stability and biological resistance of wood. The number of water hydrophilic sites of wood decreased by heat treatment and the treated wood becomes less hygroscopic. Thus, water uptake and tangential swelling of heat treated wood are decreased (Kartal *et al*. 2007).

Heat treatment causes significant changes at the chemical structure of the wood material. The change in properties is mainly caused by thermal degrading of amorphous carbohydrates. Theoretically, the available OH groups in hemicelluloses have the most significant effect on the physical properties of wood (Gunduz and Aydemir 2008).

During the heat treatment, the number of hydrophilic OH groups is decreased and replaced by hydrophobic O-acetyl groups. The latter creates cross-links between wood fibers and thus it significantly reduces the ability of the water to penetrate into the wood (Awoyemi *et al*. 2009, Poncsak *et al*. 2006). As a result of physical changes in wood material there would be reduction at the equilibrium moisture content in hygroscopicity (Awoyemi 2009).

For many years boron compounds have long been used as wood preservatives as fungicide and insecticide, relatively inexpensive and environmentally acceptable (Kartal *et al*. 2007, Thevenon *et al*. 2010). Boron-based buffers have also been used as additives in fire-retardant treatments and have been found to significantly reduce the severity of thermal degradation (Kartal *et al*. 2007). The hygroscopic nature of some boron salts may adversely affect the dimensional stability of wood under humid service conditions and may cause strength losses at high loading levels. The future of boron preservatives largely depends on enhancing their stability in wood in outdoor conditions and limits some adverse effects of boron on wood properties by supplemental treatments (Tomak *et al*. 2011, Yalınkılıç 2000, Baysal *et al*. 2006, Baysal *et al*. 2007).

The effect of impregnation treatment with boron compounds on the physical, mechanical and biological characteristics of wood material is investigated by many researchers. However, their use is limited due to its diffusibility and susceptibility to leaching. The present study examines the effects of industrial-scale heat treatment and impregnation with boron compounds on some physical properties (water uptake, tangential swelling) of spruce, pine, beech and poplar wood species.

2. EXPERIMENTAL METHODS

Raw material spruce (*Picea orientalis*), pine (*Pinus nigra)*, beech (*Fagus orientalis*) and poplar (*Populus deltoides*) wood was obtained from Black Sea Region in Turkey. The wood was cut in parallel to grain directions and sawn into specimens measuring 10 x 5 x 40 (tangential x radial x longitudinal) cm. The first part of each wood samples was impregnated with boron compounds before heat treatment whereas the other part of each wood sample was heat treated without any boron impregnation. The samples were impregnated with 4 % boric acid and 4 % borax according to the ASTM D-1413 (1976) standard method. Pine (*Pinus nigra)*, beech (*Fagus orientalis*) and poplar (*Populus *deltoides*) wood specimes treated at 600mm-Hg vacuum for 20 min. and a pressure of 5 bar for 60 min. Spruce (*Picea orientalis*) wood samples treated at 750mm-Hg vacuum for 30 min and a pressure of 5 bar for 90 min. at room temperature. The retention content for each treatment was calculated following formula (Eq.1);

$$R\ (Kg / m^3) = [G*C / V] *10 \quad (1)$$

Where;

G: (T2-T1) is the grams of treating solution absorbed by the block (initial weight of block subtracted from the initial weight plus the treating solution absorbed); C is the grams of chemical solution in 100 g of the treating solution; and V is the volume of block in cubic centimeters.

After the impregnation, the heat treatment was applied on the impregnated test samples in an industrial plant, at four different temperatures and two different durations under steam atmosphere. Soft wood and hard wood samples were subjected to the heat treatment at 212 °C - 220 °C, and at 180 °C - 190 °C, respectively, for 90 and 120 min. Two different control groups were used in the study: 1) non-heated and non-impregnated group (control-1) and 2) only heated group (control 2). After heat treatment and boron impregnations, samples treated by large-dimensions were reduced small size (3 x 3 x 1.5 cm – tangential x radial x longitudinal) to identify water uptake and tangential swelling of the samples. The tests were carried out based on TS 2472 (2005), (Can 2011).

