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ORIGINAL ARTICLE

Coloration Technology

Accelerated weathering performance of Scots pine preimpregnated with copper-based chemicals before varnish coating Part:1 coated with cellulosic and polyurethane varnishes

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Abstract
This study aimed to determine the effect of accelerated weathering on gloss, surface hardness and colour changes of Scots pine (*Pinus sylvestris* L.). Test samples were impregnated with Adolit KD-5, Wolmanit CX-8 and Celcure AC-500 covered with cellulosic and polyurethane varnishes. The results showed that the values of surface hardness and gloss increased after accelerated weathering. While the surface hardness of Scots pine was increased for impregnated and polyurethane-coated varnish, it decreased for impregnated and cellulosic varnish-coated Scots pine after 1000 hours of accelerated weathering exposure. Copper-based chemical impregnation and varnish coating developed the gloss of Scots pine specimens relative to the surface characteristics observed in single-coated Scots pine specimens. While the most appropriate chemical was Celcure AC-500 for surface hardness, it was Adolit KD-5 for the gloss of Scots pine after 1000 hours of accelerated weathering exposure. Wood specimens impregnated prior to the application of varnish were more effective in stabilising the colour of Scots pine than Scots pine only coated with varnish. Polyurethane varnish-treated Scots pine showed better colour stability for each partial and total accelerated weathering exposure period. The total colour changes were lowest for polyurethane varnish-coated Scots pine impregnated with Celcure AC-500 after 1000 hours of accelerated weathering exposure.

1 | INTRODUCTION

Wood is one of the most popular and indispensable biomaterials because it has excellent properties with high application potential and aesthetic appeal. This enables its use for furniture and in building construction as an insulation material.[1,2] However, exposed wood under external conditions must be protected from biotic and abiotic erosion.[3] When wood materials are used in outdoor applications, ultraviolet (UV) light, temperature and humidity destroy the lignocellulosic network of the wood.[4,5] Impregnation and surface coating are the most widely used methods to slow down the deterioration process and to extend the life of the wood.[3,6] Wood treated with copper preservatives gives excellent results when applied according to the specifications of preservatives.[7] It is known that copper-based compounds usually appear to be resistant to UV rays.[8]

While, in the past, copper was mixed with chromium and arsenic compounds in wood preservation, the new generation of copper-based wood preservatives is based on nanotechnology, including micronised copper and amines. Thus, copper-based wood preservatives such as Adolit-KD-5 (AD-KD-5), Tanalith-E (TN-E), Wolmanit CX-8

(WCX-8) and Celcure AC-500 (CAC-500) are now commonly being used in the forestry products industry.[1,9] The coating of varnishes is also the simplest and most common method for conserving wood under weather conditions while at the same time giving a natural appearance to wood.[10,11] Generally, chemical treatments of wood present a physical barrier by protecting the wood from weathering effects, but such treatments are inadequate. For this reason, several studies have reported that impregnation and varnishing both contribute to the long-term protection of wood surface properties against weathering.[1,12,13]

The colour changes and softening of the wood surface are defined by weathering degradation, and are followed by gloss loss, checking and roughening. All of these are caused by deformation of wood components due to weathering effects.[8] The influence of accelerated weathering on Scots pine wood samples impregnated with copper-based chemicals and coated with polyurethane varnish (PV) and synthetic varnish was studied by Baysal et al.[12] The experimental results of the study showed that accelerated weathering caused a decrease in the gloss of wood samples and an increase in the surface hardness of impregnated and varnished samples. In another study, Turkoglu et al[1] examined the weathering durability of impregnated and coated Oriental beech and Scots pine. The authors reported that, after weathering, the best colour stability was achieved by Oriental beech and Scots pine wood samples impregnated with TN-E before PV coating.

Yalcin et al[14] investigated the surface properties of Oriental beech wood samples treated with tannins and TN-E before PV, water-based varnish and cellulosic varnish (CV) after accelerated weathering. The authors found that total colour changes increased in both the control specimens and the impregnated specimens exposed to weathering periods ranging from 100 to 300 hours. After accelerated weathering, in terms of varnish type, the lowest colour change values were obtained with PV, followed by water-based varnish and then CV. The authors also reported that PV had highest surface hardness, followed by water-based and cellulosic coatings.[14] Improving the durability and surface performance of wood with various applications for weathering conditions is important for its value.

Therefore, in this study, the aim was to determine the influence on gloss, surface hardness and colour stability of Scots pine wood treated with AD-KD-5, WCX-8 and CAC-500 and covered with PV and CV after accelerated weathering.

2 | EXPERIMENTAL

2.1 | Preparation of wood specimens and chemicals

The 6 × 75 × 150 mm (radial by tangential by longitudinal) specimens were prepared from air-dried Scots pine (*Pinus sylvestris* L.) sapwood. AD-KD-5 consists of 10% didecylpolyoxethylammonium borate, 20.53% copper(II) hydroxydecarbonate and 8% boric acid. WCX-8 comprises 13.0% copper(II) carbonate hydroxide, 2.8% copper and 4.0% boric acid.[15] CAC-500 contains a quaternary system of alkaline copper comprising 5.0% boric acid, 16.63% copper(II) carbonate hydroxide and 4.8% benzalkonium chloride.[16] Aqueous solutions of chemicals with a concentration of 3% were prepared before the tests. Nine replications were produced for each group.

