POLİTEKNİK DERGİSİ

JOURNAL of POLYTECHNIC

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)
URL: http://dergipark.org.tr/politeknik

The effects of some antibacterial nano materials on varnish layer hardness

Bazı antibakteriyel nano malzemelerin vernik katman sertliğine etkileri

***Yazar(lar) (Author(s))**: Cansu ÖZDER[1], Musa ATAR[2]*

ORCID[1]: 0000-0002-9577-0571

ORCID[2]: 0000-0002-3944-5512

To cite to this article: Özder C., Atar M., "The effects of some antibacterial nano materials on varnish layer hardness", ***Journal of Polytechnic***, 26(4): 1705-1714, (2023).

Bu makaleye şu şekilde atıfta bulunabilirsiniz: Özder C., Atar M., "The effects of some antibacterial nano materials on varnish layer hardness", ***Politeknik Dergisi***, 26(4): 1705-1714, (2023).

Erişim linki (To link to this article): http://dergipark.org.tr/politeknik/archive

DOI: 10.2339/politeknik.1325355

The Effects of Some Antibacterial Nano Materials on Varnish Layer Hardness

Bazı Antibakteriyel Nano Malzemelerin Vernik Katman Sertliğine Etkileri

Highlights

- *The effect of some antibacterial nano materials and varnishes on the hardness of wood material*
- *As a result, it has been determined that nano materials reduce the varnish hardness in the binary interactions of wood and varnish type and % ratios of nano materials*
- *In the multiple interaction, the highest hardness value was found in Oriental beech+synthetic varnish+0,1% nano boron (28,00) and least Scotch pine+synthetic varnish+0,3% nano silver (11,20).*

Graphical Abstract

According to the coaction of wood and varnish type, nano material, nanomaterial % ratios, it can be said that 1st degree wood species, 2nd degree varnish type, 3rd degree nano material, 4th degree nanomaterials % ratios are effective in hardness value.

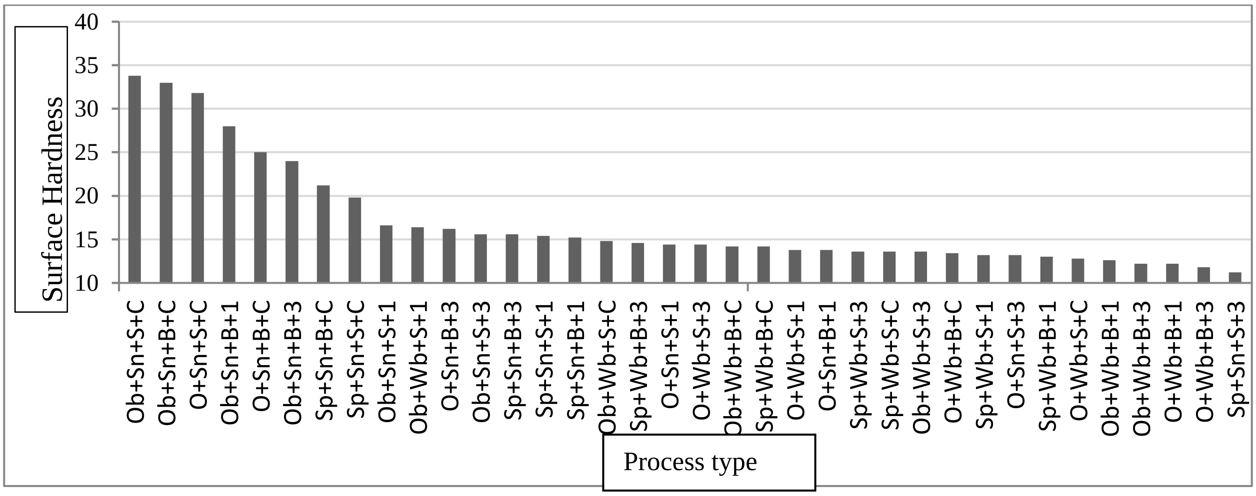

Figure. *Hardness value changes according to the process type*

Aim

To provide the hardness effect in the surface Treatment of wood material by using varnish and some nano materials

Design & Methodology

The samples were obtained by preparing the sapwood part of the wood material according to TS 1476.

Originality

The effect of wood material on hardness value in surface treatment with different nano materials and varnishes.

Findings

It can be said that the first degree wood type, second degree varnish type, third degree nano material, fourth degree nano material % ratios are effective on the varnish hardness layer values of nano materials.

Conclusion

It can be said that nano materials have a reducing effect on varnish hardness.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

The Effects of Some Antibacterial Nano Materials on Varnish Layer Hardness

Araştırma Makalesi/Research Article

Cansu ÖZDER[1*], Musa ATAR[2]

[1]Gazi University, Natural and Applied Science Institude, 06500 Ankara, Turkey
[2]Gazi University, Faculty of Technology, Department of Forestry Industrial Engineering, 06500 Ankara, Turkey

(Geliş/Received : 10.07.2023 ; Kabul/Accepted : 10.08.2023 ; Erken Görünüm/Early View : 04.09.2023)

ABSTRACT

In this study, it was researched the effect of some antibacterial nanomaterial added varnishes on the layer hardness of wood. Samples prepared from Scots pine (Pinus sylvestris L), Oriental beech (Fagus orientalis Lipsky), Sapless oak (Quercus petraea Liebl.) were mixed with 0.1%, 0.3% nano boron (NaB) and nano silver (NaAg), it is varnished with water based and synthetic varnish according to ASTM-D 3023. After varnishing, the surface hardness (oscillation) of the samples was made according to ASTM D 4366-95.

As a result; in terms of material type, the highest surface hardness value was determined in Oriental beech, synthetic varnish, nano boron and 0.1% and the lowest in Scotch pine, water based varnish, nano silver and 0.3%. In the multiple interaction, peak Oriental beech+ synthetic varnish+0.1% nano boron (28.00) and least Scotch pine+ synthetic varnish+0.3% nano silver (11.20) were obtained. Compared to the control samples, it was detected nanomaterials had a reducing impact on surface hardness of the varnishes. This may be advantage to consider in application areas where varnish hardness is important.

New ideas will emerge with the use of nanomaterials with high antibacterial properties in wood surface treatments and it will provide advantages in usage areas with high risk of abrasion.

Key Words: Wood material, hardness, varnish, nano boron, nano silver, modification.

