Article

Determination of metal corrosion of wood treated with new generation water borne preservatives combined with water repellents

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Abstract: In this study, the corrosion performances of ammonium copper quat (ACQ) and boric acid (BA) wood preservatives were investigated, with micronized copper quat (MCQ) and nano boron (NB) used as reference materials. In the study, Scots pine (Pinus sylvestris L.) wood samples were impregnated according to the full-cell process method with ACQ at 2.4% concentration, BA at 4% and MCQ and NB at 1%. The ACQ- and BA-impregnated samples were then impregnated for a second time using five different water-repellent materials: tall oil, linseed oil, sodium silicate, methyl hydrogen silicone and N'-N- (1, 8-Naphthalyl) hydroxylamine. Polyethylene glycol (PEG) 600 and aluminum sulfate were introduced as single impregnations in the form of homogeneous mixtures with the ACQ and BA. The corrosion properties of the impregnated and control samples, including metal weight loss (MWL) and corrosion depth, were examined. As a result, the MWL values of the ACQ-impregnated samples showed an increase compared to the control group. The MWL values of the MCQ-impregnated samples were lower than those of the samples impregnated with ACQ, whilst the MWL values of the BA-impregnated samples were higher than those of the samples impregnated with NB.

Keywords: alkaline copper quat (ACQ); boric acid (BA); micronized copper quat (MCQ); nano boron (NB); corrosion test

1. Introduction

Wood is a material that grows in the natural environment and, ln addition to corrosion, is affected by UV rays, humidity, rainfall, snow, moisture, white frost, wind, temperature, O_2 and polluting gases in the outdoor environment. As a result of moisture, corrosion occurs in the nails and screws used during the assembly of wooden materials used in construction, thus causing serious damage to the buildings. In the conventional sense, corrosion refers to the degradation of metals and alloys as a result of their chemical and electrochemical reactions with their surroundings. However, new findings indicate that non-metallic materials are also affected in a similar manner by environmental conditions. Corrosion is known as a surface phenomenon; in other words, it occurs at the interface, which is the place of contact between the metal and the environment [1]. Corrosion is the damage and loss incurred by metallic materials. Consequently, it leads to great loss in terms of safety issues as well as the economy. For example, fracturing in some important parts of an aircraft due to corrosion (e.g., corrosion fatigue, stress corrosion cracking) may cause the plane to crash. Corrosion is the most significant reason for the wastage of the world's limited metal resources. Almost half of the metallic materials produced annually become unusable by the end of the year because of corrosion. Although deactivated metallic materials can be partially utilized as scrap, one third of it is lost for further recycling. Corrosion pollutes the environment and also accelerates metal corrosion in the polluted environment. The loss of metal makes new metal production a necessity

and consequently, increases the amount of pollution in the atmosphere and water during its production [2].

Wood is a material that is naturally exposed to corrosion and may become more corrosive depending on the environment to which it is exposed and the modification applied. The extractive substances, wood moisture content and pH in the wood play an important role in the formation of corrosion. As a general rule, woods with a pH value of less than 4 are highly corrosive. If the ratio of moisture inside the wood is higher than 20%, corrosion formation is accelerated and the corrosion rate increases in parallel with the increase of moisture. If the wood gets wet, it can be exposed to corrosion at any temperature, but especially at high temperatures, despite being thoroughly dried. The corrosion rate values are expected to decrease in parallel with the decreasing of the absorbed water ratio. However, although chemical substances used during the impregnation process reduce the water uptake of the wood, the chemical properties of the materials cause corrosion [2-3].

The aim of this work was to determine the weight loss and corrosion of metal in contact with wood treated with ammonium copper quat (ACQ) and boric acid (BA) preservatives and to compare the findings with those of untreated wood and wood treated with micronized copper quat (MCQ) and nano boron (NB). The role of the impregnation substances in the reduction of corrosion due to the effect of moisture was also evaluated.