2.2 | Impregnation procedure

In accordance with American Society for Testing and Materials Standards (ASTM D1413-07e1), Scots pine samples were impregnated with a 3% liquid solution of CAC-500, AD-KD-5 and WCX-8.[17] In this study, a vacuum desiccator was used for the impregnation process and it was connected to a vacuum pump via a vacuum trap. A vacuum was applied for 30 minutes at 760 mm Hg before adding the solution into the chamber, followed by an additional diffusion for 30 minutes at 760 mm Hg under vacuum. The Scots pine samples were conditioned at 20°C and 65% relative humidity for 3 weeks prior to testing.

After the impregnation process, retention values were calculated using Equation 1:

$$\text{Retention} = [(G \times C)/V] \times 10 \quad (\text{kg m}^{-3}) \tag{1}$$

where $G = (T_2 - T_1)$ is the treatment solution absorbed by the Scots pine samples (g), T_1 is the dry weight of the Scots pine samples before impregnation (g), T_2 is the weight of the Scots pine samples after impregnation (g), C is the percentage concentration and V is the volume of Scots pine samples (cm^3).

2.3 | Coating of the wood surfaces

As coating materials, PV and CV were applied over impregnated Scots pine wood. In accordance with ASTM D3023-98, the varnishes were applied to the impregnated and coated Scots pine specimens with a spray gun.[18] Sufficient time for the sedimentation of the layer was left between successive applications before reaching the target retention of 100 g m^{-2} for the primary, and 100 g m^{-2} for the upper coatings, controlled by consecutive weighings. The filler was used as the first coating applied to the Scots pine surface to fill the voids, and the second and third coatings were applied to the top coat. The Scots pine wood samples were left under ambient conditions for 24 hours in accordance with the manufacturer's recommendations after the first coat, and then softly sanded using fine-grained sandpaper (220 grit) to obtain a smooth surface before the top coating. After the finishing coat of the varnishes had been applied to the wooden surfaces, the test pieces were conditioned for 3 weeks.

2.4 | Surface hardness test

The surface hardness of Scots pine wood samples was measured in accordance with ASTM D 4366-14 as the König hardness test system[19] standard.

2.5 | Gloss test

The gloss test was performed in accordance with the ASTM D523-14[20] standard. The glossiness of wood specimens was measured at a 60° angle of incidence using a gloss meter.

2.6 | Colour test

The colour parameters L^*, a^* and b^* were measured by the CIELab method. The parameters $+a^*$ and $-a^*$ indicate red and green colours, respectively. The $+b^*$ parameter is yellow, while $-b^*$ is blue. The L^* value can range from 100 (white) to zero (black).[21] The total colour change (ΔE^*) was determined for Scots pine according to ASTM–D 2244-14.[22] In this study, the colour changes were determined using Equations 2-5.

$$(\Delta E^*) = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2} \quad (2)$$

$$\Delta a^* = a_f^* - a_i^* \quad (3)$$

$$\Delta b^* = b_f^* - b_i^* \quad (4)$$

$$\Delta L^* = L_f^* - L_i^* \quad (5)$$

The values Δa^*, Δb^* and ΔL^* indicate the differences between the initial (a_i*, b_i* and L_i*) and final (a_f*, b_f* and L_f*) colour values.

2.7 | Accelerated weathering test

The accelerated weathering experiment was performed according to the American standard ASTM G154-06 in a Q-Panel Company (QUV) weathering tester with eight ultraviolet florescent lamps (UVA 340).[23] The samples were exposed to UV irradiation cycles for 8 hours, followed by condensation for 4 hours in a QUV apparatus for 250, 500, 750 and 1000 hours. During the weathering period at the maximum intensity (λ_{max} = 340 nm), the average irradiance was 0.89 W m^{-2}. The temperature was 50°C during the condensation period and it was 60°C during the light irradiation period.

2.8 | Statistical evaluations of test results

Test results were analysed by a computerized SPSS statistical program include analysis of variance and Duncan test applied at 95% confidence level. Statistical evaluations were made on homogeneity groups (HG) where different letters reflected statistical significance.

3 | RESULTS AND DISCUSSION

3.1 | Surface hardness changes

Table 1 shows surface hardness values and the retention of Scots pine wood specimens due to the chemical load. As a result of the experiments, the retention values of the Scots pine wood samples were found to be 14.36, 15.12, and 14.60 kg m^{-3} for impregnation with AD-KD-5, WCX-8 and CAC-500, respectively. Before the accelerated weathering test, the surface hardness values measured for the PV- and CV-coated Scots pine wood samples were 24.00 and 18.33, respectively. The surface hardness of PV-coated Scots pine was higher than CV-coated Scots pine wood. Thus, PV completes its polymerisation reaction on the wood surface and chemically bonds with the wood, and therefore demonstrates stronger adhesion to the surface.[24] Large molecules created by copolymerisation reactions from urethane alkyd (PV) layers and strong molecular cohesion increase pendulum hardness values.[25] Copper-based preimpregnation before both varnish coatings resulted in an increase in the wood surface hardness before accelerated weathering exposure. Toker et al[26] studied the Calabrian pine wood surface hardness characteristics. They found that borate pretreatment before varnish coating improved the surface hardness of the Calabrian wood surface. Baysal[27] investigated the surface hardness of Oriental beech wood preimpregnated with copper-chromium-boron (CCB) before varnish coating, and found that CCB pretreatment before varnish coating increased the surface hardness of the Oriental beech wood surface compared with the wood surface which was only varnish-coated. In a similar investigation, Baysal et al[12] noted that pretreatment with copper-containing preservatives such as AD-KD-5 and TN-E before PV coating improved the surface hardness of Scots pine compared with Scots pine wood surfaces which were only PV-coated. The results of this study are compatible with those conducted by Toker et al,[26] Baysal[27] and Baysal et al.[12]