Bazı Antibakteriyel Nano Malzemelerin Vernik Katman Sertliğine Etkileri

ÖZ

Bu çalışmada, bazı antibakteriyel nano malzeme katkılı verniklerin ahşap malzemede katman sertliğine etkisi araştırılmıştır. Sarıçam (Pinus sylvestris L), Doğu kayını (Fagus orientalis Lipsky), sapsız meşeden (Quercus petraea Liebl.) hazırlanan örneklere, %0,1, %0,3 nano bor (NaB) ve nano gümüş (NaAg) ilave edilmiş su bazlı ve sentetik vernik ile ASTM D-3023'e göre verniklenmiştir. Vernikleme işleminden sonra örneklerin yüzey sertliği (salınım) ASTM D 4366-95'e uyularak yapılmıştır.

Sonuç olarak; yüzey sertlik değeri malzeme çeşidi bakımından en yüksek, Doğu kayını, sentetik vernik, nano bor ve %0,1'de, en düşük sarıçam, su bazlı vernik, nano gümüş ve %0,3'de tespit edilmiştir. Çoklu etkileşimde en yüksek Doğu kayını+sentetik vernik+%0,1 nano bor (28,00)'de, en düşük sarıçam+sentetik vernik+%0,3 nano gümüş (11,20)'de elde edilmiştir. Kontrol örneklerine göre, nano malzemeler verniklerin yüzey sertliğine azaltıcı etki gösterdiği tespit edilmiştir. Bu durum, vernik sertliğinin önemli olduğu uygulama alanlarında dikkate alınması avantaj sağlayabilir. Antibakteriyel özelliği yüksek olan nano malzemelerin ahşap üst yüzey işlemlerinde kullanılması ile yeni fikirler ortaya çıkacak ve aşınma riski yüksek olan kullanım alanlarında avantaj sağlayacaktır.

Anahtar Kelimeler: Ahşap malzeme, sertlik, vernik, nano bor, nano gümüş, modifikasyon.

1. INTRODUCTION

Wood is an organic material available from nature. Although there are many alternative materials to wood, it is preferred for natural, processable, etc. or its properties. Because it is natural, it causes deformation by some external factors. For this reason, it is necessary to carry out protective processes on wood based products. Especially these processes are processes such as varnishing and impregnation. Nowadays, wooden surfaces are coated with nano technological chemicals and modified products. Nanotechnology enters our lives in different fields. These fields are especially informatics and communication, defense industry, aerospace and aircraft technologies, molecular biology [1,2]. Thanks to the developments in nanotechnology, new materials can be produced or the properties of existing materials can be improved. Nanomaterial technology, as in many areas, has been used in wood materials, chemicals and varnishes used for protection purposes, as well as in order to gain some additional and new features in processes etc.

Nowadays, one of the main uses of nanomaterials is antibacterial properties. In order to prevent the transmission of diseases in social areas such as hospitals, schools, benches, etc. and to improve the antibacterial qualities of the wooden works used in these places, it is tried to be protected by adding varnishes used in the surface treatment. For this

**Sorumlu Yazar (Corresponding Author)*
e-posta : cansuozder1@gmail.com

purpose, mostly Nano boron and Nano silver are used in certain proportions. The use of these materials is important in terms of the use of nano materials to determine the effect on other properties of varnishes such as hardness, gloss, etc. It will be understood through these tests that there is no obstacle that prevents the varnish from fulfilling the duties expected. There are studies on the effects of nano-material preservatives in the protection of wood materials.

Mechanical, optical and thermal properties were determined by adding Al_2O_3 and SiO_2 nano particles into water-based polyurethane acrylate varnishes. It was found to decrease hardness test values decreased due to clumping of nano particles on the surface, and an increase in the scratch test values with the addition of nanoparticles, despite the decrease in the hardness [3].

Its production with wood material some building with furniture/decoration elements more protective layer to protect the elements surface tools are used. For long-term and efficient use of wood-based products for protection purposes needs to be done. [4,5].

In studies with varnishes with nanoparticle addition, it has been stated that nanoparticles increase the hardness and contribute to obtaining a surface that is more resistant to abrasion and scratching [6].

The properties of conventional varnishes and commercial nanolacke ultraviolet varnish on different wood species were compared. It has been stated that the gloss, scratch, hardness and adhesion properties of commercial nanolacke ultraviolet varnish are higher than conventional varnishes [7].

The use of nanotechnology can provide wood materials with features like high resistance, water resistance, thermal stability. Thus, the service life of wooden materials can be extended [8].

The effects of impregnation and lightening on the varnish layer hardness of Oriental beech wood were researched. A range of lightening complexion {[$NaOH–Ca(OH)_2–H_2O_2$], [$NaOH–H_2O_2$], [NaOH–$MgSO4–H_2O_2$], [$NaSiO_3–H_2O_2$], [$NaHSO_3–H_2C_2O_4$], [$KMnO_4 + NaHSO_3 + H_2O_2$] } was applied to Oriental beech samples at a concentration of 18% (for bleaching) in both impregnated and non-impregnated condition. Then, water-based varnish was covered on the samples and their hardness test values were identified. Surface hardness is reduced due to chemicals used for bleaching [9].

Water-based varnishes are carried out with brush, roller, blowgun on trial panels obtained from Scots pine, Oriental beech, Oak, hardness, gloss and surface adhesion strength examined. In the examinations made, the hardness, gloss, surface adhesion strength of water-based varnishes were found to be less than solvent-based varnishes, and it was reported that application differentiation did not affect the physical properties of the varnish. The highest value in hardness measurements was obtained in acrylic emulsion varnish in Oriental beech [10].

In order to improve the undesirable surface weaknesses, low abrasion and low hardness values of water-based acrylic surface coaters, nano aluminum reinforcement was made into the mixture. It was determined that OPEO and together with nano aluminum for surface modification gave the best results in the stabilization, abrasion and hardness values of the mixture when nano aluminum was added 0.6% and 3.2 wt [11].

Impact of impregnation, bleaching of oak varnished with water-based varnish was investigated and it was determined that surface hardness is reduced due to all chemicals used for bleaching [12].

The effects of synthetic, polyurethane and acrylic varnish in different layer thicknesses on the hardness, gloss and surface adhesion resistance were investigated on the test samples obtained from Oriental beech, scots pine and sessile oak wood. It has the highest hardness value made in Oriental beech wood applied with one layer of polyurethane varnish, it has least in Scots pine wood with three layers of synthetic varnish [13].