Boron content of both heated and unheated wood samples was measured using Inductively Coupled Plasma (ICP) analysis, using an ICP spectrometer (ICP-AES, Spectro Genesis). Sample preparation was done according to AWPA A7-93 (1993). Wood samples for the ICP analysis were prepared by grinding in a Wiley mill with a mesh size of 0.5 mm (IKA MF10, IKA-Werke, Staufen, Germany) followed by oven drying at 103 ± 2ºC. One gram of ground wood was weighed to the nearest 0.01g and placed in a 100 ml flask. Nitric acid (65%) was then added to the flask, which was placed on a hot plate. After the evolution of brown fumes had ceased, hydrogen peroxide (30%) was added dropwise to clear the solution. After cooling, the contents in the flask were filtered through Whatman #4 filter paper and were diluted with distilled water for measurement. For each treatment, two replicate samples were ground and analyzed.

3. RESULT AND DISCUSSION

3.1. Retention

Retention contens of the four different wood samples are shown in Table 1. In spruce wood samples; retention ratios of BA (23.99 kg/m^3) and BX (25.58 kg/m^3) impregnations were similar to each other. The highest retension was 26.9 kg/m^3 in pine wood samples impregnated with BA (26.93 kg/m^3). Hard wood retention rate was lower than the soft wood. Nearly, 20-21 kg/m^3 retention was obtained from BA and BX impregnations in beech wood samples. The lowest retention contents were seen in poplar wood samples (14.82-15.97 kg/m^3).

Kartal (2006) obtained approximately 39.7 and 40.5 kg/m3 retention by treating sugi sapwood with 5% BA and di-sodium octoborate tetrahydrate (DOT) with the vacuum impregnation.

Table 1: Retention of the samples (kg/m^3)

Wood species	Chemical Substance	Retention [kg/m^3]	Standart deviation
Spruce	BA	23.99	0.74
	BX	25.58	0.05
Pine	BA	26.93	1.98
	BX	24.30	0.42
Beech	BA	20.09	0.77
	BX	20.70	0.56
Poplar	BA	14.82	0.62
	BX	15,97	0.69

3.2. Boron Analysis of Treated Wood

Table 2 shows the amount of BA and BX remaining in heat treated samples. According to the Table 2, remaining amount of boron in the wood species was generally high. BX significantly remained in spruce and pine wood samples, while a significant portion of BA removed from wood during the heat treatment process. Borax was more effective than the boric acid. BX less moved away from wood compared to the boric acid except for poplar wood. This might be due to the different characteristics and leaching properties of the chemicals. Kartal (2006) combined boron and heat treatment as a dual treatment to delay the boron leaching from wood and, stated that heat treatment had no effect on boron release.

As it is well known, boron compounds can easily be leached out from wood when they exposed to steam or water. Although the steam atmosphere in the oven during the heat treatment, the amount of boron leached from wood was low especially in BX treatment. So, heat treatment can be evaluated as one of the approaches to reducing boron leaching.

Table 2: Amount of BA and BX remaining in heat treated samples (%)

Wood Species	Remaining [%]	
	BA	BX
Spruce	37	63
Pine	40	80
Beech	68	95
Poplar	98	83

3.3. Water Uptake

Average water uptake ratios of the test, control 2 and control 1 samples are given in Fig. 1-4, for all wood species.

