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Effects of Nanosilver in Improving Fire-Retarding Properties of Borax in Solid Woods

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ABSTRACT

Effects of heat-transferring property of silver nanoparticles were evaluated on two solid woods of poplar and fir and in combination with Borax. Nanosilver and Borax were applied in pressure vessel using Rueping method. The size range of silver nanoparticles was 20-80 nm. Specimens of 150×130×9 mm were prepared and five fire-retarding properties were measured using a newly designed slide fire test apparatus. The obtained results indicated that most fire-retarding properties of Borax were improved in combination with nanosilver suspension. Some improvements, although not significant in most cases, were also observed in those specimens that were only impregnated with nanosilver. Significant difference was observed in the two species.Fire-retarding properties were best improved by nanosilver+Borax impregnation in poplar; however, Borax-impregnated specimens seemed to have the optimum properties in fir.

Keyword: Borax; Fire-Retarding properties; Heat-Transferring property; Metal nanoparticle; Solid woods.

1. INTRODUCTION

Wood is a unique natural products used in many applications. However, it has some disadvantages such as water absorption and thickness swelling, knots, etc. Therefore, it is sometimes modified to give better and more uniform quality [1, 2].

Fire safety is an important concern in all types of construction. Wood is exceptionally important in this concern; it burns when exposed to fire or to high temperature. Thermal degradation of wood occurs in stages. The degradation process and the exact products of thermal degradation depend on the temperature level and length of time under exposure conditions. The sequence of events for wood combustion is as follows [3, 4]:

- The wood, responding to heating, decomposes or pyrolysis into volatiles and

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char. Char is the dominant product at internal temperatures less than 300°C, whereas volatiles become much more pronounced above 300°C.

- The volatiles, some of which are flammable, can be ignited if the volatile-air mixture is of the right composition in a temperature range of 400°C to 500°C within the mixture.This gas phase combustion appears as flames.
- With air ventilation, the char oxidation becomes significant around 200°C with two peaks in intensity reported at 360°C and 520°C. This char oxidation is seen as glowing or smoldering com bustion until only ash residue remains.

Several materials have so far been tested and used to delay above-mentioned events [4, 5]. The use of inorganic salts as a treatment to render wood fire-retardant is not a modern development. Indeed, approximately eighty years ago, the wood treating industry developed and later refined a pressure impregnation process where these mineral salts were forced deep into wood cells [3]. This process resulted in a new building component known as Fire Retardant Treated (FRT) Lumber. Chemicals for FRT Lumber are used to treat wood and wood-based building materials such as plywood and structural lumber (including dimensional lumber used to fabricate roof trusses) to reduce contribution of wood to fire. Many FRT chemicals increase the temperature at which thermal degradation can occur, thereby increasing the amount of char and reducing the amount of flammable volatiles. In this regard, FRT has performed effectively. In the late 1950's and early 1960's several companies began aggressively marketing formulations of these fire retardants under various trade names. While the formulations of these products were (and still are) proprietary, and no doubt varied to a small degree, these "first generation" products contained inorganic salts, such as monoammonium Phosphate, and ammonium Sulfate.

In some cases Zinc Chloride and diammonium Phosphate were used as well [6]. Other kinds of traditional chemicals, such as lime water (alkaline aqueous solution of calcium hydroxide), have also been studied to find out their fire-retarding properties and compare with modern ones [6]. The heat-transfer property of silver nanoparticles [7-12] was also reported to improve some of the fire-retarding properties in solid woods [4]. In the U.S. building codes, Fire-Retardant-Treated Wood is defined as a wood product impregnated with the FR chemicals by a pressure process or other means during manufacture, which, shall have a flame spread index of not over 25 (based on the calibration on the testing tunnel) when tested in accordance with ASTME 84. The FRT wood shall/should show no evidence of progressive combustion when a ten-minute test is extended for an additional 20 minutes, and does not have the flame front progress 3.2 m beyond the centerline of the burner at any time during the test.