Synthetic, cellulosic, polyurethane, acid-hardened varnishes with white opaque paint were carry out to examples of Oriental beech, scots pine, oak, chestnut. After application, it was kept in open air conditions for 22 months and its effects on layer hardness were determined. As a result, there was an increase in the hardness of all varnishes except synthetic paint [14].

Nano silver has antimicrobial properties and resistance to silver against antibiotics, it has been attracting attention in science for many years because of its inability to develop it. Reducing silver to nano size bacteria and fungi further increases its impact [15].

They reported that the nanoparticles in the solution should be mixed very well so that they do not form agglomeration. They stated that when the nanoparticles added in large amounts exceed the threshold value according to the properties of the solution, there will be negative results such as aggregation, micro-cracks, and porous structure [16].

Nowadays, in order to protect against abiotic and biotic factors that damage the wood material; some studies come to the fore within the scope of wood modification such as herbal dyes with antibacterial and antifungal effects, liquid glass, paraffin, water-repellent oils, industrial wood preservatives, paints and varnishes, heat treatment (thermowood), impregnation processes [17].

So as to specified the impacts of boric acid (H_3BO_3) solution on the layer hardness value of water-based varnish, experiment examples made from Scots pine, Oriental beech and Chestnut were applied in different amounts (10%, 20%, 30%) was modified with 5% boric acid and water-based varnish was applied. Then, the hardness value on the varnished and unvarnished surfaces was determined considering ASTM D 2240 principles. Results of the research; unvarnished Oriental beech has highest hardness value [18].

The mechanical, physical specialities of scotch pine, Oriental beech woods impregnated with boron compounds were investigated. According to the results of the research; It has been reported that impregnation with boron compounds causes a reduction in bending and compressive strength, an increment in rot resistance [19].

When the effect of varnishing applied on spruce wood on brightness, hardness and color properties is examined; the highest yellow and red color value is in synthetic varnish, the lowest in polyurethane varnish; the highest gloss value was obtained in the polyurethane varnish and least in the control sample. The hardness value was the highest in polyurethane varnish [20].

Cellulosic varnish, synthetic varnish, polyurethane varnish and water-based varnish were applied to the bamboo wood material. Hardness, gloss, color change and layer thickness measurements were made on the test specimens with surface treatments. According to the data obtained, the surface hardness values of the varnishes other than the polyurethane varnish in the surface hardness measurements decreased compared to the control sample [21].

One and two component water solvent varnishes were applied to the wood surfaces of Scots pine (Pinus silvestris L.), beech (Fagus orientalis L.) and oak (Qercus petreae L.) with a brush, sponge roller and spray gun. As a result, it was determined that the application method variation was not effective on the hardness values of the varnish layers with water solvent [22].

It was investigated surface gloss, roughness, hardness, color change and adhesion resistance properties of beech wood applied with nano-graphene (NG) modified water-based varnish. The varnish solution was applied to the sample surfaces and 0.25%, 0.5% and 1% by weight of NG was added to the water-based varnish. As a result, the surface hardness value of the samples increased. Depending on the increase in the amount of NG added to the varnish, the surface gloss values of the samples decreased and significant increases up to 25% were achieved in the varnish adhesion resistance [23].

The purpose of study was to stated the effects of wood material nano boron (NB), nano silver (NaAg) and varnishes on the varnish layer hardness.

2. MATERIAL and METHOD

2.1. Wood material

As test sample in the study; Scotch pine (Pinus sylvestris L), Oriental beech (Fagus Orientalis Lipsky) and Sapless Oak (Quercus Petraea Liebl.) woods were selected. Wood materials were got from the timber operations in Ankara in accordance with the principles of ISO3129. In the selection of wood material, care was taken to ensure that the fibers were smooth, knot-free, tangle-free and not exposed to fungi and insect pests [24].

2.2. Varnishes

Water-based (Wb), synthetic (Sn) varnishes were made in the varnishing of the examples. In determining quantity of varnish to be applied, the amount of solid matter and the producers advices were taken into account. Speaciality of the varnishes used in the trials are given below.

2.2.1. Water-based Varnish

Water-based varnishes are produced from synthetic resins such as alkyd, acrylic and polyurethane that can be thinned with water, mixed with water [25]. Terms of use of the varnish used in the study; drying time is at 20°C and 40-65% relative humidity. It is dry to the touch in 30 minutes, between coats in 1.5-2 hours, and completely dry in 24 hours. The application method is done with a brush.

2.2.2. Synthetic Varnish

The melts of artificial resins in organic solvents are called synthetic varnish. It is water and moisture resistant. Viscosity is low in applications with a spray gun and high in applications with a brush [26]. Terms of use of the varnish used in the study; complete drying is 48 hours, practise temperature is between 5°C -35°C.

2.3. Nano Materials

Nano boron and nano silver (NaAg) were obtained from the manufacturers and their properties are given below.

2.3.1. Nano boron

It is boron with an atomic number of 5, an atomic weight of 10.81 g. The specific gravity of the amorphous powdery boron is 2.45 g/cm^3, and crystalline structure has 2.34 g/cm^3. Boron has not found freely in nature. Artificial boron is produced in two forms, amorphous and crystalline. While amorphous boron is black and matte in color, it becomes partially red and transparent when heated to 1260 °C. Crystal boron is black, hard and brittle. Boron mines are used in the glass industry, ceramic materials, cleaning materials and agricultural fertilizers, in the production of fire retardant or retardant materials, in metallurgy, wood industry and nuclear application areas [27]. In addition, nanomaterials can be modified to achieve better results in facilitating many different applications such as bioscience and medicine [28]. The size of the nano boron used in the study is 100 nm.

2.3.2. Nano Silver (NaAg)

Since it has a strong antibacterial effect and does not create a toxic effect, silver and silver compounds can be used by coating the surfaces during or after production on many surfaces and areas where harmful microorganisms are abundant and suitable for use in daily life. Materials with silver effect are more chemically resistant and these materials retain their antibacterial properties by keeping silver ions on their surfaces for a long time [29]. The size of nano silver used in the study is 100 nm.

2.4. Preparing of Test Examples

Experiment examples are prepared from sapwood parts of wood materials with smooth fibers, no knots, no cracks, no tulle formation, no resin, no growth defects and no reaction wood, no color and density difference, and which are not damaged by fungi and insects.