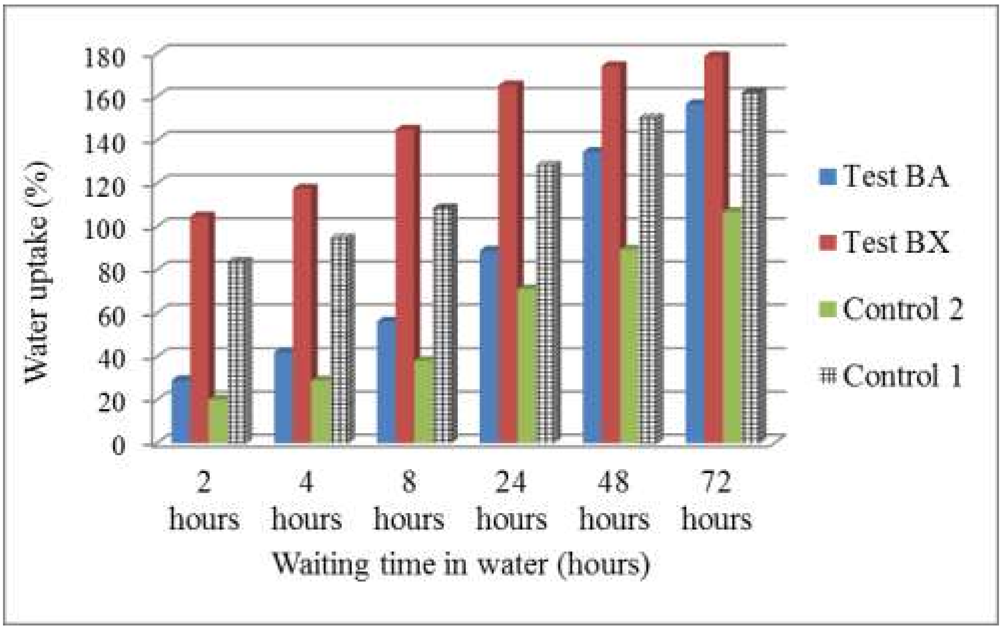

Figure 1: Water uptake ratios of spruce samples were subjected to the heat treatment at 212°C for 120 min.

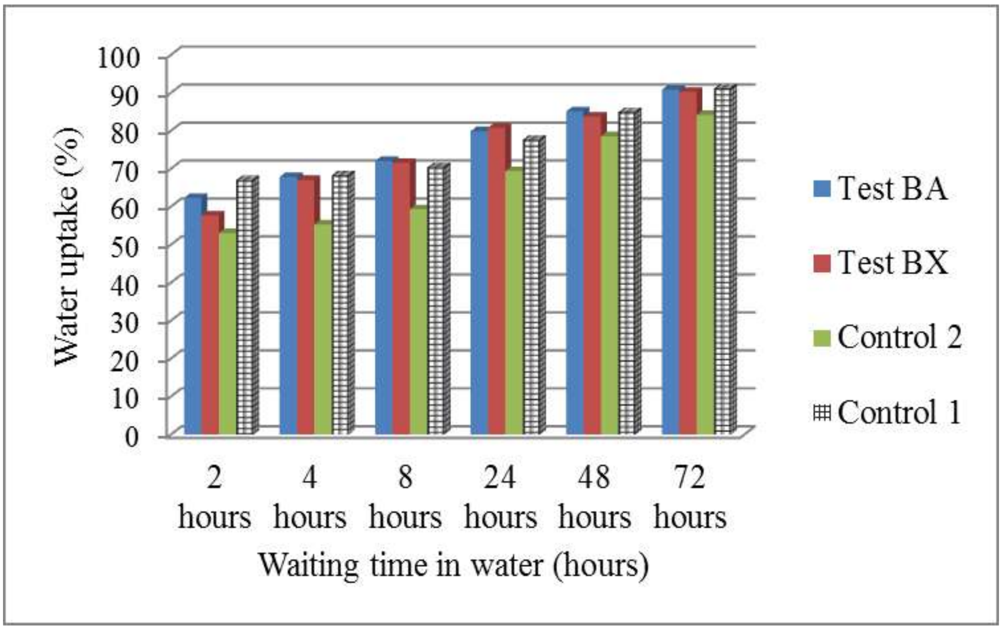

Figure 2: Water uptake ratios of pine samples were subjected to the heat treatment at 212 °C, for 120 min.