In this study, as a result of the first period of accelerated weathering (0-250 hours), all the impregnated and coated wood surfaces hardened. Surface hardness values of impregnated and CV-coated Scots pine were higher than impregnated and PV-coated Scots pine. While preimpregnation before PV coating improved the hardness of Scots pine, preimpregnation before CV coating caused a reduction in the surface hardness of Scots pine. After the second accelerated weathering period (250-500 hours), although the surface hardness values of preimpregnated and PV-coated Scots pine increased, the surface hardness of impregnated and CV-coated Scots pine decreased. Moreover, decreases in the surface hardness of Scots pine which was only CV-coated were greater than those in impregnated and CV-coated Scots pine. After the third accelerated weathering period (500-750 hours), the surface hardness of impregnated and coated Scots pine decreased. This decrease was greater for impregnated and PV-coated Scots pine compared with impregnated and CV-coated Scots pine. After the fourth accelerated weathering period (750-1000 hours), although surface hardness values of impregnated and PV-coated Scots pine slightly increased, they decreased by 17.88%-23.95% for impregnated and CV-coated Scots pine. The Scots pine wood surface hardened over the total exposure time (0-1000 hours); surface hardness increased by 38.89%-60.91% for impregnated and PV-coated Scots pine, and increased by 13.78%-70.30% for impregnated and CV-coated Scots pine. The results showed that although preimpregnation with chemicals before PV coating caused an increase in surface hardness, it caused a decrease in impregnated and CV-coated Scots pine. Also, impregnated and CV-coated Scots pine wood surfaces softened during the second, third and fourth accelerated weathering exposure periods, but hardened by 13.78%-70.30% after 1000 hours of accelerated weathering exposure. Except for the third exposure period (500-750 hours), impregnated and PV-coated Scots pine wood surfaces were hardened by all accelerated weathering exposure periods, and by 38.89%-60.91% after 1000 hours of accelerated weathering exposure. The results showed that impregnated and coated Scots pine wood surfaces hardened after 1000 hours of exposure to weathering conditions. While copper-based chemical treatments reduced the degradation of PV-coated Scots pine wood specimens after 1000 hours of accelerated weathering, they softened CV-coated Scots pine specimens after 1000 hours of accelerated weathering exposure. Yalinkilic et al[28] studied the surface hardness of Scots pine wood and chestnut wood preimpregnated with CCB before PV coating after outdoor exposure, and reported that preimpregnated and PV-coated Scots and chestnut wood surfaces became harder under outdoor exposure conditions. Baysal et al[12] investigated the hardness of Scots pine wood samples treated with copper-containing chemicals before PV surface coating, and found that accelerated weathering improved the hardness of impregnated and varnished Scots pine. In another study, Turkoglu et al[1] tested the surface hardness of wood pretreated with copper-containing impregnates before PV coating after 3 months of outdoor exposure. The authors found that the surface hardness of Oriental beech and Scots pine wood before PV coating preimpregnated with chemicals was higher than PV-coated Oriental beech and Scots pine wood after 3 months of outdoor exposure. The results of this study are in good agreement with the aforementioned studies.[1,12,28] The importance of the type of varnish upon surface hardness has been demonstrated.[29] Atar et al[30] noted that polyurethanes are a unique class of polymers that can be used in many applications because their properties

TABLE 1 Surface hardness values of Scots pine wood specimens before and after each accelerated weathering (AW) period

Impregnation chemicals and varnish application	Retention, kg m^{-3}	Before AW	AW: After the first period (0-250 h) Mean	Change, %	After the second period (250-500 h) Mean	Change, %	After the third period (500-750 h) Mean	Change, %	After the fourth period (750-1000 h) Mean	Change, %	Comparison of before AW and after 1000 h AW, %
PV	–	24.00	31.89	32.87^{F}	36.78	15.33^{C}	33.00	−10.27^{DE}	33.33	1.01^{C}	38.89^{D}
AD-KD-5 + PV	14.36	26.33	39.00	48.10^{E}	42.67	9.40^{D}	39.44	−7.55^{CE}	40.44	2.54^{B}	53.59^{C}
WCX-8 + PV	15.12	26.33	35.22	33.76^{F}	44.11	25.24^{A}	39.22	−11.08^{E}	39.89	1.70^{BC}	51.48^{C}
CAC-500 + PV	14.60	24.44	33.00	35.00^{F}	39.56	19.87^{B}	37.78	−4.49^{A}	39.33	4.12^{A}	60.91^{B}
CV	–	18.33	49.11	167.88^{A}	42.00	−14.48^{F}	40.89	−2.65^{A}	31.22	−23.64^{F}	70.30^{A}
AD-KD-5 + CV	14.36	30.11	50.56	67.90^{D}	47.33	−6.37^{E}	44.11	−6.81B^{C}	36.22	−17.88^{D}	20.30^{F}
WCX-8 + CV	15.12	28.22	49.11	74.02^{C}	45.33	−7.69^{E}	42.22	−6.86^{BC}	32.11	−23.95^{F}	13.78^{G}
CAC-500 + CV	14.60	22.44	45.89	104.46^{B}	40.44	−11.86^{F}	38.78	−4.12^{AB}	30.56	−21.20^{E}	36.14^{E}

Note: AD-KD-5, Adolit KD 5; AW, accelerated weathering; CAC, Celcure AC-500; CV, cellulosic varnish; h, hour; PV, polyurethane varnish; WCX, Wolmanit CX. Capital letters represent homogenity groups obtained by statistical analysis.