2. Materials and methods

Scots pine (Pinus sylvestris L.) timber having oven-dry density of 0.49 g/cm³ and average growth ring width of 0.2 cm was purchased from the Kartal Ahşap Company in Bartin, Turkey. The wood was cut into small-sized samples with the dimensions of 20 x 20 x 45 mm. The samples were free of knots and showed no visible evidence of infection by mold or fungi. The Alkaline copper quat (ACQ) and Micronized copper quat (MCQ) wood preservative were purchased from the Koppers Company, the boric acid (BA) from Eti Maden İşletmeleri and nano boron (NB) from Ege Nanotek Kimya Sanayi. Sodium silicate (SS), Aluminum sulphate (AS), Polyethylene glycol (PEG), methyl hydrogen silicone (MHS), N'-N- (1, 8-Naphthalyl) hydroxylamine (NHA-H) were purchased from Duzey laboratory chemicals and devices, all in Turkey.

The concentrations of the preservatives and their various formulations are listed in Table 1 together with the treatment descriptions. The variations formulated with BA.

Wood preservatives were prepared at different concentrations (Table 1) and were impregnated for 30 min under vacuum and then for 60 min under a pressure of 6 bar. The weight of the samples was recorded before impregnation (Mf) and after impregnation (Ms). The retention of the samples was calculated using Equation (1) below. Later, the samples were conditioned for two weeks in a climate-controlled cabinet at 20 °C and 65% relative humidity.

After the conditioning process, the samples to be subjected to the second impregnation process were dried at 103 °C until they reached oven dry weight. After recording the oven dry weights of the samples (M1), they were impregnated with the solutions prepared at different concentrations (Table 1) for 30 min under vacuum and then for 60 min under a pressure of 6 bar. After the second impregnation process, the samples were conditioned for one week in a climate-controlled cabinet at 23 °C and 65% relative humidity. After conditioning, the samples were allowed to dry at 80 °C for 2 d (M2). The weight percentage gain values (WPG%) of the samples after the impregnation were calculated using Equation (2).

For the tall oil (TO) impregnation, the oil/water emulsions were prepared with tall oil at the ratio of 1/1 (weight/weight). Sodium lauryl sulfate (SLS) was added at the ratio of 15% as the surface active agent. In preparation of the emulsion, the oil and surface active agent were thoroughly mixed with a blender (3000 rpm) and pure water was slowly added while the mixing continued. The prepared emulsion was then mixed in a magnetic mixer for 1 h. The NHA-H was prepared with a 0.1% concentration of methanol. Pure water was used for the preparation of the solutions of MHS, LO and SS.

Table 1. Impregnation Method of Variations and Samples Created.

Variations *	Treatment Description
2.4% ACQ	Impregnated with ACQ only
2.4% ACQ + 50% TO	1st impregnation with ACQ then 2nd impregnation with TO
2.4% ACQ + 100% LO	1st impregnation with ACQ then 2nd impregnation with LO
2.4% ACQ + 30% SS	1st impregnation with ACQ then 2nd impregnation with SS
2.4% ACQ, 20% PEG	Single impregnation by mixing ACQ and PEG
2.4% ACQ, 5% AS	Single impregnation by mixing ACQ and AS
2.4% ACQ + 5% MHS	1st impregnation with ACQ then 2nd impregnation with MHS
2.4% ACQ + 0.1% NHA-H	1st impregnation with ACQ then 2nd impregnation with NHA-H
1% MCQ	Impregnated with MCQ only
1% NB	Impregnated with NB only
TO	Impregnated with TO only
LO	Impregnated with LO only
SS	Impregnated with SS only
PEG	Impregnated with PEG only
MHS	Impregnated with MHS only
NHA-H	Impregnated with NHA-H only
* Variations with ACQ were also formulated with BA.	

Retention (kg/m3) = GxCX10/V (1)

where G is the amount of the impregnated material absorbed by the sample (Ms-Mf) (g), C is the concentration of the impregnation solution (%) and V is the sample volume (cm^3).