Fire-retardant treatments may affect wood from different perspectives: increased hygroscopicity, reduced strength, dimensional stability changes depending on treatment, wood degradation, corrosion of metal fasteners, adhesion problems, increased abrasiveness, and leaching of treatments. As evidenced by recent structural problems with fire-retardant-treated plywood, fire-retardant chemicals and high temperature environments can degrade the strength properties of wood [13]. It is suspected that the combination of acidic fireretardant chemicals and elevated temperatures increases the rate of acid hydrolysis in the wood, thereby causing a loss in strength [14]. In the meantime, the effects of fire-retardant chemicals is so important that designers intending to use fire-retardant-treated materials in areas of elevated temperatures, such as roof decks, should ask suppliers the initial effects of fire-retardant formulations on wood strength, stiffness, and fastener corrosion [5].

The problem with the use of these salts as fire retardants is that, firstly, they are highly hygroscopic. That is, they will absorb moisture from the air when relative humidity becomes high. It has been reported that some products were so hygroscopic that they would actually drip solution at relative humidity of approximately 90% [3]. Initial problems included corrosion of metal

fasteners and fittings (such as metal truss plates). Secondly, the smoke and gases produced by fire are toxic and dangerous for health. The term smoke is frequently used in an all-inclusive sense to mean the mixture of pyrolysis products and air that is present near the fire site. In this context, smoke contains gases, solid particles, and droplets of liquid. Smoke presents potential hazards because it interacts with light to obscure vision and because it contains noxious and toxic substances. Two approaches are usually used to deal with the smoke hazards: limit smoke production and control the smoke that has been produced [3]. The control of smoke flow is most often a factor in the design and construction of large or tall buildings. In these buildings, combustion products may have serious effects in areas remote from the actual fire site.

Based on the above mentioned literature review, fire-retardant chemicals may be assessed from three main perspectives beyond flammability: reduced strength on wood and corrosion on fasteners, increased hygroscopicity, and the amount of toxic and smoke gases produced. Although all these perspectives are considered over the years and in the new fire-retardant formulations nearly all requirement are met, the properties of these fire-retardant chemicals are yet to be improved.

In this connection, nanotechnology was used in many sciences, such as fluid transfer in porous media [15, 16], enhancement of antibacterial and antimicrobial effects of silver, thermal conductivity [17], heat treatment, filtration, wood densification [18], shape controlling [19], DNA detection [20], electrode position, semiconductors and molecular electronics [21], extraction of materials, missing data [22], and many others. Silver nanoparticles were reported to improve some of the fire-retarding properties of impregnated solid woods [4]. The present study was therefore designed to evaluate the potentiality of its combination with Borax, as a former well-known fire-retardant. However, as the standard fire testing apparatuses such as the cone calorimeter are not readily available in all laboratories, two innovative fire-testing apparatuses were designed and built that nearly all laboratories can afford. In the meantime, apart from the ignitability and weight loss properties that are always measured for reporting purposes of fire-retarding chemicals, these apparatuses can measure spread of flame over time which is important for safety purposes.

2. MATERIALS AND METHODS

2.1. Specimen Procurement

One hardwood and one softwood species of rather the same density values were chosen based on their importance in various industrial applications in Iran; the hardwood was poplar (*Populus nigra*) with 0.53 g/cm^3 of density; and the softwood was silver fir (*Abies Alba*) with 0.44 g/cm^3 of density. Specimens of each species were divided into four treatment groups: control, nano-silver, Borax and NS+Borax-impregnated specimens. For every species, 10 specimens free of knots, fissures, and checks were randomly chosen for each group; 40 specimens for the four treatments per species, totally 200 specimens. The size of the specimens was 150 (length) × 130 (width) × 9 (thickness) mm. The length of specimens was in longitudinal, and the width in tangential direction.