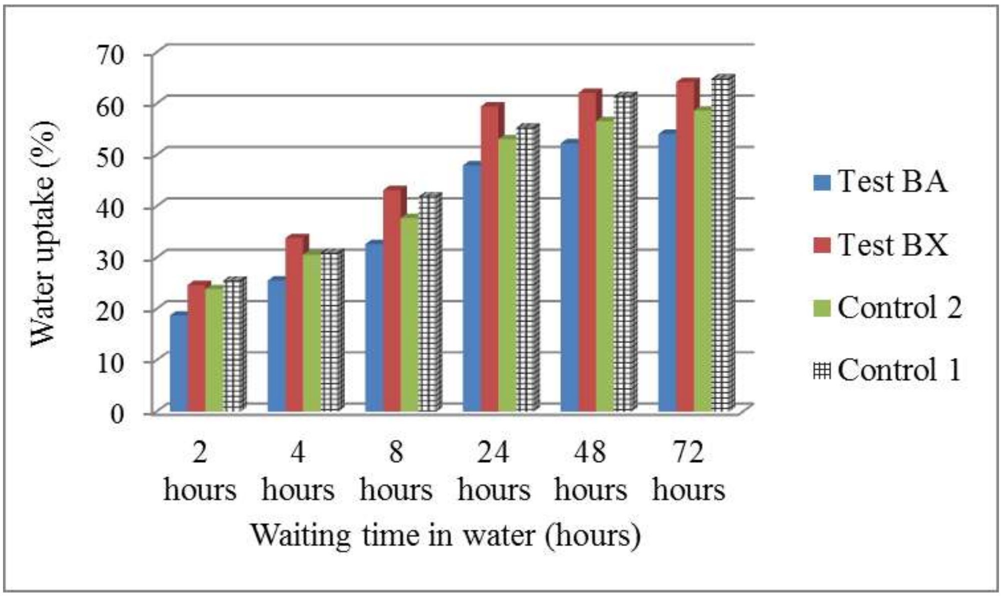

Figure 3: Water uptake ratios of beech samples were subjected to the heat treatment at 180 °C, for 120 min

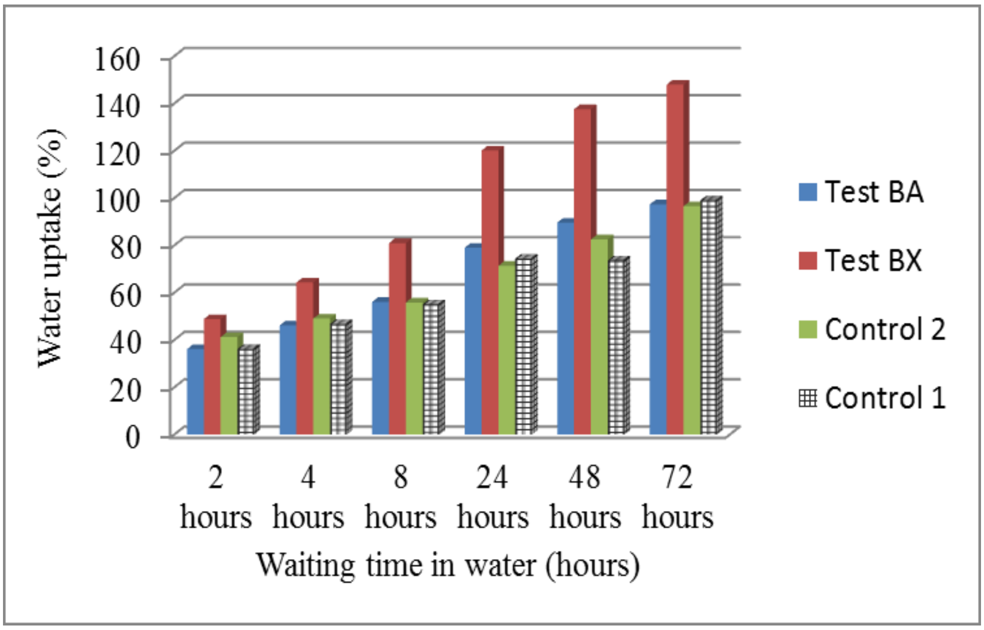

Figure 4: Water uptake ratios of poplar samples were subjected to the heat treatment at 180 °C, for 120 min.

As can be seen in figure 1-4, the water uptake was found lower for control 2 than control 1, from 2 hours to 72 hours for all wood species. The most obvious difference between control 1 and 2 was observed in spruce wood samples.

Results of the study shows that heat treatment were affected to the reduction of water uptake of heat treated samples. The water uptake ratios of untreated spruce, pine, beech and poplar samples wich were 161%, 91%, 64% and 98% was reduced 97%, 90%, 58% and 86% respectively, at the and of the 72 hours, after heat treatment. Tjeerdsma (2005) revealed that heat treatment reduced water absorption of oil heat treated spruce wood.