WPG (%)= (M2-M1)/M1 X 10 (2)

where M2 is the dry weight after impregnation (g) and M1 is the oven dry weight before impregnation (g).

The AWPA E12 [4] standard was used for the corrosion test. The wood samples were prepared in dimensions of 20 x 20 x 45 mm. The screws used were in diameters of 2.35 mm and 30 mm. Five samples were used for each variation. Screws were driven in the middle of the 45 x 20 mm surfaces of the air-dried samples.

Prior to being driven into the wood samples, the screws were washed with ethanol in order to clean them of any grease and sediments. The cleaned screw samples were numbered and their pre-test weights (M1) were determined at a sensitivity of 0.0001 g. The area of the metal was 0.000381465 m2 and the density was 1.18 kg/dm3. The samples were kept at 25 °C and 97% relative humidity for eight weeks.

After the test, the wood samples were split and the screws removed. The screw samples were cleaned by washing with 10% ammonium citrate. After cleaning, the screws were weighed (M2). By means of this data, the metal weight loss (MWL) in the screw samples was calculated using the formula given in Equation (3) and the depth of the formed corrosion was calculated via the formula in Equation (4).

Metal weight loss (g/m^2) = ((M1-M2))/(Metal area (m^2)) (3)

Corrosion (µm) = (Metal weight loss (g/m^2))/(Metal density (kg/dm^3)) (4)

Data were analyzed using the SPSS version 16.0 statistical package program based on a 95% confidence level. The data and the statistical differences between them were calculated by multiple variance analysis. The Duncan test was conducted in order to determine differences in the variances.

3 Results and discussion

The weight gain (%) values of the 20 x 20 x 45 mm samples used for the corrosion test after impregnation are presented in Figure 1.
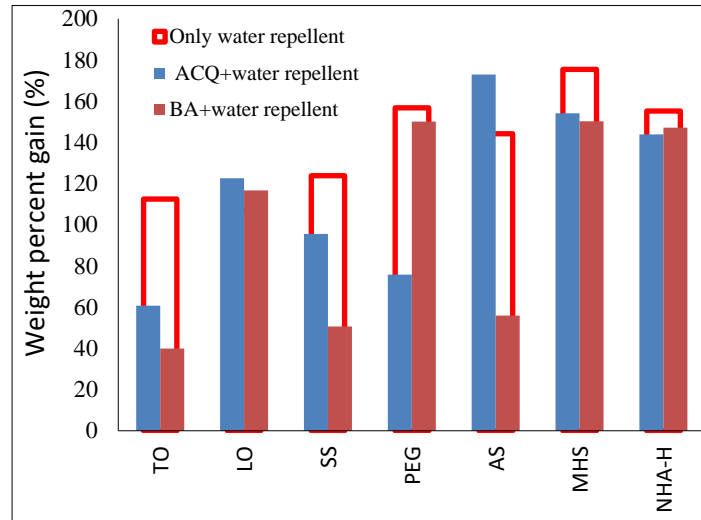

Figure 1. Weight percent gain values (%) of samples after impregnation.