2.2. Impregnation Process

Impregnation with either Borax or nanosilver (NS) suspension was completed using empty-cell process at 3 bar pressure . A 400 ppm aqueous dispersion of silver nanoparticles was made using an electrochemical technique in. The size range of silver nanoparticles was measured to be 20 to 80 nm. The pH of the suspension was 6-7; two kinds of surfactants (anionic and cationic) were used in the suspension as stabilizer. Each specimen was weighted just before and after the impregnation to measure nano-silver solution uptake.

Extreme cautions were made to make sampling process with the highest possible similarity. The amount of Borax retention was 8.5-10% based on the dry weight basis of solid woods due to variability of permeability in different parts of woods [23-25].

After impregnation, all specimens were mildly

dried to the moisture content of 10%. They were then kept at room temperature (30-35°C and 45-50% relative humidity) along with control specimens for three months. The moisture content (MC) of all the specimens was 7.5% at the time of testing. Scanning Electron Microscope (SEM) micrographs were carried out on NS-impregnated specimens before the fire tests. SEM imaging was done at thin-film laboratory, FE-SEM lab (Field Emission), School of Electrical & Computer Engineering, The University of Tehran; a field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial.

2.3. Fire-Retardant Testing Apparatus

Due to the unavailability of the standard tests by

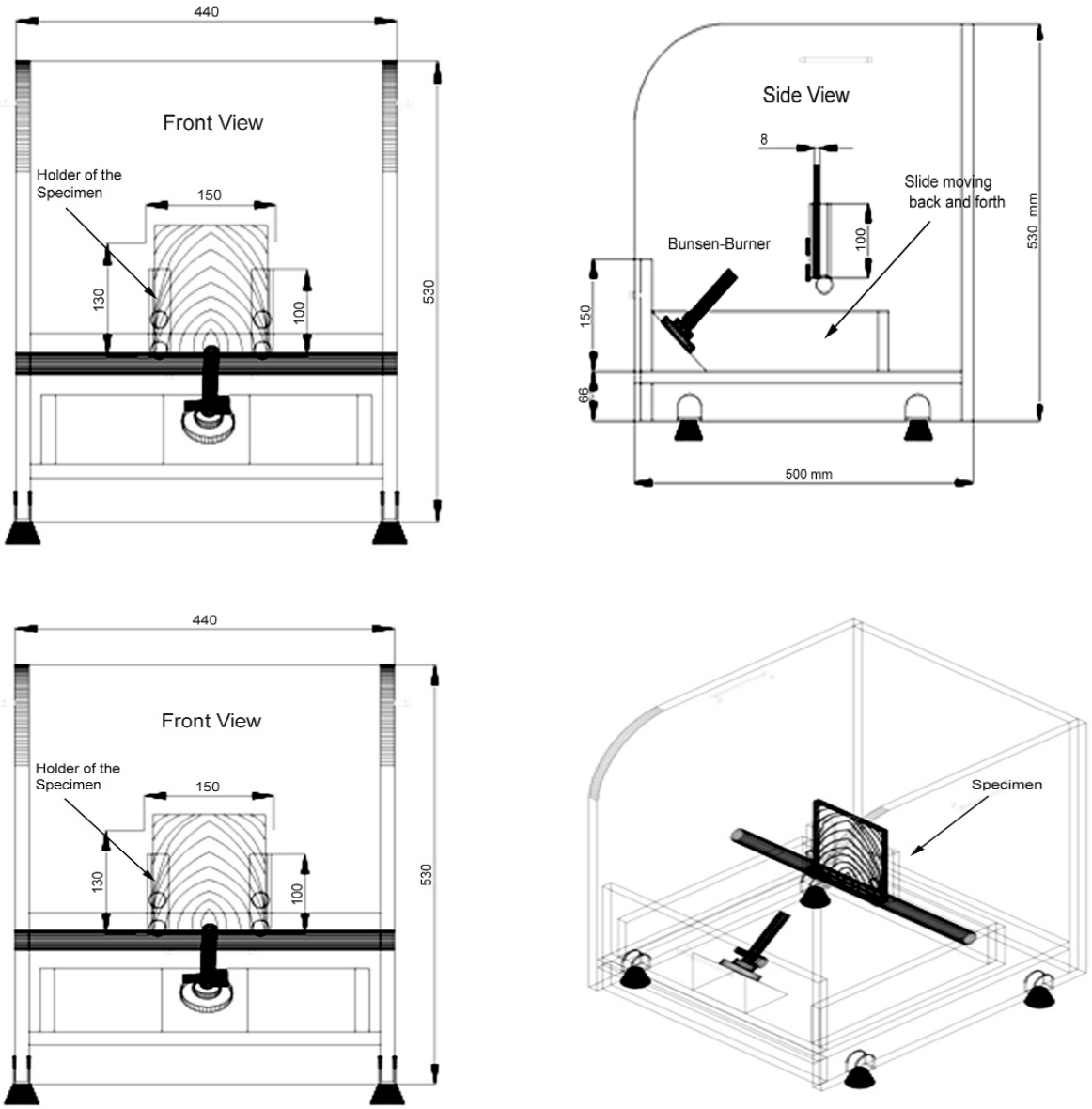

Figure 1: *Schematic picture of the slide fire testing apparatus (SFTA) (invented by the second author under Iranian Patent No. 67232; approved by Iranian Research Organization for Science and Technology under license No. 3407).*

cone calorimeter and heat release measurement apparatus, Slide Fire Test Apparatus (SFTA) was designed and built by the second author, using piloted ignition [3] (Figure 1).

The fuel in the present study was natural gas comprised of mainly methane CH_4 (90-98%); however, other hydrocarbons were also reported by the supplier to be accompanied (C_2H_6: 1-8%; C_3H_8: 2%; H_4H_{10}+C_5H_{12}: less than 1%; and also N_2 + H_2S + H_2O: less than 1.5%).