TABLE 2 Changes in gloss values of Scots pine wood specimens before and after each accelerated weathering (AW) period

Impregnation chemicals and varnish application	Before AW	AW: After the first period (0-250 h) Mean	Change, %	After the second period (250-500 h) Mean	Change, %	After the third period (500-750 h) Mean	Change, %	After the fourth period (750-1000 h) Mean	Change, %	Comparison of before AW and after 1000 h AW %
PV	98.97	112.56	13.73^{E}	107.44	−4.54^{E}	104.76	−2.50^{C}	105.13	0.35^{E}	6.23^{F}
AD-KD-5 + PV	95.40	110.78	16.12^{D}	108.30	−2.24^{D}	107.89	−0.38^{A}	108.38	0.45^{DE}	13.60^{D}
WCX-8 + PV	97.68	111.22	13.87^{E}	105.07	−5.53^{F}	104.11	−0.91^{AB}	104.99	0.84^{C}	7.48^{F}
CAC-500 + PV	94.70	111.78	18.03^{C}	105.20	−5.88^{F}	104.26	−0.89^{AB}	104.72	0.44^{DE}	10.58^{E}
CV	72.86	79.21	8.72^{F}	81.37	2.72^{C}	79.58	−2.20^{C}	80.02	0.56^{D}	9.84^{E}
AD-KD-5 + CV	47.42	58.31	22.96^{A}	61.60	5.64^{B}	61.23	−0.60^{AB}	62.18	1.54^{A}	31.12^{A}
WCX-8 + CV	58.93	66.63	13.07^{E}	71.48	7.27^{A}	70.77	−0.99^{B}	71.64	1.24^{B}	21.57^{C}
CAC-500 + CV	53.20	64.52	21.28^{B}	68.20	5.70^{B}	67.54	−0.97^{B}	67.96	0.62^{D}	27.74^{B}

Note: AD-KD-5, Adolit KD 5; AW, accelerated weathering; CAC, Celcure AC-500; CV, cellulosic varnish; h, hour; PV, polyurethane varnish; WCX, Wolmanit CX.
Capital letters represent homogenity groups obtained by statistical analysis.

can be adapted to suit the variation of their components. The polyurethane coating improves the surface hardness of the wood more than the synthetic varnish coating.[10,31] The results showed that among impregnation chemicals, CAC-500 was found to be the most suitable impregnation chemical followed by AD-KD-5 and then WCX-8 in terms of surface hardness changes after 1000 hours of accelerated weathering exposure.

3.2 | Gloss changes

The results of gloss values for Scots pine wood before and after accelerated weathering are given in Table 2. Glossiness is an important property of coated wood materials when the objective is to give the surface a decorative or aesthetically pleasing appearance.[32,33] The gloss values of PV-coated Scots pine were much higher than those of CV-coated Scots pine prior to accelerated weathering. The gloss values measured before accelerated weathering testing were 98.97 and 72.86 for the PV- and SV-coated Scots pine wood samples, respectively. Pretreatment with copper-containing chemicals caused a reduction in gloss values of Scots pine for both varnish types, in particular for the CV-coated wood surface. Baysal[34] determined that copper-chromium arsenic (CCA) impregnation limited the lightness received by a Scots pine prior to accelerated exposure to the weather. Ozdemir et al[35] found that water-based wood preservatives increased the porosity of the surface and that the gloss values of the wood decreased. Chemicals can limit the gloss to a certain extent in test specimens before weathering. These results may be due to the absorption and dispersion of the rays reflected by the salt crystals that dominate in the lights of the vessels in large sections of the first grains of wood. Photoactive ions present on the surface of wood are assumed to cause gloss loss of the coated wood prior to weathering.[28] This result is consistent with the gloss values of the CCB-treated pine, as well as TN-E- and AD-KD-5-impregnated Scots pine and Oriental beech before varnish coating.[1,28]

After the first accelerated weathering period (0-250 hours), gloss values of all the impregnated and coated wood surfaces increased. This increase was from 13.73% to 18.03% and 8.72% to 22.96% for impregnated, and PV- and CV-coated Scots pine, respectively. Impregnation with chemicals before both varnish coatings caused an increase in the gloss values of Scots pine wood. At the end of the second accelerated weathering period (250-500 hours), while the gloss values of pretreated and PV-coated wood specimens decreased from 5.88% to 2.24%, gloss values of treated and CV-coated wood specimens increased by 2.72% to 7.27%. After the third accelerated weathering period (500-750 hours), gloss values of impregnated and both coated varnishes slightly increased from 2.5% to 0.38% and from 2.20% to 0.6% for PV- and CV- coated Scots pine, respectively. After the fourth accelerated weathering period (750-1000 hours),

TABLE 3 Colour changes in Scots pine wood specimens before and after each accelerated weathering (AW) period

