



Evaluation of the weathering resistance of waterborne acrylic- and alkyd-based coatings containing HALS, UV absorber, and bark extracts on wood surfaces

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Abstract In this study, tree bark extracts were assessed as functional additives to provide protection in waterborne acrylic- and alkyd-based coatings. Tree bark extracts acted as natural photostabilizers and inhibited UV degradation with high UV absorption capacity. The coating systems comprising bark extracts were compared to the control coating groups comprising ultraviolet light absorbers (UVA) of the hydroxyphenyl-*s*-triazine (HPT) for acrylic and nonbasic amino ether (NOR) hindered amine light stabilizers (HALS) for alkyd. Scots pine surfaces coated with acrylic and alkyd coatings were exposed to artificial weathering for 2016 h. Three different trees (maritime pine, alder and Calabrian pine) with high antioxidant activity and phenol content were used for this purpose. The chemical structure of acrylic and alkyd coating systems was also examined using ATR–FTIR spectroscopy. The weathering resistance of coating systems containing extracts was evaluated in terms of their color changes and surface roughness through macroscopic evaluation, and they were compared to commercial UV absorber. The lowest color change was

observed in the alkyd-based coatings with the bark extract. For the alkyd coatings, the color change (ΔE) in the control samples was 24.85, whereas it was found to be 4.68, 5.92 and 7.80 in the test samples containing Calabrian pine, maritime pine and alder bark, respectively. However, color stabilization of the acrylic coatings with UV absorber was found to be much better than the acrylic coatings with extracts. The alkyd coating systems with extracts did not exhibit the same performance for surface roughness. The alkyd coating with the UV absorber provided a smoother surface than that with bark extracts. The acrylic coatings with alder and maritime extracts provided the best results. Acrylic coating may be compatible with (Calabrian) bark extracts. According to the obtained results, it was seen that tree bark extracts in wood coating systems have a potential to substitute commercial UV absorbers as a natural product.

Keywords Artificial weathering, ATR–FTIR spectroscopy, Bark extracts, UV absorber, Waterborne acrylic coating

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Introduction

Wood is a popular engineering material which is also preferred in outdoor conditions. Depending on its area of use, several defects including surface erosion, cracks, and color changes occur due to weathering conditions such as UV radiation, humidity, and temperature. Degradation of wood with combination of some factors such as chemical factors, mechanical factors, and UV light is called “weathering.”^{1,2} It is a phenomenon commonly seen in outdoor conditions. UV absorption starts the degradation mechanism, and humidity, temperature, wind, atmosphere gases, and other factors accompany this process. As a result, the wood’s color turns from yellow to brown.³ Color changes may be

accepted as an indicator of chemical changes in the wood cell wall. Previous studies clearly revealed that lignin, which absorbs UV light between 300 and 400 nm, is responsible for color changes.^{4,5} Therefore, lignin's removal from wood surface by water results in a cellulose-rich surface which increases the surface roughness of wood and causes cracks and erosion.⁶

Today, various methods are preferred for inhibiting and/or minimizing the effects of degradation factors of weathering. One of the methods used to protect wood materials in outdoor conditions is impregnating wood with water-soluble salts such as chromium, iron, and copper.⁷ Chemical modification is also a significant alternative applied for protecting wood surfaces.^{8,9} Another method used to protect wood surfaces against weathering is preventing UV light and water contact with the wood surface by using coating systems. Several studies have been carried out on resistance of surface applications of acrylic/alkyd coatings to exterior conditions. Waterborne transparent acrylic coatings, which are applied without any protection, do not provide color stabilization under outdoor conditions.^{10,11} However, in order to protect wood surfaces and coating layers against outdoor conditions, various UV absorbing and stabilizing agents such as organic absorbents and hindered amine light stabilizers (HALS) are added to coating formulations.^{12–16} Most of these protective additives commonly used in acrylic coating systems contain toxic chemicals.^{17–19} Because of the increased awareness of these environmental issues, these chemicals which pose threats not only to human health but also the environment are being forbidden, and in this context, manufacturers are looking for more environment-friendly and organic-based coating systems.