The flow rate was 0.096 liters/s. The specimen was vertically mounted on a holder up-straight and exposed to a Bunsen-type burner hold at 45 degrees to the surface of the specimen for 120 seconds in accordance with the standard ISO 11925-3. The burner nozzle internal diameter was 11 mm. The burner was fixed on a slide, moving back and forth, equipped with an adjustable stop to keep flame at a certain distance from the specimen. While the slide was back, the burner was turned on; the slide was thenpulled forward abruptly to expose the flame to the specimen. The time for each specimen to catch fire with an evident visible flame on the spot nearest to the Bunsen-type burner, as well as the time the spot started to glow, were registered as ignition and glowing times. After 120 seconds, the slide was pulled back to prevent over-exposure of the specimen to the flame. The time the specimen showed a visible fire, after the removal of the burner, was also registered as fire endurance time (the duration time of a visible flame).

Once the flame was extinguished and the specimen was no longer burning, the length and width of burning were measured. The weight was also measured just before, as well as 2 hours after the test, to measure the weight loss. The whole structure of the apparatus was placed in a three-wall-compartment in order to protect the burning flame from wind and air movements.

2.4. Statistical Analysis

Statistical analysis was conducted using SAS software program, version 9.1. Two-way analysis of variance (ANOVA) was performed on the data to conclude significant differences at the 95% level of confidence. Hierarchical cluster analysis, including dendrogram and using Ward methods with squared Euclidean distance intervals, was carried out by SPSS/16.

3. RESULTS

3.1. Ignition Time

The highest ignition time was found in poplar specimens, impregnated with NS+Borax (28.4 s); and the lowest was found in fir specimens, impregnated with NS (13.64 s) (Figure 2). The highest ignition times in the two species were found in different treatments of Borax-impregnated (in fir) and NS+Borax-impregnated (in poplar).