Before impregnation with the water-repellent agents, a retention value of 14.95 kg/m3 was obtained in the samples impregnated with ACQ, 26.71 kg/m^3 in the samples impregnated with BA, 6.32 kg/m3 in the samples impregnated with MCQ and   6.63 kg/m^3 in samples impregnated with NB. When the samples were impregnated with water-repellent agents after the first impregnation with ACQ and BA, a lower WPG value was obtained (except for LO) compared to samples treated with the water-repellents alone. In the samples which were subjected to the second impregnation process after the impregnation with ACQ, the lowest weight gain (60.73%) was with TO and the highest (154.12%) was with the MHS. The polyethylene glycol (PEG), which was applied in a single impregnation mixed with the ACQ, demonstrated a WPG value of 75.82%, while 172.95% was obtained with the aluminum sulfate (AS) mixture.
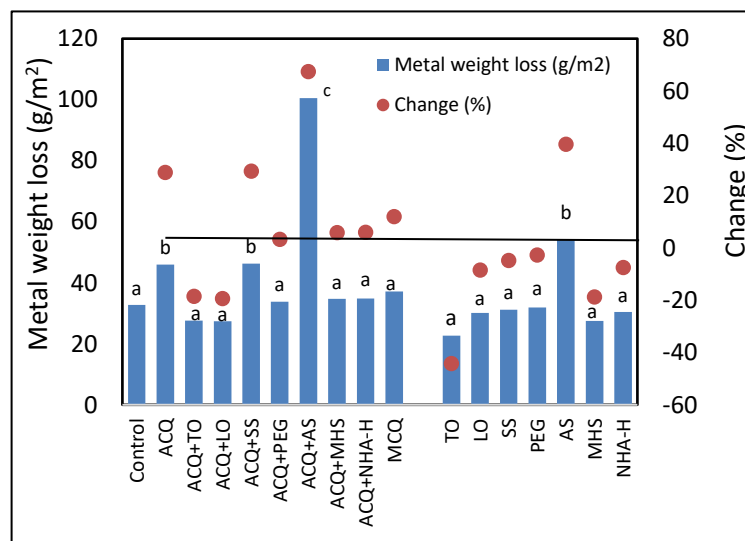

Figure 2. Metal weight loss (g/m^2) of samples impregnated with copper compounds and metal weight loss change (%) compared to the control.
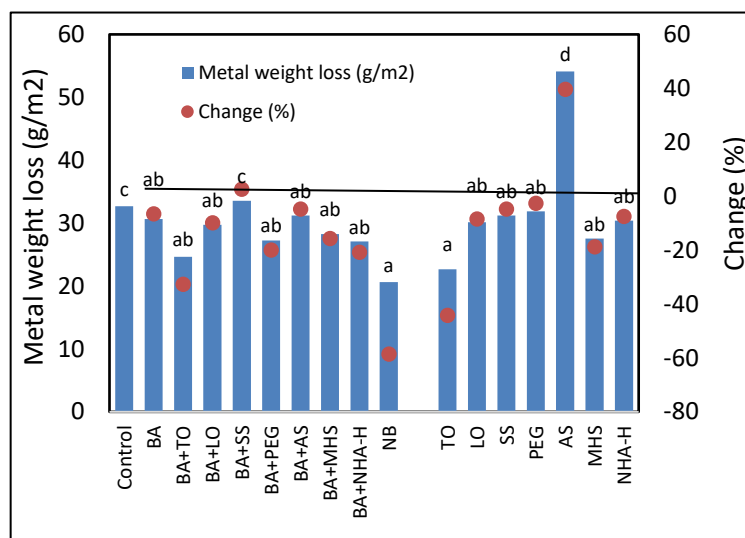
Figure 3. Metal weight loss (g/m²) of samples impregnated with boron compounds and metal weight loss change (%) compared to the control.

In the samples which were subjected to the second impregnation process after the impregnation with BA, the lowest weight gain (39.96%) was obtained with the TO and the highest (150.33%) with the MHS. The PEG, which was applied in a single impregnation mixed with the BA, yielded a WPG value of 150.09%, while 156.78% was obtained with the AS mixture. The weight gain values obtained were higher than the weight gain values obtained in samples impregnated with ACQ. High weight gain values were observed in the impregnation processes with water-repellent materials only. The highest weight gain (175.48%) was observed with MHS and the lowest in samples impregnated with LO.