In order for the rough cut samples to become airdry, experiment examples were hold in the air-conditioning room at 20 ± 2ºC and 65± 5% relative humidity till their weight became unchanged. The air-dried samples were cut to the dimensions of 100x100x10 mm in a circular saw machine. A total of 150 test specimens were prepared, wood type (3), varnish (2), nanomaterial (2) and for control specimens.

The varnishing process of the test samples was made in according to specified in ASTM-D 3023 [30] .Before the measurements, examples were kept in the air conditioning room till they reached a constant weight in an region of 23 ± 2°C and 50 ± 5% relative humidity, according to the principles of TS ISO 13061-1 [31] .

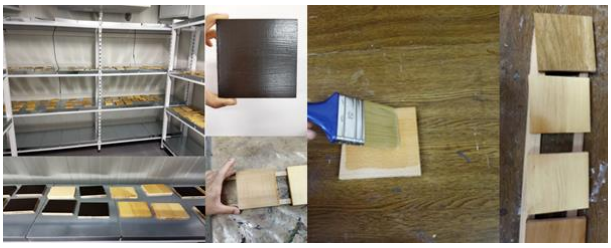

Figure 1. Varnishing of test samples

2.4.1. Varnishing

ASTM-D-3023 was considered for the varnishing process. Accordingly; the surfaces to be treated were sanded in such a way that the fiber swellings were removed, and after the dust was removed, they were varnished in accordance with the manufacturer's recommendations. In the varnishing of the samples, 0.1% and 0.3% nano materials were added into the water-based and synthetic varnish. It was mixed for 30 minutes with a special equipment. Water-based varnish 160 gr/m^2 and synthetic varnish 120 gr/m^2 were applied in 3 coats with a brush. Varnishing was applied below 20±2 °C temperature , 65±3 % relative humidity states.

3. TEST METHOD

3.1. Pendulum hardness determination

Hardness measurements were made with a pendulum hardness measuring device so as to specify the strength of the surface layer against mechanical effects. The Köning method was based and made in according to determined in ASTM D 4366-95 [32]. The working principle of the device is to measure the layer hardness according to the oscillations of two balls with a diameter of 5±0.0005 mm and a pendulum between 3º-6º oscillating with a hardness of 63±3.3 HRC. Surfaces with a high number of oscillations are considered harder, and surfaces with a low number of oscillations are considered as low hard surfaces [32] "Pendulum hardness measuring device" is Figure 2.

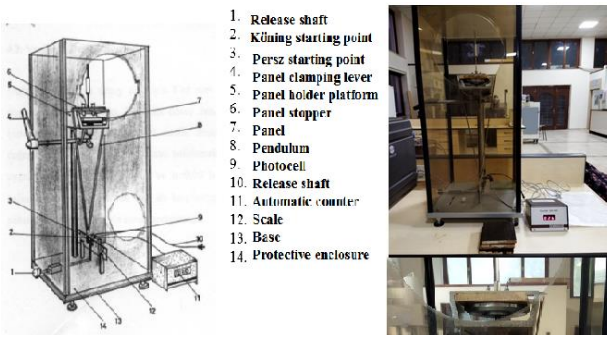

Figure 2. Pendulum hardness tester (13) and surface hardness measurement

3.1.2. Statistical evaluation

In the consideration of the statistical, the "MSTAT-C" program was made. Multiple variance (MANOVA) analysis was used to determine the effects of nanomaterials, nanomaterials % ratios on the hardness in wood material. If the variation among the groups was important, the degree of impact compared with Duncan test.

3.1.3. Determination of the amount of solids

The purpose of determining the amount of solid matter; it is to determine the layering feature of the top surface material in order to prepare a layer of equal thickness on the test sample surfaces. For this purpose, the varnishes used in the coating of the test sample surfaces were weighed as 5±0.2 grams on a 75±5 mm concave watch glass, which was previously tared, in according to TS EN ISO 3251 [33] then in an oven fixed at 60 °C left until it reaches constant weight. It was then weighed again and calculated with the following formulas [34].

Km = [(Vu- Çb) / Vu] X 100	
Vu = G – D	Çb = G – E

In this place;

Vu = Varnish applied (gr) G = wet weight (g)

Çb = Evaporated solvent (g) D = Tare (gr)

Km = Solids (%) E = Dry weight (g)

4. RESULTS

4.1. Varnish

The solid matter amount of the synthetic varnish used in experiments was specified as 53.6%, the solid matter amount of the water-based varnish was stated as 42%. Layer thicknesses were measured 120 µm for synthetic varnish and 100 µm for water-based varnish.

4.2. Pendulum (Oscillation) Surface Hardness

The varnish layer hardness values obtained as far as wood, varnish type, nanomaterial and nanomaterial % ratio are Table 1.

Wood Type*	$\bar{X}$ (Oscillation)	HG
Oriental beech (Ob)	19.57	A
Oak (O)	16.07	B
Scots pine (Sp)	15.05	C
Varnish Type**		
Synthetic (Sn)	20.21	A
Water-based (Wb)	13.58	B
Nano Material**		
Nano boron (B)	17.23	A
Nano silver (S)	16.56	A
% Of Nano Material *		
Control (C)	20.63	A
0.1 % (1)	15.38	B
0.3 % (3)	14.67	B
LSD*= 0.8331, LSD **=0.6802		
Oriental beech:Ob, Oak:O, Scots pine:Sp, Synthetic:Sn, Water-based:Wb, Nano boron:B, Nano silver:S, Control:C 0.1%:1, 0.3%:3		

Surface hardness value (Oscillation) is highest in Oriental beech (19.57), lowest in Scots Pine (15.05), in terms of varnish type, in synthetic varnish (20.21), lowest in water-based varnish (13.58), the highest nano boron (17.23) in terms of nanomaterial, the lowest nano silver (16.56), the highest 0.1% (15.38) nanomaterial percentage, the lowest 0.3% it was found in (14.67). The bilateral interaction values related to the surface hardness of wood type, varnish type, nanomaterial, nano equipment % ratios are given in Table 2.