Natural components such as aldehydes, alkaloids, phenols, terpenoids, and tannins have been considered as natural preservatives in wood preservative industry because of their nontoxic nature.^{20–23} Moreover, polyphenolic substances such as flavonoids, lignans, tannins, and quinones have a light absorbing ability due to chromophoric groups which allow them to take control of photodegradation.^{23–25} Flavonoids containing a 5-OH group inhibit the detrimental effects of sunlight, transform photon energy to heat, and provide natural protection.^{26,27} They play an important role in slowing down the UV degradation mechanism owing to the high light absorption capabilities of phenolics.^{25,28} Therefore, it may be stated that their high antioxidant capacity and phenol content make extracts favorable as natural photostabilizers.^{3,29} Galiñanes et al. demonstrated that, since it has the highest phenol content and antioxidant activity, pine extract hinders UV oxidation and thus exhibits better performance than other preservatives against UV degradation.³⁰ Moreover, Yalcin et al. stated that wood could be better preserved with impregnated tannins before varnishing.³¹ Similarly, it was reported in the literature that tannin-reinforced films improve durability against UV irritations as they reduce oxidation.³² Chang et al. also proved that extracts have photostabilizing effects

and diminish UV degradation by means of flavonoids that have UV absorbing capacity.³³

The objective of this study was to investigate the performance of artificial weathering of waterborne acrylic- and alkyd-based wood coatings comprising HALS, UV absorbers, and tree bark extracts. The extracts were obtained from barks of alder, Calabrian pine, and maritime pine trees by using the alcohol-benzene extraction method. Evaluation of coatings was conducted in two stages. First, antioxidant capacity of the extracts was determined to assess the effect of their protection against artificial weathering. Wood coating systems were examined using ultraviolet–visible (UV–Vis) and attenuated reflectance–Fourier transform infrared (ATR–FTIR) spectroscopies for the first stage. After that, UV exposure was facilitated to evaluate the performance of coatings in an accelerated weathering chamber. The changes in the color and surface roughness on wood surface were determined after weathering exposure. The effects of weathering (cracks, discoloration, surface erosion, etc.) were also evaluated by visual assessment.

Experimental

Wood and bark samples

The barks were peeled off from 20 to 30-year-old alder (*Alnus glutinosa*), Calabrian pine (*Pinus brutia*), and maritime pine (*Pinus pinaster*) trees that were cut down in the Black Sea Region in northern Turkey. In the extraction analysis, the TAPPI T 257 cm-12³⁴ and TAPPI T 264 cm-07³⁵ standard methods were used for preparing and chopping the tree barks.

Scots pines (*Pinus sylvestris* L.) were used in the study as defect-free samples. Wood samples with dimensions of 150 mm (longitudinal) by 70 mm (tangential) by 20 mm (radial) were prepared for artificial weathering.

Bark extraction and coating system process

All tree barks were air-dried at room temperature and then ground with a laboratory-scale Wiley mill to obtain 40–60-mesh wood powder. To obtain extracts, the bark powders were extracted in a Soxhlet extractor. The bark powder (25 g each) was soaked in 300 mL of ethyl alcohol: benzene (1:2 v/v). The solvents from each extract were removed using a rotary evaporator at 50°C and stored in sealed flasks at 4°C until use.

Total polyphenols analysis, antioxidant activity, and UV–Vis spectroscopy

Total phenolic content was analyzed using the Folin–Ciocalteu method at a wavelength of 765 nm,¹⁴ and UV

spectrophotometry (PG Instruments, T60/Leicestershire, the UK) was used. The amount of total phenolic content (TPC) is expressed in gallic acid equivalent per g of dried matter (mg-GAE/g-DM).