Water uptake of the samples which impregnated with boric acid and borax had nearly equivalent water uptake of the control 1 samples even in the first two hours due to the hygroscopic structure of boron compounds. Although the heat treatment provides water repellency in wood, boron compounds can affect water uptake by hygroscopic nature (Kartal *et al*. 2007). The absorbed water rate of the samples impregnated with BX was more than the control 1 sample for spuce and poplar wood within the all periods of 2 hours to 72 hours. When it's looked at to water uptake of the pine samples, it can be said that the difference between the test variations unable to change the amount of water intake too much. This difference was observed especially in spruce and poplar test samples. In generally (except for pine), the water uptake ratios of the samples impregnated with BX was found higher than impregnated with BA. Being more clearly in spruce and poplar wood samples, it's found that water uptake of the samples impregnated with BX was higher than the samples impregnated with boric acid. Poplar wood samples impregnated with BX was absorbed more water than impregnated with BA compared to the control 1 and control 2 (Fig. 4). This situation can be attributed that the different structure of boric acid and borax chemicals. Additionally, because of boric acid easily moved away from the wood, provided better performance in terms of water uptake. However, the samples impregnated with borax had greater values of water uptake because of the amount of borax leached from wood was little (Table 2).

A study by Kartal *et al*. (2007) reported that in the DOT (disodium ocatborate tetrahydrate;a mixture of borax and boric acid) treatments, the specimens at 180 C for 4 h showed slightly less water absorption than the boric acid treated ones. Toker (2007) also reported that borax treated wood exhibited greater hygroscopicity than boric acid treated material.

In a study, at the end of 72-hour period, it was found that amount of water uptake of soft wood was higher than the water uptake of hard wood (%95, %79). The lowest water uptake was seen in beech wood, the highest water uptake was achieved in spruce wood samples. After heat treatment, knots are separated from wood and annual ring structure is relaxed. In this case, after heat treatment of spruce wood is composed of some structural gaps. Hence, water absorption rate of spruce wood increased to some extent (Fojutowski *et al*. 2009, Yildiz, 2002). Soft wood cellulose has lower thermal stability than hard wood cellulose and have been reported broken down at temperature above 150 ºC (Feist and Sell 1987).

3.4. Tangential Swelling

Tangential swelling ratios of the test, control 2 and control 1 samples for each wood species are given in Fig. 5.

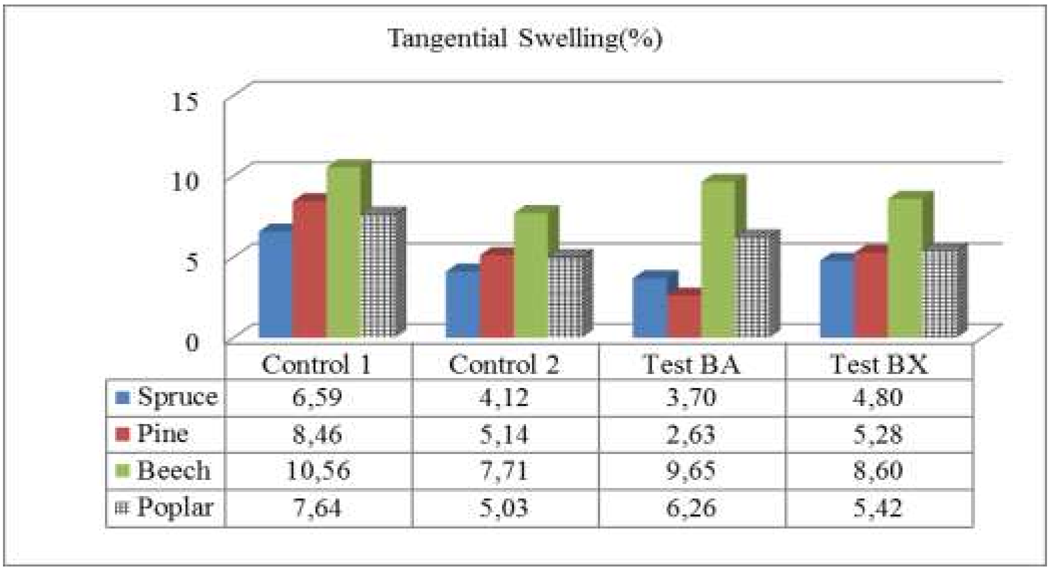

Figure: 5 Tangential swelling ratio of spruce, pine, beech and poplar (%)

As can be seen in Fig. 5; tangential swelling of untreated spruce, pine, beech and poplar samples wich were 6.59%, 8.46%, 10.56%, and 7.64 was reduced 4.12%, 5.14%, 7.71% and 5.03% respectively, after heat treatment. Heat treatment significantly reduces the tangential swelling of wood and provides dimensional stabilization to it (Yildiz 2002). Gündüz and Aydemir (2008) found that heat treatment at 200 ºC in 2, 4, 6, 8 and 12 hours significantly reduce the tangential, radial and longitudinal swelling. The effect of heat treatment in terms of reduced swelling and shrinkage of wood was clearly.