Impregnation chemicals and varnish application	Before AW			After the first AW period (0-250 h)				After the second AW period (250-500 h)				After the third AW period (500-750 h)				After the fourth AW period (750-1000 h)			
	L_i^*	a_i^*	b_i^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*
PV	65.8	9.7	39.4	−9.4	5.6	7.5	13.2^{B}	−1.3	0.9	−4.5	4.8^{C}	−1.6	0.8	−0.1	1.7^{CD}	−1.6	1.1	−0.7	2.0^{DE}
AD-KD-5 + PV	36.8	3.1	24.6	−1.7	5.2	2.0	5.8^{F}	−0.9	1.0	3.2	3.5^{E}	0.6	0.3	−0.3	0.7^{E}	−1.3	1.0	2.2	3.0^{DE}
WCX-8 + PV	46.6	3.7	28.4	−4.4	7.0	6.7	10.7^{C}	−0.2	0.9	−3.5	3.6^{DE}	−1.0	1.0	1.7	2.2^{C}	−1.3	1.1	0.8	1.9^{E}
CAC-500 + PV	40.8	4.8	28.7	−3.1	5.1	4.2	7.3^{E}	0.8	0.2	−3.9	4.0^{DE}	1.0	0.5	−0.9	1.0^{DE}	−1.3	1.1	2.2	2.8^{D}
CV	66.7	10.2	34.2	−15.7	8.6	13.0	22.1^{A}	−5.8	4.9	1.7	7.7^{A}	−7.0	4.0	−4.3	9.1^{A}	−5.1	0.2	−9.2	10.5^{A}
AD-KD-5 + CV	39.2	3.0	25.4	−1.8	6.2	6.6	9.2^{D}	−2.8	3.8	−0.6	4.8^{C}	−3.6	2.8	−7.2	8.5^{A}	−4.6	2.1	−0.3	5.1^{C}
WCX-8 + CV	49.8	3.5	31.9	−7.0	9.2	5.0	12.6^{B}	−4.5	4.4	0.8	$6.^{B}$	−3.7	2.4	−7.6	8.8^{A}	−6.1	1.8	−4.2	7.7^{B}
CAC-500 + CV	44.5	5.1	30.2	−3.8	9.6	5.0	11.5^{C}	−4.0	0.9	−0.8	4.2^{D}	−3.8	2.4	−4.5	6.4^{B}	−4.1	0.9	−6.0	7.3^{B}

Note: AD-KD-5, Adolit KD 5; AW, accelerated weathering; CAC, Celcure AC-500; CV, cellulosic varnish; h, hour; PV, polyurethane varnish; WCX, Wolmanit CX.L^*, a^* and b^*, colour parameters; Δa^*, Δb^* and ΔL, changes between the initial and final interval values; ΔE^*, total colour difference.
Capital letters represent homogenity groups obtained by statistical analysis.

gloss values of impregnated and both coated varnishes slightly increased from 0.35% to 0.84% and from 0.56% to 1.54% for PV- and CV-coated Scots pine, respectively. After the total exposure time (0-1000 hours), gloss values of the Scots pine wood surface increased. Gloss values for impregnated and PV-treated Scots pine increased from 6.23% to 13.60%, and increased from 9.84% to 31.12% for impregnated and CV-coated Scots pine. A slight effect on the gloss of wood specimens was observed as a result of accelerated weathering.[12] Scrinzi et al[36] reported that UV radiation had no major effect on the glossiness of coatings. According to the results of this study, preimpregnation with chemicals before both varnish coatings increased the gloss values of Scots pine after 1000 hours of accelerated weathering. While gloss values of treated and PV-coated test specimens of Scots pine slightly decreased after the second accelerated weathering (250-500 hours), during the third accelerated weathering period (500-750 hours) they decreased only slightly for impregnated and CV-coated Scots pine wood. In terms of gloss changes, after 1000 hours of accelerated weathering exposure, among the impregnation chemicals, AD-KD-5 was found to be the most appropriate to use, followed by CAC-500 and WCX-8.

3.3 | Colour changes

Table 3 displays ΔL^*, Δa^*, Δb^* and ΔE^* values of Scots pine before accelerated weathering periods and for accelerated weathering periods of 0-250, 250-500 and 750-1000 hours. The colour changes in wood samples before and after 1000 hours of accelerated weathering are given in Table 4. Figures 1 and 2 show the colour changes in impregnated and PV- and CV-coated Scots pine before and after each accelerated weathering period.

The L^* values measured before the accelerated weathering test were 65.8 and 66.7 for the PV- and SV-coated Scots pine wood samples, respectively. Pretreatment with copper-containing formulations resulted in a decrease in L^* values of wood for both types of varnish. Baysal et al[12] investigated colour changes in Scots pine wood specimens, which were impregnated with TN-E, Wolmanit CB (Copper Based) and AD-KD-5 and coated with polyurethane and synthetic varnishes. The authors found that preimpregnation with chemicals before varnish coating caused a decrease in L^* values. In another study, Turkoglu et al[13] examined the L^* values of Oriental beech treated with copper-containing chemicals, and reported that the L^* values of impregnated and coated Oriental beech were lower than those for Oriental beech which was only coated. The results of this study are compatible with the findings of the aforementioned research, and showed that a^* and b^* values of impregnated and coated Scots pine wood samples were lower than Scots pine wood samples which were only coated.