2,2-Diphenyl-1-picrylhydrazyl (DPPH), gallic acid, Folin-Ciocalteu reagent, and sodium carbonate were purchased from Sigma-Aldrich Co. (Germany). Antioxidant activity by DPPH assay was analyzed using the method proposed by Galiañes et al.³⁶ with some modifications (at 517 nm against a blank sample without DPPH) as previously stated. The ability to inhibit the DPPH radical was calculated by using the following equation:

$$AA (\% \text{ inhibition}) = \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \times 100 \quad (1)$$

where A_{control} is the absorbance of the control sample, which is the DPPH solution without the extract, and A_{sample} is the absorbance of the test sample. Statistical analysis on the means of total polyphenols and antioxidant activity analysis were performed via analysis of variance (ANOVA) test of the InStat® (GraphPad, San Diego, CA, USA) software (version 3.0). Tukey's test of significance between means was applied for indication of significance.

Extracts were redissolved in water, and the UV spectra of the solutions were measured in Agilent 8453 UV-visible spectrophotometer equipment using water as reference.

Application and preparation of coating systems

The raw materials of acrylic and alkyd coating system products were supplied from the BASF Company in Turkey. The waterborne acrylic-based coating system was formulated from the commercial acrylic coating, a poly(methyl acrylate/methyl methacrylate/butyl acrylate) copolymer dispersion. In order to increase the effects of other additives on photostabilization, only a small amount of defoamer and 2,2,4-trimethyl-1,3-pentandiolemonoisobutyrate was used in the formulation as a coalescent agent. A commercial 1 K alkyd topcoat-based 1-component alkyd coating, dry solution, and dispersing agent were used as additives in the formulation of waterborne alkyd-based coating systems. Acrylic- and alkyd-based coating systems comprising bark extracts were compared to the control coating groups comprising UVA of a hydroxyphenyl-s-triazine class (HPT) for acrylic and nonbasic amino ether (NOR) hindered amine light stabilizer (HALS) for alkyd. These formulation products were supplied from the BASF Company for the wood coatings (Tables 1 and 2).

For the artificial weathering test, the back, end-grain, and side faces of wood samples were covered with 2-epoxy white paint with a brush, and the front

side was left uncoated for the experiments. The commercial water-based impregnation product with active ingredients of 1.20% propiconazole and 0.30% iodopropynyl butylcarbamate was used as a primer for protecting the samples against any biological deterioration such as soft rot and blue stain. The primer was applied to the samples with a brush at a spreading rate of 120 g/m². The first layers of the topcoats were also applied to each sample with a brush at a spreading rate of 100 g/m². Later, the specimens were sanded with a 240-grit size of sandpaper and kept at room temperature for two days before applying the second layer of the topcoat. After the top coatings, the samples were conditioned at 20°C and 65% RH for 2 weeks.

Chemical analysis of coating systems

The absorbance spectra of liquid coating systems diluted with 1/100 and 1/200 water were measured using a UV-Vis spectrophotometer (Libra/Biochrom S80, UK) at 190–1100 nm to determine the performance of coating systems as potential UV absorbers. The solid content and UV absorbance of the liquid waterborne acrylic and alkyd coating systems are shown in Table 3.

FTIR measurements with the attenuated total reflection technique (ATR) were recorded using a Thermo Nicolet iS50 FTIR (Thermo Fisher Scientific Co., Waltham, MA, USA) spectrometer equipped with a single bounce diamond crystal and a deuterated triglycine sulfate (DTGS) detector. The FTIR spectra of the dry film coatings were acquired in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ before weathering. Each spectrum was collected at 32 scans in the absorbance mode.

Artificial weathering test

All wood samples containing bark extracts and mineral UV absorber on which coating systems were applied were subjected to an artificial weathering process by means of exposing them to 340 fluorescent UV lamps in a QUV/spray accelerated weathering tester (Q-Lab Products, Cleveland, USA) for 2016 h in accordance with the EN 927-6 standard.³⁷ The weathering experiment was conducted by cycles of UV-light irradiation for 2.5 h at 60°C followed by a water spray for 0.5 h, and then, condensation was performed for 24 h at 45°C in an accelerated weathering test cycle chamber.