Table 2.Hardness values of wood, varnish type, nanomaterial, nanomaterial % ratio obtained according to the binary interaction (Oscillation)

Transaction Type					
Wood Type+Varnish type*	$\bar{X}$	HG	Wood Type+ Nano Material *	$\bar{X}$	HG
Ob+Sn	25.17	A	Ob+B	20.67	A
O+Sn	19.07	B	Ob+S	18.47	B
Sp+Sn	16.40	C	O+S	16.73	C
Ob+Wb	13.97	D	Sp+B	15.63	CD
Sp+Wb	13.70	D	O+B	15.40	D
O+Wb	13.07	D	Sp+S	14.47	D
Varnish Type+Nano Material **					
Sn+B	21.33	A	Wb+S	14.02	C
Sn+S	19.09	B	Wb+B	13.13	C
Wood Type+Nano Material % ratios ***					
Ob+ C	23.95	A	Ob+3	16.35	D
O+C	20.75	B	Sp+1	14.20	E
Ob+1	18.40	C	O+3	13.90	E
Sp+C	17.20	D	Sp+3	13.75	E
Varnish Type+Nano Material % Ratios *			**Nanomaterial+Nanomaterial % Ratios ***		
Sn+C	27.43	A	S+C	21.10	A
Sn+1	17.23	B	B+C	20.17	A
Sn+3	15.97	C	B+1	15.80	B
Wb+C	13.83	D	B+3	15.73	B
Wb+1	13.53	D	S+1	14.97	B
Wb+3	13.37	D	S+3	13.60	C
LSD*= 1.178, LSD**=0.9620, LSD***= 1.443					

Surface hardness (oscillation) value was highest in wood type+ varnish type interaction, highest Oriental beech+ synthetic varnish (25.17), leastt in Oak+ waterbased varnish (13.07), highest in wood type+ nanomaterial interaction Oriental beech + nano boron (20.67), lowest Scotch pine+ nano silver (14.47), highest synthetic varnish+ nano boron (21.33) in varnish type+ nano material interaction, lowest water-based varnish+ nano boron (13.13), wood type + nanomaterial % ratio interaction, the highest is Oriental beech + 0.1% (18.40), the lowest is Scotch pine + 0.3% (13.75), varnish type + nanomaterial % ratios interaction the highest synthetic varnish + 0.1% (17.23), the lowest water-based varnish + 0.3% (13.37), the highest nano-boron + 0.1% in the interaction of nanomaterial + nanomaterial % ratio (15.80), the lowest hardness was found at nano silver+0.3% (13.60).

The triple interaction values related to the surface hardness of wood, varnish type, nano material, nano material % ratios are Table 3.

Table 3. Hardness values of wood type, varnish type, nanomaterial and nanomaterial % ratio obtained according to triple interaction (Oscillation)

Wood Type + Varnish Type + Nano Material*					
Process type	**X̄**	**HG**	**Process type**	**X̄**	**HG**
Ob+Sn+B	28.33	A	Ob+Wb+S	14.93	EF
Ob+Sn+S	22.00	B	Sp+Wb+B	13.93	EFG
O+Sn+S	19.80	C	O+Wb+S	13.67	EFG
O+Sn+B	18.33	CD	Sp+Wb+S	13.47	FG
Sp+Sn+B	17.33	D	Ob+Wb+B	13.00	G
Sp+Sn+S	15.47	E	O+Wb+B	12.47	G
Wood Type + Varnish Type + Nano Material % Ratios **					
Process type	**X̄**	**HG**	**Process type**	**X̄**	**HG**
Ob+Sn+C	33.40	A	Sp+Wb+3	14.10	E
O+Sn+C	28.40	B	O+Sn+1	14.10	E
Ob+Sn+1	22.30	C	Sp+Wb+C	13.90	E
Sp+Sn+C	20.50	CD	Sp+Sn+3	13.40	E
Ob+Sn+3	19.80	D	Sp+Wb+1	13.10	E
Sp+Sn+1	15.30	E	O+Wb+3	13.10	E
O+Sn+3	14.70	E	O+Wb+C	13.10	E
Ob+Wb+1	14.50	E	O+Wb+1	13.00	E
Ob+Wb+C	14.50	E	Ob+Wb+3	12.90	E

Wood Type+ Nanomaterial+ Nanomaterial % Ratios **					
Process type	**X̄**	**HG**	**Process type**	**X̄**	**HG**
Ob+S+C	24.30	A	Sp+B+3	15.10	FGH
Ob+B+C	23.60	A	Ob+S+3	14.60	FGHI
O+S+C	22.30	AB	Sp+S+1	14.30	GHI
Ob+B+1	20.30	BC	Sp+B+1	14.10	HI
O+B+C	19.20	CD	O+S+1	14.10	HI
Ob+B+3	18.10	DE	O+B+3	14.00	HI
Sp+B+C	17.70	DE	O+S+3	13.80	HI
Sp+S+C	16.70	EF	O+B+1	13.00	HI
Ob+S+1	16.50	EFG	Sp+S+3	12.40	I
Varnish Type+ Nano Material % Ratios *					
Process type	**X̄**	**HG**	**Process type**	**X̄**	**HG**
Sn+S+C	28.47	A	Wb+B+C	13.93	DE
Sn+B+C	26.40	B	Wb+S+3	13.87	DE
Sn+B+1	19.00	C	Wb+S+C	13.73	DE
Sn+B+3	18.60	C	Sn+S+3	13.33	E
Sn+S+1	15.47	D	Wb+B+3	12.87	E
Wb+S+1	14.47	DE	Wb+B+1	12.60	E
LSD*= 1.666 , LSD**=2.041					

Surface hardness (oscillation) value is highest in wood type+ varnish type+ nano material interaction Oriental beech+ synthetic varnish+ nano boron (28.33), lowest Oak+ water-based varnish+ nano boron (12.47), wood type+ varnish variety+ nano material % ratio interaction, the highest Oriental beech+ synthetic varnish+ 0.1% (22.30) the lowest Oriental beech+ water-based varnish+ 0.3% (12.90) wood type+ nano, in the interaction of material+ nanomaterial % ratios, the highest Oriental beech+ nano boron+0.1% (20.30) and the lowest Scotch pine+nano-silver+0.3% (12.40) varnish type+ nano material In the interaction of % ratios, the highest synthetic varnish + nano boron + 0.1% (19.00) was found, the lowest was water-based varnish + nano boron + 0.1% (12.60).

The results of multivariance analysis regarding the surface hardness of wood, varnish type, nanomaterial, nano material % ratios are Table 4.