At the end of the first accelerated weathering period (0-250 hours), ΔL^* values of all the impregnated and coated wood surfaces decreased. Impregnation with chemicals

TABLE 4 Colour changes in Scots pine wood specimens before and after 1000 hours of accelerated weathering

Impregnation chemicals and varnish application	Before accelerated weathering			After 1000 h of accelerated weathering			After 1000 h of accelerated weathering			
	L_i*	a_i*	b_i*	L_f*	a_f*	b_f*	ΔL*	Δa*	Δb*	ΔE*
PV	65.8	9.7	39.4	52.1	18.0	41.8	−13.8	8.3	2.3	16.3^{E}
AD-KD-5 + PV	36.8	3.1	24.6	33.5	10.7	31.7	−3.3	7.6	7.1	10.9^{G}
WCX-8 + PV	46.6	3.7	28.4	39.7	13.7	34.2	−6.9	9.9	5.8	13.4^{F}
CAC-500 + PV	40.8	4.8	28.7	37.2	11.7	30.3	−3.6	6.9	1.6	7.9^{H}
CV	66.7	10.2	34.2	33.3	27.9	35.3	−33.5	17.7	1.2	37.9^{A}
AD-KD-5 + CV	39.2	3.1	25.4	26.5	17.9	23.9	−12.7	14.8	−1.5	19.6^{D}
WCX-8 + CV	49.8	3.5	31.9	28.5	21.3	25.9	−21.3	17.8	−6.0	28.4^{B}
CAC-500 + CV	44.5	5.1	30.2	28.8	18.9	23.9	−15.7	13.8	−6.3	21.9^{C}

Note: AD-KD-5, Adolit KD 5; AW, accelerated weathering; CAC, Celcure AC-500; CV, cellulosic varnish; h, hour; PV, polyurethane varnish; WCX, Wolmanit CX.L*, a* and b*, colour parameters; Δa*, Δb* and ΔL, changes between the initial and final interval values; ΔE*, total colour difference.
Capital letters represent homogenity groups obtained by statistical analysis.

before both varnish coatings caused ΔL* and ΔE* values of Scots pine to decrease. For example, ΔL* was only −9.4 and −15.7 for PV- and CV-coated Scots pine, respectively. ΔL* changed from −1.7 to −4.4 for impregnated and PV-coated Scots pine, and from −1.8 to −7.0 for impregnated and CV-coated Scots pine wood. The positive Δa* and Δb* values indicated that wood specimens maintained their reddish and yellowish tones, respectively. After the second accelerated weathering period (250-500 hours), except for CAC-500 impregnated and PV-coated Scots pine, all of the treated groups gave negative values. While ΔL* changed from −1.3 to 0.8 for impregnated and PV-coated Scots pine, it changed from −2.8 to −5.8 for impregnated and CV-coated Scots pine wood. Impregnation with chemicals before both varnish coatings caused decreases in ΔL* and ΔE* values of Scots pine. Impregnated and coated Scots pine showed positive Δa* values, indicating that the wood specimens maintained a reddish tone. After the third accelerated weathering period (500-750 hours), ΔL* values for impregnated and CV-coated Scots pine changed from −3.7 to −7.0. While the ΔL* values were negative for only PV-coated and WCX-8 + PV-treated Scots pine, they were positive for AD-KD-5 + PV- and CAC-500 + PV-treated Scots pine. Impregnation with chemicals before both varnish coatings generally caused the ΔL* and ΔE* values of Scots pine to decrease. While positive Δa* values indicate that wood specimens maintained a reddish tone, except for WCX-8 + PV-treated Scots pine, all of the other treatment groups showed negative Δb* values, indicating that the wood specimens turned a bluish tone.

After the fourth accelerated weathering period (750-1000 hours), while ΔL* changed from −1.3 to −1.6 for impregnated and PV-coated Scots pine, it changed from −4.1 to −6.1 for impregnated and CV-coated Scots pine wood. Impregnation with chemicals before both varnish coatings generally caused a decrease in ΔL* values for Scots pine. Impregnated and coated Scots pine showed positive Δa* values, indicating that wood specimens maintained a reddish tone. While impregnated and CV-coated Scots pine gave negative Δb* values, except for Scots pine which was only PV-coated, all of the other impregnated and PV-coated Scots pine samples gave positive Δb* values.

For the total exposure time (0-1000 hours), ΔL* changed from −3.3 to −13.8 for impregnated and PV-coated Scots pine, and from −12.7 to −33.5 for impregnated and CV-coated Scots pine wood. Impregnation with chemicals before both varnish coatings caused the ΔL* and ΔE* values of Scots pine to decrease. This may have been due to the varnish, which acts as a multilayer coating that can further reduce the diffusion of sunlight into the wood.[28] Impregnated and coated Scots pine showed positive Δa* values, indicating that wood specimens maintained a reddish tone after 1000 hours of accelerated weathering. While impregnated and PV-coated Scots pine showed positive Δb* values, except for CV-coated Scots pine, all the other impregnated and CV-coated Scots pine samples gave negative Δb* values after 1000 hours of accelerated weathering. Negative lightness stability values (ΔL*) show that wood tends to darken after accelerated weathering. The darkening of Scots pine may be due to the degradation of non-cellulosic polysaccharides and lignin.[37-39] As reported, ΔL* is one of the most important parameters for demonstrating wood surface quality.[40] In general, for the partial and the total accelerated weathering exposure time periods, ΔL* and ΔE* values of impregnated and CV-coated Scots pine were higher than those of impregnated and PV-coated Scots pine. For the partial and the total accelerated weathering exposure time periods, Scots pine gave positive values of Δa*, indicating that the wood tends to turn reddish. The results also showed that the ΔL* and ΔE* values of impregnated and coated Scots pine specimens were lower than those for Scots pine specimens which were only coated, for the partial and the total accelerated weathering exposure time