Color measurement

The color measurements were taken using a Minolta CM-600d spectrophotometer (Konica Minolta, Japan) equipped with an integrating sphere in accordance with

Table 1: Formulations of acrylic-based wood coating systems

Formulation products	Content (%)	Acrylic			
		A (Alder)	B (Calabrian pine)	C (Maritime pine)	D (control)
Acrylic Resin	72.5	x	x	x	x
UVA	3.0	–	–	–	x
Bark extract	5.0	x	x	x	–
Film-forming agents	0.67	x	x	x	x
Defoamers	1.0	x	x	x	x
Dispersing agent	0.6	x	x	x	x
Rheology modifier	1.3	x	x	x	x
Distilled water	18.88	x	x	x	–
Distilled water	20.88	–	–	–	x
Anhydrous ammonia	0.05	x	x	x	x

Table 2: Formulations of alkyd-based wood coating systems

Formulation products	Content (%)	Alkyd			
		A (Alder)	B (Calabrian pine)	C (Maritime pine)	D (control)
Alkyd Resin	75.0	x	x	x	x
HALS	3.0	–	–	–	x
Bark extract	6.0	x	x	x	–
Film-forming agents	0.55	x	x	x	x
Resin solvent	2.4	x	x	x	x
Distilled water	17.0	x	x	x	x
Distilled water	19.0	x	x	x	–
Anhydrous ammonia	0.05	–	–	–	x

Table 3: Solid content and UV–visible spectroscopy values of coating systems

Resin type	Coatings groups	Solid content (%)	UV absorbance (abs.) at 340 nm
Acrylic	Alder	32.09	0.447
	Calabrian	41.18	0.364
	Maritime	42.09	0.400
	Control	35.47	0.357
Alkyd	Alder	51.12	0.487
	Calabrian	59.27	0.447
	Maritime	41.90	0.419
	Control	36.24	0.364

the CIE $L^*a^*b^*$ system.³⁸ The reflection spectrum of the Konica Minolta CM-600d instrument was acquired from an area with an 8-mm diameter with 10° in the 400–700 nm wavelength range. Five measurements were recorded for each sample. The color measurement was taken at 24, 48, 224, 448, 672, 896, 1120, 1344, 1568, 1792, and 2016 h of the artificial weathering test.

Surface roughness measurement and macroscopic evaluations

A Mitutoyo Surfest SJ-301 instrument (Japan) was utilized for measuring surface roughness. The Ra and

Rz roughness parameters were measured to evaluate the surface roughness of the nonweathered and weathered (untreated and treated) samples in accordance with DIN 4768.³⁹ Ra is an arithmetic mean of the absolute values for profile departures within the reference length, and Rz is the arithmetic mean of the 5-point height of irregularities.³⁹ The cutoff length was 2.5 mm, the sampling length was 12.5 mm, and the detecting tip radius was 5 mm in the surface roughness measurements.

After the weathering test, macroscopic changes (erosion, checks, and cracks) on the sample surfaces were evaluated according to the ASTM D 660,⁴⁰ ASTM D 661,⁴¹ and ASTM D 662⁴² standards. The

samples were visually rated on a scale of 0–10 with 0 indicating a surface with high-level degradation and 10 indicating a flawless surface with no degradation. Photographs of the samples were also taken with a NIKON D7500+AF-S DX NIKKOR 18-105 VR Digital SLR camera.

Statistical analysis

The data were analyzed with the SPSS 19.0 statistical package program based on a reliability level of 95%. Shapiro–Wilk normality test was carried out for parameters related to color and roughness changes in alkyd- and acrylic-based test and control coatings due to outdoor exposure. After this test, the independent samples *t* test was applied on the parameters showing normal distribution. For the nonnormally distributed parameters, Mann–Whitney *U* test was performed. However, if the surface color and roughness values between the test samples of the alkyd- and acrylic-based coatings and their control samples were to be compared before and after the artificial weathering test, Shapiro–Wilk normality test was performed. When the parameters were found to be normally distributed, the paired samples *t* test was carried out. When the parameters were not normally distributed, a comparison was made with Wilcoxon signed-rank test.

Results and discussion

Total polyphenols analysis, antioxidant activity, and UV spectroscopy

The antioxidant activity of the tree bark extracts obtained through alcohol-benzene extraction was determined using a DPPH assay as shown in Fig. 1.