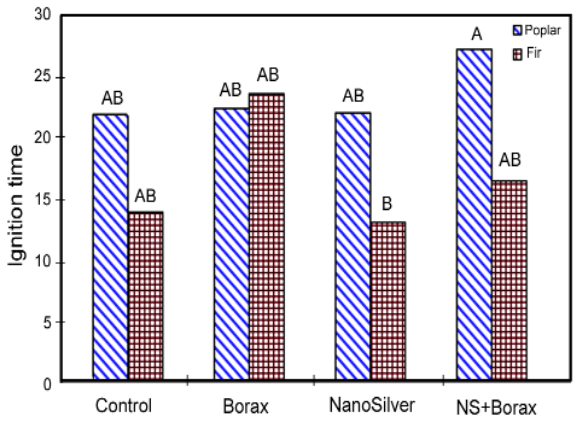

Figure 2: *Ignition time of the four treatments of both species of poplar and fir (s) (NS=nanosilver) (letters on each column indicate Duncan grouping at 95% confidence level).*

3.2. Glowing Time

Glowing time didn't show much difference between the four treatments in poplar, although NS+Borax were a little higher (Figure 3). The highest glowing time in fir was found in Borax-impregnated specimens, similar to the results of ignition time.

3.3. Fire Endurance

The lowest fire endurance time was found in poplar impregnated with NS+Borax (0.66 s) (Figure 4). Also, the lowest fire endurance in fir was found in Borax-impregnated specimens (0.8 s). Impregnation

of poplar specimens with NS+Borax increased fire endurance time by 79.4%.

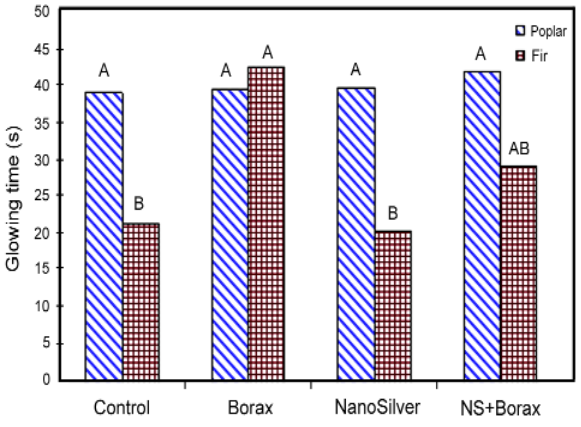

Figure 3: *Glowing time of the four treatments of both species of poplar and fir (s) (NS=nanosilver) (letters on each column indicate Duncan grouping at 95% confidence level).*

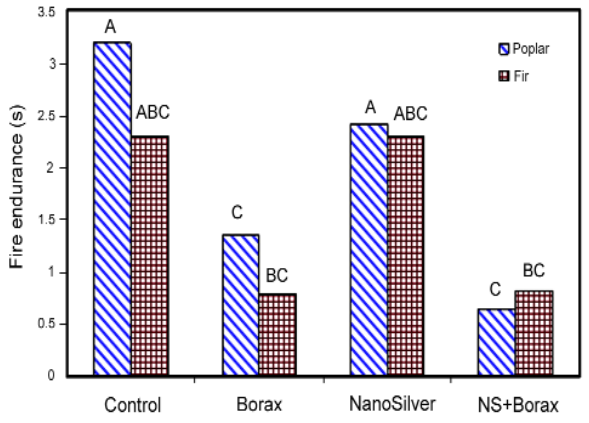

Figure 4: *Fire endurance of the four treatments of both species of poplar and fir (s) (NS=nanosilver) (letters on each column indicate Duncan grouping at 95% confidence level).*

3.4. Carbonized area

The lowest carbonized area was found in fir specimens, impregnated with NS+Borax (Figure 5). The next lowest rank belonged to the same treatment of poplar. Interesting point is that the control treatments of these two species showed quite different results, although they had nearly similar density; that is, the higher carbonized area was found in fir specimens.