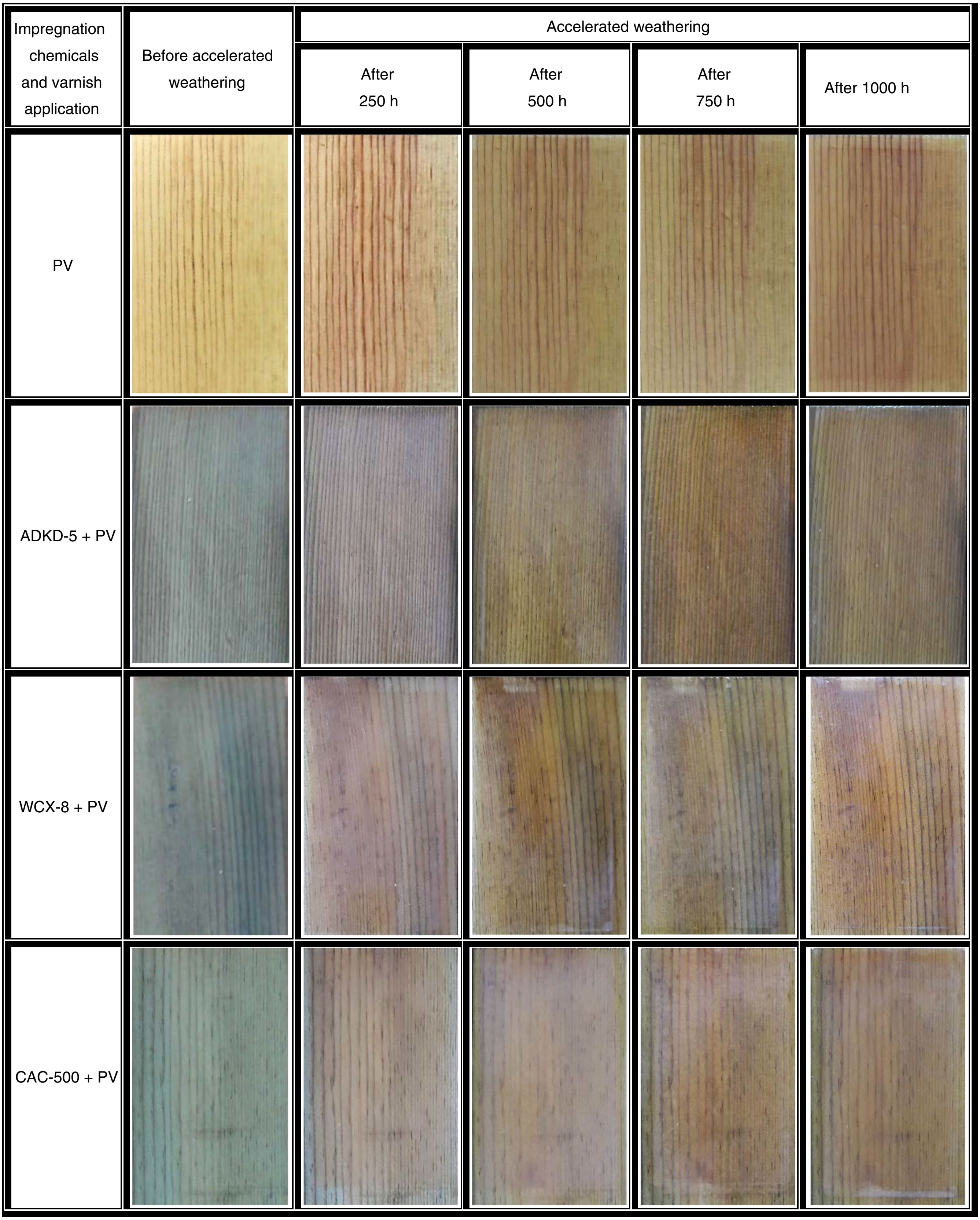

FIGURE 1 Colour changes of impregnated and polyurethane varnish (PV)-coated Scots pine samples before and after each accelerated weathering period. AD-KD-5, Adolit KD 5; CAC, Celcure AC-500; CV, cellulosic varnish; PV, polyurethane varnish; WCX, Wolmanit CX