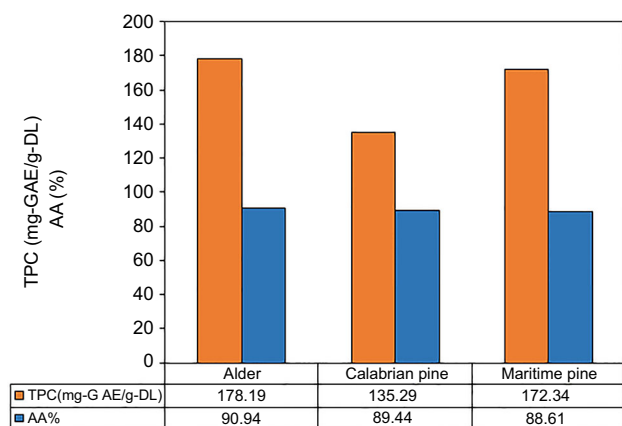


Fig. 1: Total polyphenols content (TPC) and antioxidant activity (AA) of the tree bark extracts

The antioxidant activity (AA) and total phenol content (TPC) of the extracts were found to be substantially high, which meant that the bark extracts had high UV absorbance capacity.^{43,44} High antioxidant properties are in parallel with high content of phenols which act as a singlet oxygen quencher or free radical scavenger as well as peroxide decomposers and enzyme inhibitors to hinder UV degradation.^{45,46} The AA values of the three bark extracts were close. Significant differences in the TPC values were determined. Although the values were similar for all tree species, the highest TPC and AA values were obtained from the alder extract, while the lowest ones were obtained from Calabrian pine. However, the Calabrian pine extract exhibited the best performance against artificial weathering. As the phenol content increased, UV absorbance capacity also increased. Therefore, these phenomena might cause much more degradation in the chemical structure of coating and result in high levels of color change.⁴⁴ Likewise, the high antioxidant capacity of extracts restrains UV radiation and moderates color change on wood surfaces.

The UV absorbability performance of control and test coating systems was determined in the 190–1100 nm wavelength range (Table 3). In this study, the UV absorption effect of natural extracts, commercial UV absorber, and HALS in the waterborne acrylic varnish was investigated using antioxidant activity test, total polyphenols, and UV–Vis spectroscopy analysis. These analyses have gathered some important findings that reveal bark extracts as functional coating additives to stabilize acrylic coatings against weathering. Grigsby also evaluated various tannins and chemically modified derivatives, coating concentrations, and different acrylic coating systems. The findings showed that the addition of tannin materials as functional additives to the coatings can help to protect and prolong the life of the coating.⁴⁷

The absorption spectra of different concentrations of bark extract have already been reported by Vázquez et al. and Galiñanes et al.^{48,36} In this present study, the absorption spectra of the Calabrian pine, alder, and maritime pine bark extracts at three different concentrations (2%, 5%, and 8% w/w) were compared with the commercial UV absorber and HALS (Fig. 2). As shown in Fig. 2, bark extracts presented a single absorption maximum at 250–270 nm, characteristic of proanthocyanidins.⁴⁸ The absorption test results (Fig. 2) showed that the bark extract at 2% concentration had poor absorption capacity in the UV range compared to the commercial UV absorber and HALS. Absorption lower than that of the commercial UV absorber and HALS was observed up to 250 and 400 nm for 2% of Calabrian pine, alder, and maritime pine bark extract, respectively. High absorption in the UV range allows the UV light to eventually reach the wooden surface, which begins to deteriorate shortly after exposure to outdoor conditions.⁴⁵ Among all bark extract concentrations, the bark extracts at a concentration of 5% provided the primary criteria of the UV absorber. In