Table 4. Multiple variance analysis of wood, varnish type, nanomaterial, nanomaterial % ratios on surface hardness

Variance Source	Degrees of Freedom	Sum of Squares	Mean Square	F Value	P<0.05
Factor A	2	673.678	336.839	62.9932	0.0000
Factor B	1	1980.050	1980.050	370.2951	0.0000
AB	2	550.900	275.450	51.5127	0.0000
Factor C	1	20.672	20.672	3.8660	0.0512
AC	2	99.011	49.506	9.2582	0.0002
BC	1	110.450	110.450	20.6556	0.0000
ABC	2	153.433	76.717	14.3470	0.0000
Factor D	2	1273.544	636.772	119.0847	0.0000
AD	4	144.822	36.206	6.7709	0.0001
BD	2	1101.100	550.550	102.9600	0.0000
ABD	4	130.000	32.500	6.0779	0.0002
CD	2	71.078	35.539	6.6462	0.0017
ACD	4	41.089	10.272	1.9210	0.1101
BCD	2	165.433	82.717	15.4691	0.0000
ABCD	4	103.733	25.933	4.8499	0.0011
Error	144	770.000	5.347		
Total	179				
Factor A:Wood, Factor B:Varnish, Factor C:Nano material, Factor D:%					

The hardness value effects of wood, varnish type, nano,nano material % ratios were statistically significant (α=0.05) in respect to wood type, varnish type, nano material % ratio interactions, and insignificant in terms of nano material type. The Duncan test results, which were performed to state among which groups the distinction was significant, are given in Table 5.

Table 5.Hardness values of wood, varnish type, nanomaterial, nanomaterial % ratio obtained compared to the quadruple interaction (Oscillation)

Process type	$\bar{X}$	HG	Process type	$\bar{X}$	HG
Ob+Sn+S+C	33.80	A	O+Wb+S+3	14.40	FGHIJK
Ob+Sn+B+C	33.00	A	Ob+Wb+B+C	14.20	FGHIJK
O+Sn+S+C	31.80	A	Sp+Wb+B+C	14.20	FGHIJK
Ob+Sn+B+1	28.00	B	O+Wb+S+1	13.80	FGHIJK
O+Sn+B+C	25.00	C	O+Sn+B+1	13.80	FGHIJK
Ob+Sn+B+3	24.00	CD	Sp+Wb+S+3	13.60	FGHIJK
Sp+Sn+B+C	21.20	DE	Sp+Wb+S+C	13.60	FGHIJK
Sp+Sn+S+C	19.80	E	Ob+Wb+S+3	13.60	FGHIJK
Ob+Sn+S+1	16.60	F	O+Wb+B+C	13.40	FGHIJK
Ob+Wb+S+1	16.40	FG	Sp+Wb+S+1	13.20	FGHIJK
O+Sn+B+3	16.20	FGH	O+Sn+S+3	13.20	FGHIJK
Ob+Sn+S+3	15.60	FGHI	Sp+Wb+B+1	13.00	GHIJK
Sp+Sn+B+3	15.60	FGHI	O+Wb+S+C	12.80	HIJK
Sp+Sn+S+1	15.40	FGHI	Ob+Wb+B+1	12.60	IJK
Sp+Sn+B+1	15.20	FGHIJ	Ob+Wb+B+3	12.20	IJK
Ob+Wb+S+C	14.80	FGHIJ	O+Wb+B+1	12.20	IJK
Sp+Wb+B+3	14.60	FGHIJK	O+Wb+B+3	11.80	JK
O+Sn+S+1	14.40	FGHIJK	Sp+Sn+S+3	11.20	K
LSD*= 2.886					

Surface hardness (oscillation) value is peak in Oriental beech+ synthetic varnish+0.1% nano boron (28.00) in the coaction of wood+varnish type+ nanomaterial+ nanomaterial % ratio, and the lowest is Scots pine+ synthetic varnish+% it was found in 0.3 nano silver (11.20).

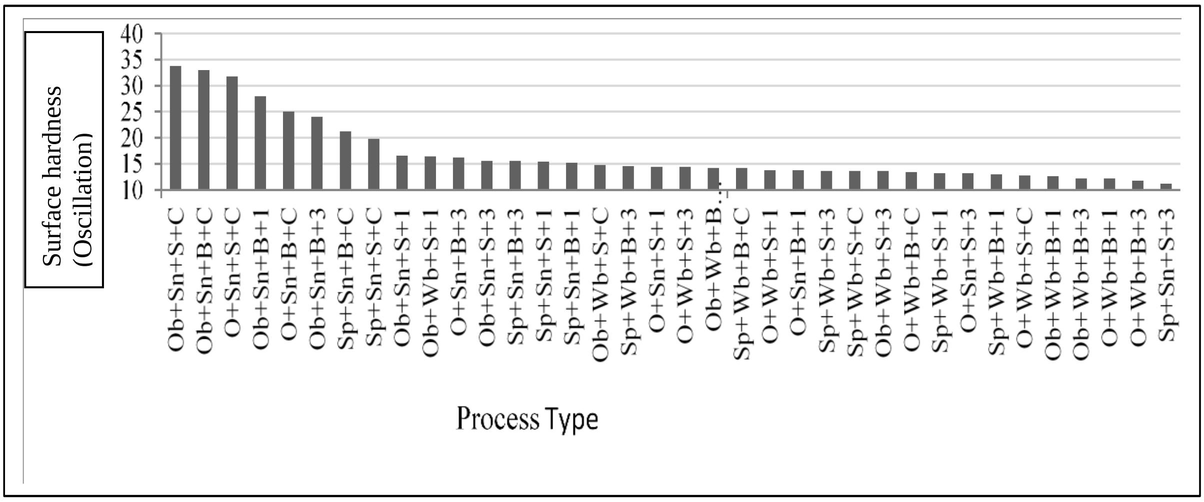

Figure 3. Surface hardness value changes according to the process type

5. CONCLUSIONS

Varnish hardness was different between wood types. As a matter of fact, the hardness value (oscillation) was found 24% higher in Oriental beech than Scots pine and 18% higher than Oak. This may be due to the anatomical structure differences of the wood materials.

Synthetic varnish was %33 high according to waterbased varnish. This may be due to the varnish feature.

The hardness value was found to be approximately equal in nano boron, nano silver and % ratios. However, the hardness of the varnishes modified with nanomaterials was lower than the control samples. It can be said that nano materials have a reducing effect on the hardness value of the varnish.

In the interaction of wood type and varnish type, the hardness value was highest in Oriental beech synthetic varnish, while the lowest was found in Oak water-based varnish. It can be said that wood type and varnish type are effective in varnish hardness.