3.5. Weight Loss

The highest weight loss was observed in nanosilver impregnated specimens of poplar, showing 36.8% increase in comparison to control specimens (Figure 6). However, no significant difference was observed in weight losses of the four treatments in fir.

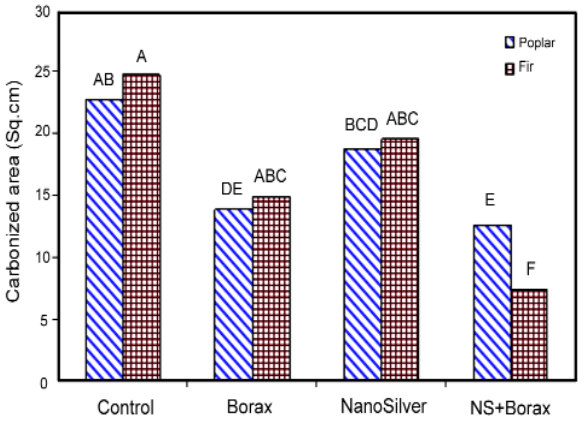

Figure 5: *Carbonized area of the four treatments of both species of poplar and fir (cm^2) (NS=nanosilver) (letters on each column indicate Duncan grouping at 95% confidence level).*

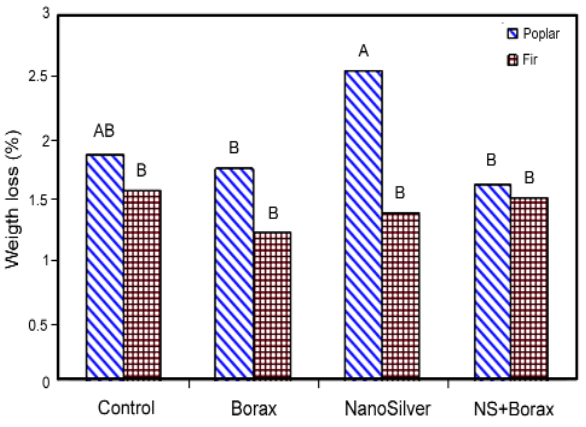

Figure 6: *Weight loss of the four treatments of both species of poplar and fir (%) (NS=nanosilver) (Letters on each column indicate Duncan grouping at 95% confidence level).*

4. DISCUSSION

In all cases, significant difference was observed between the controls treatments of the two species of poplar and fir, although their density was rather close. This may imply that the structure of the species may be significant with regard to the fire-retardant properties of a particular species. Also, the results of the four properties showed that in both species, NS-impregnated specimens were rather close to control treatment although there were some improvements in fire-retarding properties. Similar conclusions were previously reported using another kind of apparatus [4]. Only the weight loss showed a significant increase in NS-impregnated poplar specimens. This significant increase in weight loss was due to the heat-transferring property of silver nanoparticles [7-12] resulting in weight loss being also occurred in the deeper parts as well as the surrounding areas of the burning spot.

Cluster analysis was carried out to give an overall perspective on the similarity or diversity among the four treatments of poplar based on the