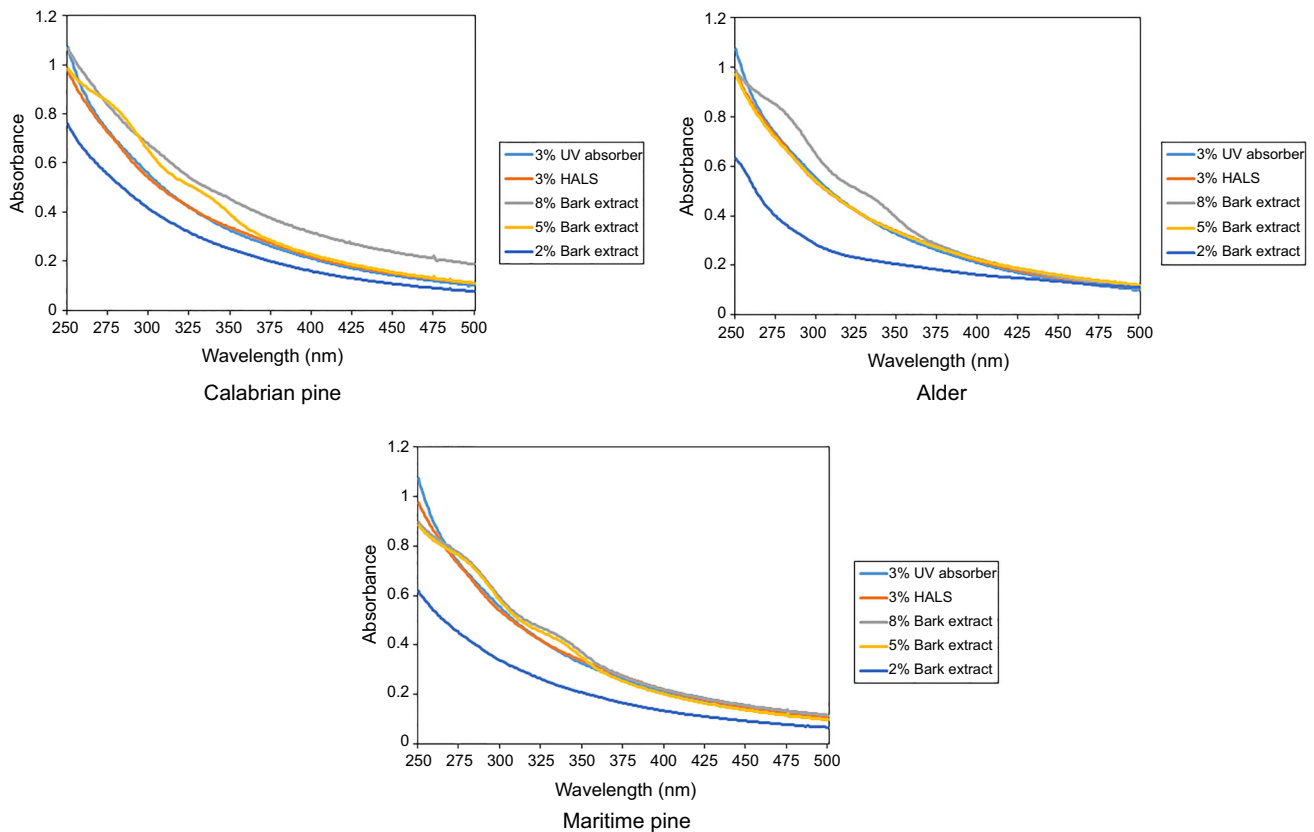


Fig. 2: Absorption spectra of commercial UV absorber, HALS and different bark extracts for three different concentrations

addition to their antioxidant activity, the bark extracts also functioned as UV absorbers, although the mechanisms of energy diffusion are still unknown. However, further testing is required to conclude the effectiveness of the bark extract. From the total polyphenols analysis, antioxidant activity, and UV-Vis spectroscopy results, a 5% concentration of bark extract was selected for further testing.