It has been determined that nanomaterials reduce the varnish hardness in the binary interactions of wood type, varnish type and % ratios of nano materials. The most reducing effect was observed in varnish and then nano silver. As a matter of fact, this situation can be understood from the F values of variance table.

According to triple interaction of wood type, varnish type, nano-material and nano-material % ratios, it can be said that 1st degree wood species, 2nd degree varnish type, 3rd degree nano material, 4th degree nano material % ratios are effective in hardness value. The hardness value decreases follow this order from the largest to the smallest.

In multiple interactions, the peak hardness value was found in Oriental beech + synthetic varnish + 0.1 % nano boron (28.00), least in Scotch pine + synthetic varnish + 0.3% nano silver (11.20). Oriental beech+ synthetic varnish+0.1% nano boron hardness value was 96% higher than Scots pine+ synthetic varnish+0.3% nano silver.

Human beings now use nano-technological product/product formations at every stage of today's life. Although nano refers to a small structure, this term is also described as smart. It is used in the construction / wood, textile industry, medicine, military materials (information systems / aircraft-space industry), for the destruction of all kinds of biological struggles (germs / bacteria); nanotechnological formation has emerged as a technological breakthrough (revolution) [35].

It can be said that nano-materials used on the surfaces to which antibacterial properties are desired have a reducing impact on the hardness of the varnish layer. The hardness value, synthetic varnish + nano silver interaction was 54% lower in Oriental beech, 59% in Oak and 44% in Scots pine compared to the control samples. Synthetic varnish + nano boron interaction was 28% lower in Oriental beech, 36% in Oak, and 27% synthetic varnish + nano boron interaction was 28% lower in Oriental beech in Scots pine. Compared to the control groups, nano silver showed a reducing effect on varnish hardness.

It was applied to the wood surfaces of Scots pine (Pinus silvestris L.) and beech (Fagus orientalis L.) tea dye and water-solvent varnish, developed as a top surface material. The changes in the hardness value were calculated. According to the test results; the highest hardness value was obtained in water solvent varnish (37.60) beech wood application, the lowest hardness value (17.60) was obtained in beech wood application of tea dye [36].

The samples were prepared from oriental beech (Fagus orientalis Lipsky) and sessile oak (Quercus petreae Lipsky) woods. After they were impregnated with boric acid and borax by vacuum method, their surfaces were covered with cellulosic, synthetic, polyurethane, water-based, acrylic and acid-hardened varnishes. After the varnishing process, the layer hardness of the samples was determined. According to this; the highest in terms of hardness value, wood type, impregnation material and varnish type interaction; sessile oak+borax+acrylic varnish, lowest; Obtained in oak+borax+synthetic varnish [37].

The hardness value, water-based varnish + nano silver interaction, was found to be 8% lower in Oriental beech, 12% higher in Oak compared to the control samples and it did not show any effect in Scots pine. Water-based varnish + nano boron interaction was 15% lower in Oriental beech, 12% lower in Oak, and 3% higher in Scots pine.

Hardness is important in furniture decoration etc. application areas. Taking this into account may be advantageous in terms of usage. It is thought that it can be used in hospitals, children's playgrounds, etc. where antibacterial properties are required. By increasing the nanomaterial % ratios, studies can be made in different variations where hardness is considered important.

DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Cansu ÖZDER: She conducted the experiments and analyzed the results. She wrote the article.

Musa ATAR: He analyzed the results and made additions to the article.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

ACKNOWLEDGEMENT

This work has been supported by Gazi University Scientific Research Projects Coordination Unit under grant number FDK-2022-7848

REFERENCES

[1] Nanoteknoloji strateji grubu., Nanobilim ve nanoteknoloji stratejileri, Vizyon 2023 projesi, TÜBİTAK, 18 sayfa, Ankara, (2004)

[2] Bozkurt A. Y., Erdin N., "Ağaç Teknolojisi" İstanbul Üniversitesi Orman Fakültesi ,yayın no: 445, ISBN: 975-404-449-X. İstanbul, (1997).

[3] Sow, C.; Riedl, B; Blanchet, P., UV-waterborne polyurethane-acrylate nanocomposite coatings containing alumina and silica nanoparticles for wood: mechanical, optical, and thermal properties assessment. Journal of Coatings Technology and Research, 8(2): 211-221., (2011)

[4] Kurtoğlu A., Ağaç malzeme Yüzey İşlemleri, genel bilgiler, Cilt I, İstanbul Üniversitesi Yayınları, İstanbul Üniversitesi Yayın no: 4262 (2000)

[5] Vardanyan V., Galstian T., Riedbl B., Effects of addition of cellulose nanocrystals to wood coatings on color changes and surface roughness due to accelerated weathering, Journal of Coatings Technology and Research, 12(2), 247-258, (2015)

[6] Frigione, M; Lettieri, M., Novel attribute of organic–inorganic hybrid coatings for protection and preservation of materials (stone and wood) belonging to cultural heritage. Coatings, 8(9): 319, (2018)

[7] Kaygın, B.; Akgün, E., A nano-technological product: An innovative varnish type for wooden surfaces. Scientific Research and Essay, 4 (1): 1-7, (2008)

[8] Candan, Z., "Ahşap Sandviç Panel ve Laminat Parke Üretiminde Nanopartikül Kullanımı ve Teknolojik Özellikler Üzerine Etkisi", İstanbul Üniversitesi, Doktora Tezi, İstanbul, (2012)

[9] Atar, M.; Keskin, H.; Yavuzcan, H. G., Varnish layer hardness of oriental beech (Fagus orientalist L.) wood as affected by impregnation and bleaching. Journal of Coatings Technology and Research, 1(3), 219–224, (2004)

[10] Yakın, M., "Su bazlı verniklerde sertlik, parlaklık ve yüzeye yapışma mukavemetinin tespiti, Yüksek Lisans Tezi", Gazi Üniversitesi, Ankara, (2001)

[11] Long, L.; Xu, J.; Wan, X; Qian, L., Surface modification of nano-alumina and its application in preparing polyacrylate water-based wood coating. Journal of Polymer Engineering, 33(8): 767-774, (2013)

[12] Keskin, H.; Atar, M.; Yavuzcan, H. G., Impact of impregnation and bleaching on the surface hardness of oak (Quercus petraea L.) wood. Journal of Applied Polymer Science, 93(2), 498–504., (2004)

[13] Budakçı, M., "Ahşap verniklerinde katman kalınlığının sertlik, parlaklık ve yüzeye yapışma mukavemetine etkileri". Yüksek Lisans Tezi, Gazi Üniversitesi Fen Bilimleri Enstitüsü, Ankara, 68. (1997).