The ACQ and BA materials in combination with water-repellents, the MCQ and NB samples and the MWL values (g/m²) obtained with them, their control samples and the different values of the formulated variations compared to the controls are shown in Figures 2 and 3. In addition, the corrosion depth (µm) of the samples and the differences generated by the variations compared to the control are shown in Figures 4 and 5.
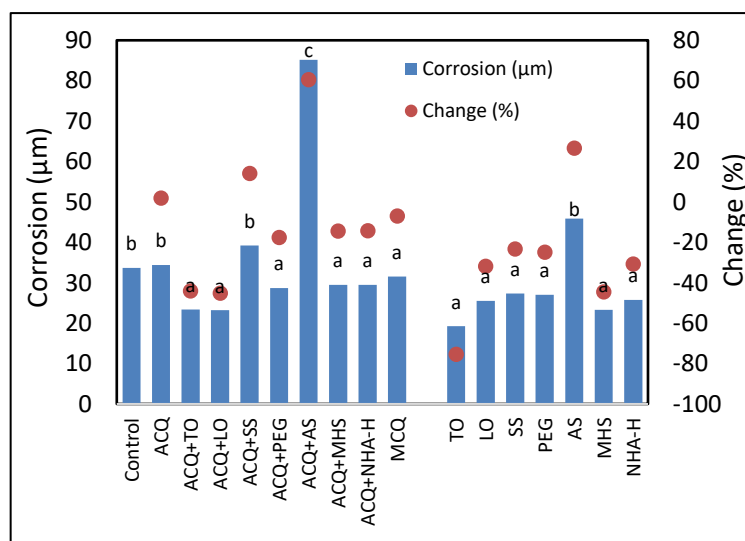

Figure 4. Corrosion depth (µm) of samples impregnated with copper compounds and corrosion depth change (%) compared to the control.
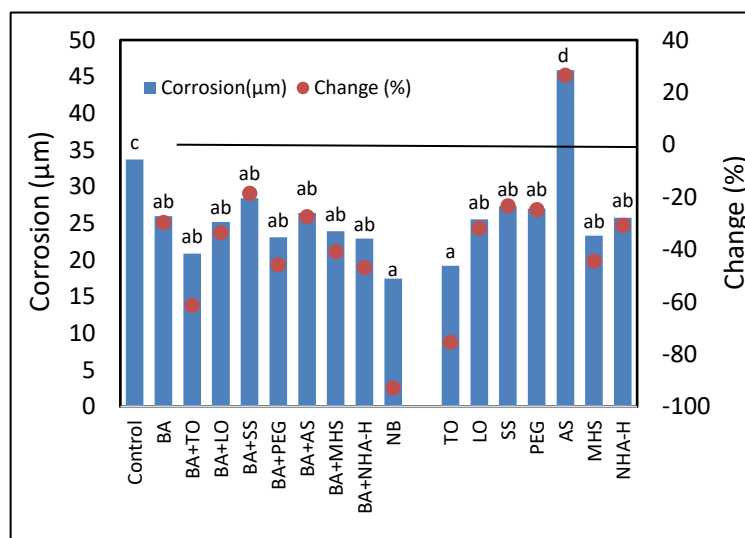
Figure 5. Corrosion depth (μm) of samples impregnated with boron compounds and corrosion depth change (%) compared to the control.

The MWL with the Scots pine wood samples used in the study was found to be 32.70 g/m² and the corrosion depth was found to be 33.70 μm.1 In corrosion studies using spruce and black larch, metal weight losses of 301.2 g/m², 256.6 g/m² and corrosion depths of 38.61 μm and 32.9 μm were obtained, respectively. The low MWL values obtained in this thesis study can be attributed to the differences between the wood and the metal used. After the impregnation process, the MWL values with the ACQ-impregnated samples increased compared to the control, which showed a statistical difference between the control and the ACQ (p >0.05). Corrosion formation was increased due to the Cu+ ions in the wood materials that were impregnated with copper compounds [5-6]. Studies In the literature have emphasized that the corrosion rate increases in parallel with the increase of copper concentration [5,7-8].