Chemical characterization of coating systems by using ATR-FTIR spectrometry

The performance of tree bark extracts and UV absorbance with acrylic and alkyd coatings on the wood surface against weathering conditions was investigated using ATR-FTIR spectrometry. The changes in the vibrational bands recognized as characteristic peaks are clearly shown in Figs. 3 and 4. The intensity of peaks changed depending on the chemical structure of the coatings. The bands located at 2925 and 2955 cm^{-1} were C-H bonds that occurred during chemical characterization of acrylic and alkyd coatings.⁴⁹ These peaks were found to be higher in the alkyd-based coating system than in the acrylic-based coatings. Likewise, the intensity of peaks was more

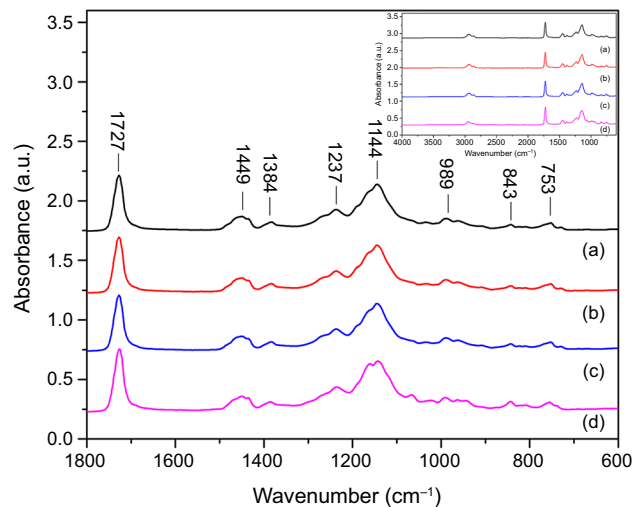


Fig. 3: Absorption spectra of waterborne acrylic-based coating systems: (a) Alder, (b) Calabrian pine, (c) Maritime pine, and (d) Control

dominant for the coatings containing UV absorber in comparison with the extracts. The peaks at 1718–1740 cm^{-1} were described as the absorption of carbonyl

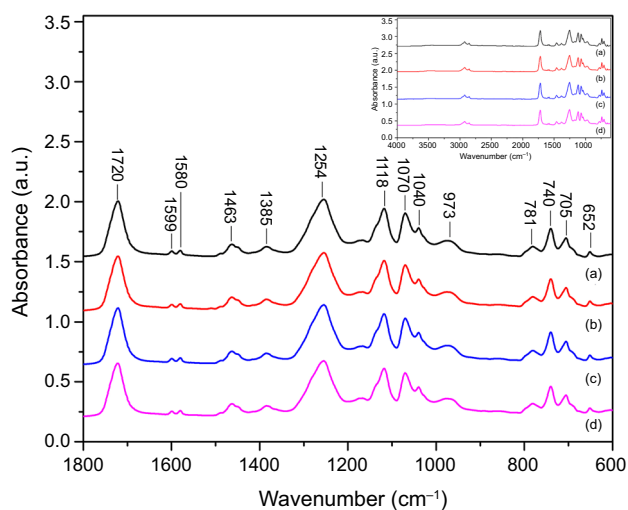


Fig. 4: Absorption spectra of waterborne alkyd-based coating systems: (a) Alder, (b) Calabrian pine, (c) Maritime pine, and (d) Control

and carboxyl groups on the wood surface. The absorption at these peaks demonstrated C=O stretching vibrations in the aldehydes, ketones, esters, and carboxylic acids.^{15,50} The changes in these peaks were more prominent in the acrylic-based coatings, which were associated with extensive degradation. The coating systems rich in hydroxyl groups became oxidized, which led to an increase in the intensity of peaks.⁵¹ The high water content in acrylic coating systems also caused the heights of the peaks to increase.