[14] Özen, R; Sönmez A., Özen, R., Sönmez A., Ahşap verniklerin harici etkilere karşı dayanıklılığına ilişkin araştırmalar, Devlet Planlama Teşkilatı Araştırma Projesi Kesin Raporu, Ankara. (1996).

[15] Rai, M.K., Yadav, A.P., Gade, A.K., "Silver nanoparticles as a new generation of antimicrobials", Biotech Adv., 27 (1):76-82 (2009).

[16] Dhoke S.; Mahajan P.; Kamble R.; Khanna A.; Effect of Nanoparticles Suspension on the Growth Mung (Vigna radiata) seedlings by foliar spray method, India, volume:3 no:1 (2013)

[17] Atılgan A., Peker H., Atar M., "Çevreci organik üst yüzey işlem maddesinin ahşap malzemede uygulanması ve bazı yüzey özelliklerine etkisi" *Journal of the Faculty of Engineering and*

Architecture of Gazi University, 37:1 107-120, (2022).

[18] Budakçı, M.; Uysal B.; Esen R.,). Borik asit modifikasyonunun su bazlı vernik sertlik değerine etkisi, 5. Uluslararası İleri Teknolojiler Sempozyumu (IATS'09), Karabük-Türkiye, 1160, (2009).

[19] Şimşek, H., "Ülkemiz için yeni bazı borlu bileşiklerin ağaç malzemenin yoğunluk, mekanik özellikler, biyolojik direnç ve üst yüzey özellikleri üzerine olan etkilerinin belirlenmesi", Yüksek Lisans Tezi, Muğla Üniversitesi Fen Bilimleri Enstitüsü, Muğla, (2009).

[20] Örs Y.; Özçiftçi A.; Şahinkol H.; Yapıcı F., "Üstyüzey işlemlerinin Doğu ladini (*Picea orientalis L.*) odununun renk, parlaklık ve pandüllü sertlik değerine etkisi", *Ladin Sempozyumu*, Trabzon, 994–1005, (2005)

[21] Aykaç S., Sofuoğlu D. S., "Bambu ağaç malzemede vernik tiplerinin yüzey özellikleri üzerine etkisinin incelenmesi" Politeknik Dergisi, 24(4): ss 1353-1363, (2021)

[22] Sönmez A., Budakçı M., ve Yakın M., "Ağaç Malzemede Su Çözücülü Vernik Uygulamalarının Sertlik, Parlaklık ve Yüzeye Yapışma Direncine Etkileri" Politeknik Dergisi, cilt 7, sayı:3, ss 229-235, (2004)

[23] Pelit H., Korkmaz M., "Kayın Kayın (*Fagus orientalis* Lipsky) Odununun Yüzey Özelliklerine Nano-Grafen Katkılı Su Bazlı Verniklerin Etkisi" Politeknik Dergisi, 22(1), ss.203-212, (2019)

[24] ISO 3129 "Wood-Sampling methods and general requirements for physical and mechanical testing of small clear wood specimens. İsviçre: International Organization for Standardization, (2019).

[25] Baykan, İ.; Kılıç, Y.; Bakır, K.., Mobilya Endüstrisinde Üstyüzey İşlemleri, Ankara, 102-104, (2000)

[26] Temiz, A.; Gezer, E. D.; Yildiz, U. C.; Yildiz, S., Combustion properties of alder (Alnus glutinosa L.) Gaertn. subsp. barbata (C.A. Mey) Yalt. and southern pine (Pinus sylvestris L.) wood treated with boron compounds. Construction and Building Materials, 22(11), 2165–2169, (2008)

[27] Lines, M.G., Nanomaterials for practical functional uses, Journal of Alloys and Compounds. 449-(1-2), Australia, (2008)

[28] DPT, "Bor Tuzları–Trona–Kaya Tuzu–Sodyum Sülfat–Stronsiyum. Çalışma Grubu Raporu", Cilt, Ankara, (2001)

[29] Cansızı, E.; Kırmusaoğlu, S., "Nanoteknolojide nano gümüşün antibakteriyel özelliği" Haliç Üniversitesi, Fen Edebiyat Fakültesi, Moleküler Biyoloji ve Genetik Bölümü, İstanbul, (2018).

[30] ASTM-D3023., "Standard practice for determination of resistance of factory-Applied coatings on wood products to stains and reagents". American Society for Testing and Materials, U.S.A., (2017)

[31] TS ISO 13061-1., "Odunun fiziksel ve mekanik özellikleri – Kusursuz küçük ahşap numunelerin deney yöntemleri" - Bölüm 1: Fiziksel ve mekanik deneyler için nem muhtevasının belirlenmesi. Ankara: Türk Standardları Enstitüsü, (2021).

[32] ASTM D 4366 -95, "Standard test methods for hardness of organic coatings by pendulum damping tests". American Society for Testing and Materials", U.S.A., (1984)

[33] TS EN ISO 3251., "Boyalar, vernikler ve plastikler - Uçucu olmayan madde içeriğinin tayini. Türk Standardları Enstitüsü, Ankara, (2019).

[34] Sönmez, A., "Ağaçtan yapılmış mobilya üst yüzeylerinde kullanılan verniklerin önemli mekanik, fiziksel ve kimyasal etkilere karşı dayanıklılıkları". Doktora Tezi, Gazi Üniversitesi Fen Bilimleri Enstitüsü, Ankara, 142, (1989)

[35] Peker H., Ulusoy H., "Ahşapta nanoteknolojik vernik/tutkal kullanımı ve etkileri" 3nd International Symposium on Innovative Approaches in Scientific Studies, April 19-21, Ankara, (2019)

[36] Peker H., "Atık çay ekstrakt boyasının çeşitli mordan-su çöüzücülü vernikle ahşapta kullanımı ve sertlik değişimine etkisi", Politeknik Dergisi, 18 (2) : 73-78, (2015)

[37] Örs Y., Atar M., Çolakoğlu H.M., "Impact of ımpregnation with boron compounds on the surface hardness of varnished wood", Journal of Applied Polymer Science, cilt.105, sa.4, ss.2327-2331, (2007)