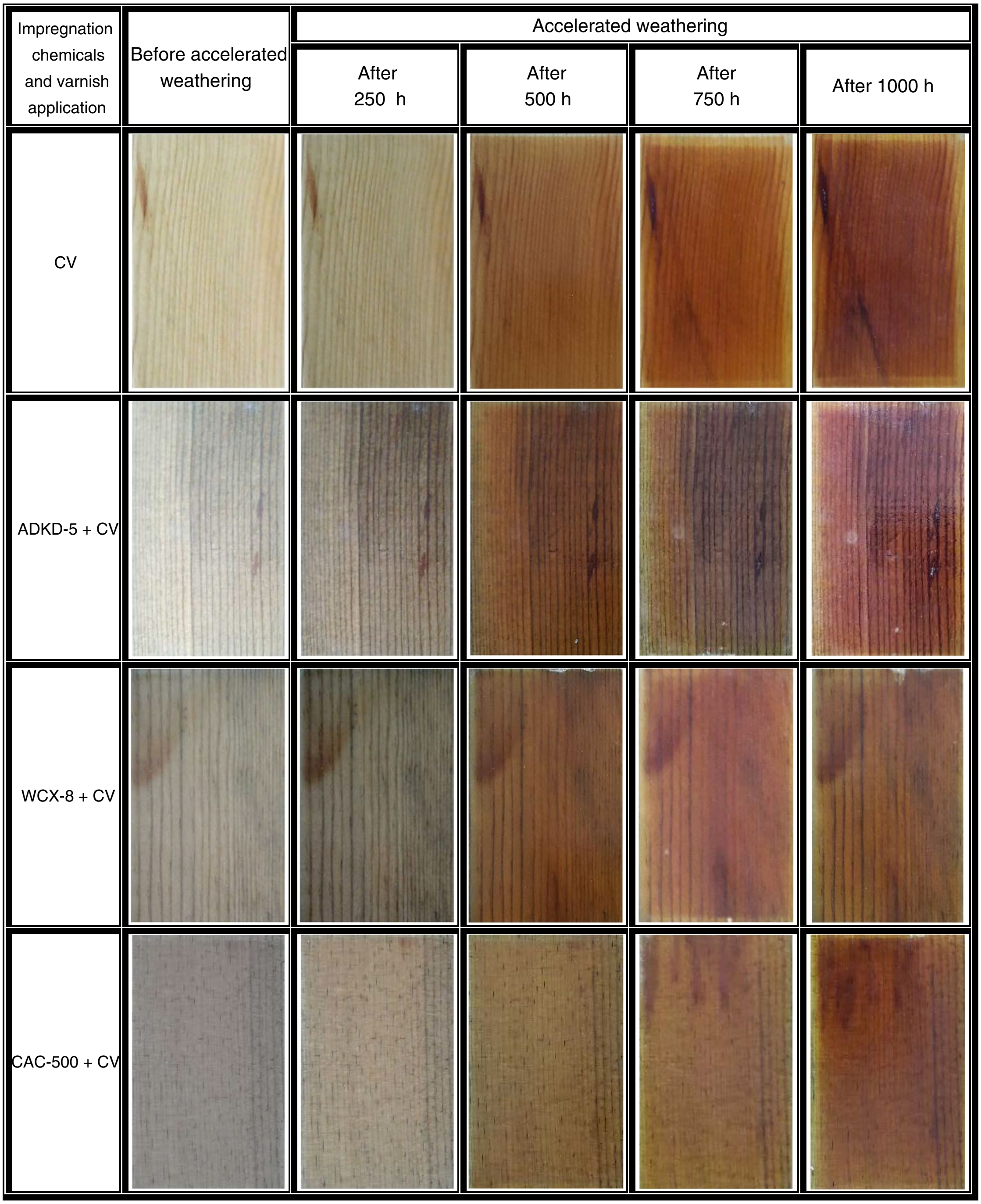

FIGURE 2 Colour changes of impregnated and cellulosic varnish (CV)-coated Scots pine samples before and after each accelerated weathering period. AD-KD-5, Adolit KD 5; CAC, Celcure AC-500; CV, cellulosic varnish; PV, polyurethane varnish; WCX, Wolmanit CX

periods. Preimpregnation with copper-based chemicals before varnish coating prevented lignin degradation and retarded the degradation of varnishes during weathering exposure. This may be because wood-ion complexes formed on copper-impregnated Scots pine wood surfaces thus ensuring photoprotection by blocking the free phenolic groups, the reactive sites in photochemical reactions.[37,41] These complexes could reduce radials, thus stabilising the colour of the wood. The mechanism of action of copper-containing preservatives has been reported by Schmid et al.[42] Also, Temiz et al[40] reported that copper-based impregnation formulations such as WCX-8, Ammonium Copper Quat (ACQ)-2200, CCA, ACQ-1900 and TN-E 3491 improved the wood colour stability of Scots pine and alder.

4 | CONCLUSIONS

The surface properties of Scots pine coated with PV and CV preimpregnated with CAC-500, AD-KD-5 and WCX-8 after accelerated weathering were investigated.

Preservative-impregnated and PV-coated Scots pine wood surfaces were only softened in the third period (500-750 hours). Preservative-impregnated and CV-coated Scots pine were softened, except for after the first accelerated weathering period (0-250 hours). According to these results, the hardness of wood specimens increased remarkably for both preservative- treated and coated wood pine specimens after the first exposure period. While treatment with copper-based formulations before both varnish coatings improved the hardness of both impregnated and PV-coated Scots pine, it was decreased for impregnated and CV-coated Scots pine after 1000 hours of total accelerated weathering. Whereas the gloss values of the impregnated Scots pine coated with PV decreased during the second and third periods of exposure, it only decreased after the second exposure period for impregnated and CV-coated Scots pine. But these decreases were fairly low for both varnishes. According to the results of this study, treatment with copper-based formulations before both varnish coatings increased the gloss values of Scots pine compared with Scots pine which was only varnish-coated after 1000 hours of total accelerated weathering. But this effect was not observed for each exposure period. Of the impregnation chemicals, AD-KD-5 gave the most appropriate results for gloss value changes, while CAC-500 was the most suitable chemical to provide hardness changes in wood specimens after accelerated weathering. Stability at negative lightness values shows that the wood surface tends to darken after accelerated weathering. Preimpregnated and PV-coated Scots pine appeared to have better colour characteristics than preimpregnated and CV-coated Scots pine at both the partial and at the total accelerated weathering exposure time periods. Impregnation with copper-containing chemicals before varnish coating improved the colour stability at both the partial and at the total accelerated weathering exposure time periods. After 1000 hours of accelerated weathering exposure, the best colour stabilisation of Scots pine wood was obtained for samples which were impregnated with CAC-500 and were PV-coated.

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