Maximum tangential swelling ratios in control 1 samples was seen in beech wood (10.56%). The tangential swelling ratios in contol 2 samples was found lower than the tangential swelling ratios in contol 1. After the heat treatment, the tangential swelling ratios of spruce, pine, beech and poplar wood samples improved by 38%, 39%, 27% and 35%, respectively compared to the control 1.

The lowest tangential swelling ratios in contol 2 was seen in spruce wood (4.12%). The tangential swelling of the test samples were lower than the control 1. While the highest tangential swelling of the test samples were obtained from beech wood (9.65), lowest tangential swelling was obtained from pine wood (2.63) in boric acid impregnation. In spuce and pine wood samples, tangential swelling ratio of BX impregnation was higher than the BA impregnation. This might be due to more hydrophobic nature of borax compared to boric acid. When compared on the basis of the amount of boron remaining in the wood (Table 2); since the amount of BX leached from wood was little, BA showed a better performance than the BX in terms of the tangential swelling ratios. After the BA impregnation, the tangential swelling ratios of heated spruce and pine samples improved by 44% and 69%, respectively compared to the control 1.

Kartal *et al*. (2007) reported that water absorption of the wood specimens treated with boron compounds followed by heat treatment increased more than those of the only heat treated ones. Accordingly, boron compounds may affect the water absorption of heat treated wood in spite of hydrophobication provided by heat treatment. Bazyar *et al*. (2010) noted that radial, tangential and volumetric swelling of control samples were decreased 4.39%, 8.99% and 12.95% percent respectively while have 2.99%, 6.98% and 9.8% percent of heat treated samples

The heat treatment provides the dimensional stability and for this reason, tangential swelling is decreases. At the study reported by Ghalehno (2011), has found a decrease of 40% tangenteil swelling and 37,15% of radial expansion compared to control after heat treatment (190 ºC-9 hours) (Ghalehno 2011). Gunduz *et al*. (2009), reported that heat treatment reduces the tangential swelling by 2,6% with 180 ºC for 10 hours and wild pear (*Pyrus elaeagnifolia*) wood species.

4. CONCLUSIONS

The effects of industrial-scale heat treatment and impregnation with boron compounds on some physical properties of spruce, pine, beech and poplar were investigated.

Results indicated that the highest retension was 26.9 kg/m^3 in pine wood samples impregnated with BA (26.93 kg/m^3). Hardwood retention was lower than soft wood retention. In generally, water uptake and tangential swelling ratios of only heated samples was found lower than non-treated control samples.The combination of heat treatment and BX impregnation was negatively affected water uptake especially in spruce and poplar wood. Borax was more hygroscopic than boric acid. The tangential swelling rates of four wood species impregnated with boric acid and borax were found lower than the non-treated control samples. The tangential swelling rates of spruce and pine wood samples impregnated with boric acid decreased compared to the only heated samples. Heat treatment process significantly affected the remaining boron compounds in wood. Although the steam atmosphere in the oven during the heat treatment, the amount of boron leached from wood was low especially in BX treatment.

Heat treatment process significantly affected the remaining boron compounds in wood. Although the steam atmosphere in the oven during the heat treatment, the amount of boron leached from wood was low especially in BX treatment. Chemical structure of boron compound affects the amount of boron remaining in wood. Therefore there is need to investigate boron remaining in wood after heat treatment with different heat treatment parameters and different boron compounds.

5. REFERENCES

ASTM-D 1413-76 (1976): Standard Method of Testing Wood Preservatives By Laboratory Soil block Cultures.

AWPA A7-93 (1993): Standard for Wet Ashing Procedures for Preparing Wood for Chemical Analysis, American Wood Preservers' Association Standard.

Awoyemi, L (2009): Differential response of Heartwood and Sapwood to Heat Treatment. *The Journal of the Institute of Wood Science vol*. 19. The Wood Technology Society of the Institute of Materials, Minerals and Mining.

Awoyemi, ., Jarvis, M C, Hapca, A (2009): Effects of preboiling on the acidity and strength properties of heat-treated wood. *Wood Science and Technology,* **43**:97–103.