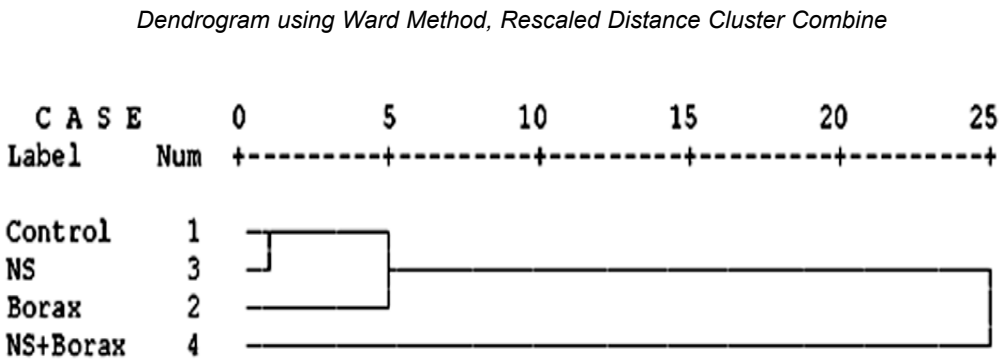

Figure 7: *Cluster analysis of the four treatments of poplar based on the five fire-retarding properties (ignition time, glowing time, fire endurance, carbonized area, and weight loss) (NS=nanosilver).*

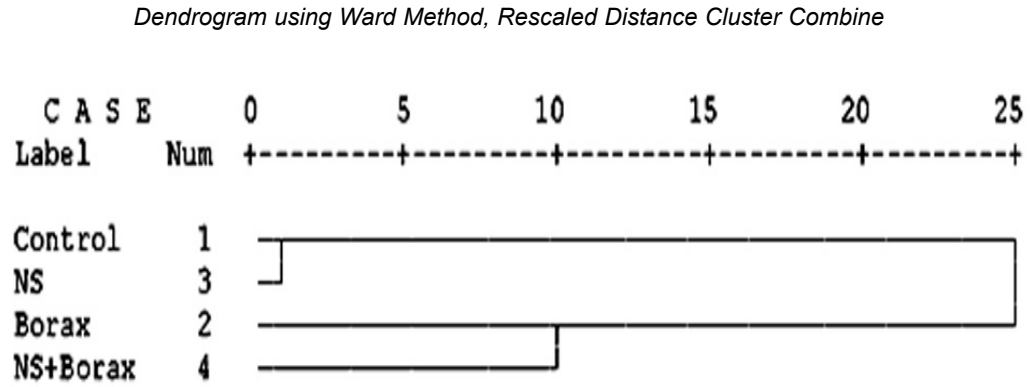

Figure 8: *Cluster analysis of the four treatments of fir based on the five fire-retarding properties (ignition time, glowing time, fire endurance, carbonized area, and weight loss) (NS=nanosilver).*

five fire-retarding properties (ignition time, glowing time, fire endurance, carbonized area, and weight loss). The obtained results from the cluster analysis indicated that control and nanosilver-impregnated specimens were clustered closely (Figure 7). Also, Borax-impregnated specimens showed significant difference in most properties (Figures 2-6); so it could have been expected that it would be clustered differently from control treatment (Figure 7).

Combination of the heat-transferring property of silver nanopartilces and fire-retarding property of Borax resulted in a significant improvement in fire-retarding properties in poplar; NS+Borax-impregnated treatment was therefore clustered quite differently from other treatments in poplar (Figure 7). However, the results of cluster analysis showed rather different results in the softwood species. The fire-retarding properties of Borax-impregnated specimens showed the best results in fir (Figures 2-6); so, it was quite predictable that this treatment be clustered quite differently from control and NS-impregnated treatments.

NS+Borax-impregnated treatment showed more similarity to Borax-impregnated treatment in fir (Figure 8). Cluster analyses of the two species (Figures 7 and 8) clearly show the difference in reaction of the combined nanosilver+Borax suspension. In poplar, the best overall results were found in NS+Borax treatment (Figure 7), while in fir the best overall results were observed in Borax-impregnated specimens (Figure 8).

However, as to the vital importance of smoke production in the finaldetermination of the suitability of a new fire-retardant, the smoke production aspect of wollastonite nano-fibers should still will be studied in further research projects.

5. CONCLUSIONS

1- Softwoods and hardwoods react differently in their fire-retarding properties when impregnated with fire-retarding chemicals.

2- Combination of heat-transferring property of silver nanopartilces and fire-retarding properties of Borax results in improvement in the overall fire-retarding properties of both softwoods and hardwoods.

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