When examining the combinations of ACQ with water-repellent agents, the MWL values decreased in all variations except for that of the AS. The minimum MWL was obtained as 27.39 g/m² with LO used at 100% concentration, while the maximum MWL was obtained as 100.49 g/m² with AS used at a concentration of 5%. The ACQ (67% copper oxide, 33% DDAC) and AS [Al2 (SO₄)₃] materials were mixed together for the single impregnation. It was thought that the copper oxide in this mixture formulation reacted to the sulfate and formed copper (II) sulfate (CuSO₄) and that this resulting CuSO4 increased the MWL values. In contrast, the MWL with the single impregnation using the BA and AS mixture was not as high as that of the variation using ACQ (100.49 g/m²) [9]. As in all copper compounds, copper sulfate also possesses a highly corrosive characteristic. One study in the literature pointed out that aluminium sulfate used as a fire retardant demonstrated a corrosive characteristic [10].

The LO and TO significantly reduced the MWL values. This is mainly due to the low water intake of the oil-treated wood samples. Although the moisture content of the control samples was 22.64% at the end of the test, the moisture content values of the samples impregnated with TO and LO were 18.14% and 13.50%, respectively. After the impregnation process, the water intake rate of the wood decreases because the hemicelluloses and OH groups connected to the cellulose are blocked as the cell walls are filled with oil and thus, the moisture content, which accelerates the formation of corrosion, can be lowered [11].

The BA, which is not as corrosive as ACQ, reacts like a mild acid and may cause corrosion in metals. In the wood samples impregnated with BA, 30.67 g/m² of MWL occurred. Statistically, this was at the same level as the control (p >0.05). The lowest MWL with the variations formulated with BA was obtained in the samples impregnated with TO (24.64 g/m²) and the highest in samples impregnated with SS (33.55 g/m²). In the case of water-repellent agents used alone, the maximum MWL value was obtained in samples impregnated with AS (54.13 g/m²), while the minimum MWL

value was obtained in samples impregnated with TO (22.68 g/m²). When examining the chemical substances used in micro and nano sizes, it was observed that the metal loss and the corrosion depth generated were significantly reduced with both MCQ and NB compared with macro-sized agents. The MWL was found to be 37.16 g/m² and the corrosion depth 31.49 μm in the sample groups impregnated with MCQ, whereas the MWL was 20.62 g/m² and the corrosion depth 17.48 μm in the sample groups impregnated with NB. The MWL that occurred in the NB stood out as the lowest MWL among all variations. The MCQ material with its copper content had an MWL value close to the control (37.16 g/m²) and statistically, there was no difference between them. Studies in the literature examining corrosion properties of impregnated materials emphasized that MCQ impregnation materials had a less abrasive impact [5]. Furthermore, in another study it was stated that the copper content in MCQ was higher than the copper content in ACQ, but that it had a less abrasive effect due to the fact that the copper in MCQ is water insoluble [12-13].

4. Conclusion

As is known, copper compounds cause corrosion in metals. In our study, the MWL values obtained using the variations formulated with ACQ were found to be higher than in the control samples. There were statistically significant differences in metal weight losses between the samples impregnated with ACQ and the control samples (p <0.05). The maximum MWL was obtained in samples impregnated with ACQ+AS. With some formulation variations, the corrosive impact of the ACQ material was reduced.

The MWL values of the samples impregnated with MCQ were lower than of those impregnated with ACQ.

The samples impregnated with BA exhibited results similar to those of the control samples. The MWL values of the samples impregnated with NB were lower than those of the samples impregnated with BA.

In samples impregnated with water-repellent agents only, the maximum MWL values were obtained with samples impregnated with AS.

Corrosion is an important problem with copper compounds. The results we have obtained in our study confirm this situation. In the variations formulated with ACQ, the MWL values after corrosion testing were significantly reduced with some of the variations. It is recommended that, for use in places where corrosion risk is high, wooden materials be impregnated with ACQ variations formulated with water-repellent agents.

Author Contributions: A.C. and H.S. designed the research; A.C. performed the experiment, H.S. performed chemical analyses; A.C. analyzed the data; A.C. and H.S. wrote the paper. All authors discussed and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest

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