Baysal, E, Sonmez, A, Colak, M, Toker, H (2006). "Amount of leachant and water absorption levels of wood treated with borates and water repellents". *Bioresource Technology,* **97 (18):** 2271-2279.

Baysal E, Yalinkilic, M K., Altinok, M, Sönmez, A, Peker, H, Çolak, M (2007). Some physical, wood polymer biological, mechanical, and fire properties of composite (WPC) pretreated with boric acid and borax mixture. *Construction and Building Materials*, **21(9)**: 1879-1885.

Bazyar, B, Parsapajouh, D, Khademieslam, H (2010): An Investigation on Some Physical Properties of Oil Heat Treated Poplar Wood. *41st IRG Annual Meeting*, France.

Can, A, (2011): The effects of Industrial-Scale Heat Treatment and Impregnation with Boron Compounds on Some Physical, Mechanical and Biological Properties of Wood. Karadeniz Technical University, M.Sc. Thesis, Trabzon, Turkey.

Feist, W C., Sell, J (1987): Weathering Behavior of Dimensionally Stabilized Wood Treated by Heating under Pressure of Nitrogen Gas, *Wood and Fiber Science*, **19(2)**: 185-195.

Fojutowski, A, Kropacz, A, Noskowiak, A (2009): The Resistance of Thermo-Oil Modified wood Against Decay and Mould Fungi. *40th IRG Annual Meeting*, China.

Ghalehno, D M (2011): Changes in the Physical and Mechanical Properties of Iranian Hornbeam Wood (*Carpinus betulus*) with Heat Treatment. *European Journal of Scientific Research*, **51(4)**: 490-498.

Gunduz, G, and Aydemir, D (2008): The Effect of Heat Treatment on Water Absorption and Dimensional Stability of Anatolian Chestnut (*Castanea sativa* Mill.) Wood. *39th IRG Annual Meeting* İstanbul, Turkey.

Gündüz, G, Aydemir, D, Karakaş, G (2009): The effects of thermal treatment on the mechanical properties of wild Pear (Pyrus elaeagnifolia Pall.) wood and changes in physical properties. *Materials and Design* **30**: 4391–4395.

Kartal, S N (2006): Combined Effect of Boron Compounds and Heat Treatments on Wood Properties: Boron Release and Decay and Termite Resistance, *Holzforschung*, **60**: 455– 458.

Kartal, S N, Hwang, W J, Imamura, Y (2007): Water Absorption of Boron-Treated and Heat-Modified Wood. *Wood Science and Technology,* **53**: 454-457.

Poncsak, S, Kocaefe, D, Bouazara, M, Pichette, A (2006): Effect of High Temperature Treatmenton the Mechanical Properties of Birch (*Betula papyrifera*). *Wood Science and Technology,* **40**: 647-663.

Tjeerdsma, B, Militz,H (2005): Chemical Changes in Hydroheat Wood: FTIR Analysis of Combined Hydroheat and Dry Heat-Treated Wood.*Holz als Roh und Werkstoff*, **63**:102-111.

Thevenon, M F, Tondi, G, Pizzi, A (2010): Environmentally friendly wood preservative system based on polymerized tannin resin-borix acid for outdoor appliations. Maderas. Ciencia y Tecnologia*, 12 (3): 253-257.*

Toker, H (2007): The Effects of Boron Compounds on the Properties of Physical, Mechanical and Biological of Wood. PhD Thesis, Gazi University, Ankara, Turkey.

Tomak, E D, Viitanen, H, Yıldız, Ü C, Hughes, M (2011): The combined effects of boron and oil heat treatment on the properties of beech and Scots pine wood. Part 2: Water absorption, compression strength, color changes, and decay resistance. *Journal of Material Science*, **46**:608–615.

TS 2472. (2005): Wood - Determination of Density for Physical and Mechanical Tests, Turkish Standard.

Welzbacher, C R, Rapp, A O (2002): Comparison of Thermally Modified Wood Originating from four Industrial Scale Processes – durability. *39rd IRG Annual Meeting* Cardiff, Wales.

Yalinkilic, M K (2000): Improvement of boron immobility in the borate treated wood and composite materials. PhD Thesis, Kyoto University, p 151.

Yildiz, S (2002): Physical, mechanical, Technological and Chemical Properties of *Fagus orientalis* and *Picea orientalis* Wood Treated by Heat, PhD Thesis, Karadeniz Technical University, Trabzon, Turkey, p: 245.