The bands located at 1580–1599 cm^{-1} and 1450–1465 cm^{-1} , which were considered to be characteristic lignin peaks, are benzene rings and C–H deformation in the lignin and hemicellulose, respectively.^{52,53} The absorption at 1580–1599 cm^{-1} was more intense for the alkyd-based coatings, while the absorption at 1450–1465 cm^{-1} was more intense for the acrylic-based coatings. The chemical changes in lignin are responsible for color changes of coating systems on the wood surface.^{54,55} The color of the wood surface turning grey indicates degradation of hemicellulose and lignin.⁵⁶

The peaks at 1384–1385 cm^{-1} refer to C–H degradation in the cellulose and hemicellulose.⁵⁷ The changes in CO stretching and vibration at the guaiacyl ring in lignin and hemicellulose were followed from the peaks at 1237–1254 cm^{-1} . The changes in these bands indicate degradation of hemicellulose and delignification of lignin on the wood surface.⁵⁶ The bands at 1140 and 1144 cm^{-1} and 1070 and 1118 cm^{-1} indicate C–O–C symmetric stretching and OH association in cellulose, respectively.^{58,59} The vibration in the bands centered at 973 cm^{-1} and 989 cm^{-1} referred to C–H bonds in alkane for the alkyd and acrylic coatings, respectively. The intensity of the functional groups in the IR bands was generally dominant for UV absorbance. The

carbonyl absorption of the related peak heights of acrylic and alkyd wood coating systems are given in Table 4. The ATR–FTIR results supported the macroscopic evaluation as well as other results and revealed that the best performance was obtained from the commercial UV absorber.

Color change

The performance of the acrylic- and alkyd-based coatings containing tree bark extracts and UV absorbance was evaluated depending on color changes during the 2016 h weathering process. The changes in color due to intensive weathering conditions are shown clearly in Fig. 5. As a general trend, the tree bark extracts provided the best color stabilization against the extensive artificial weathering conditions. High antioxidant properties of tree bark extracts inhibit oxidation reactions which occur in cell wall components, especially in lignin.^{29,45} Therefore, tree bark extracts improved weathering resistance significantly. ΔE values represent the general changes in the color of coating systems on wood surfaces. Although the ΔE values of the control and test samples were close to each other for the alkyd coating, the least amount of color change was obtained from the Calabrian pine extract for both the acrylic and alkyd coatings. While the color changes increased gradually at the 2016th hour for the acrylic coating, the tree bark extracts ensured that the color change remained lower for the alkyd coating. Oxidation reactions induced by weathering conditions (combination of UV radiation, high humidity and temperature) caused deformation in the coating structure and influenced coating adhesion and cohesion.^{60,61} Therefore, UV rays reached the wood surface, and degradation occurred on the surface. Incompatibility of tree bark extracts could also weaken the acrylic coating structure and result in low weathering resistance. In our study, the results showed that the tree bark extracts were more compatible with the alkyd coating and provided more color stabilization than the acrylic coating in general.

The comparison of color change values of the acrylic- and alkyd-based coating systems containing bark extracts and commercial UV absorber after 2016 h of the QUV test is given in Table 5. For this comparison, Mann–Whitney U test was performed on the nonnormally distributed parameters. As $p < 0.05$, a significant difference was found between the alkyd- and acrylic-based coating groups containing the whole bark extract and the commercial UV absorber, respectively. After the 2016th hour of the QUV test, the color stabilization of the Scots pine wood was found to be high the alkyd in group B, the alkyd in group C, and the acrylic in group D.

In the test and control groups of the acrylic- and alkyd-based coating systems applied to Scots pine, the color change values after QUV exposure were com-

Table 4: Carbonyl absorption of related peak heights of acrylic and alkyd wood coating

Acrylic	989 cm ⁻¹	1144 cm ⁻¹	1449 cm ⁻¹	1727 cm ⁻¹	2925 cm ⁻¹	2955 cm ⁻¹
A	0.033	0.277	0.097	0.455	0.063	0.064
B	0.034	0.281	0.097	0.453	0.064	0.064
C	0.035	0.283	0.098	0.456	0.066	0.065
D	0.026	0.281	0.096	0.510	0.045	0.062
Alkyd	973 cm ⁻¹	1118 cm ⁻¹	1580 cm ⁻¹	1720 cm ⁻¹	2925 cm ⁻¹	2955 cm ⁻¹
A	0.059	0.262	0.035	0.439	0.068	0.031
B	0.057	0.254	0.031	0.424	0.068	0.031
C	0.058	0.265	0.035	0.447	0.066	0.031
D	0.055	0.248	0.031	0.421	0.063	0.031

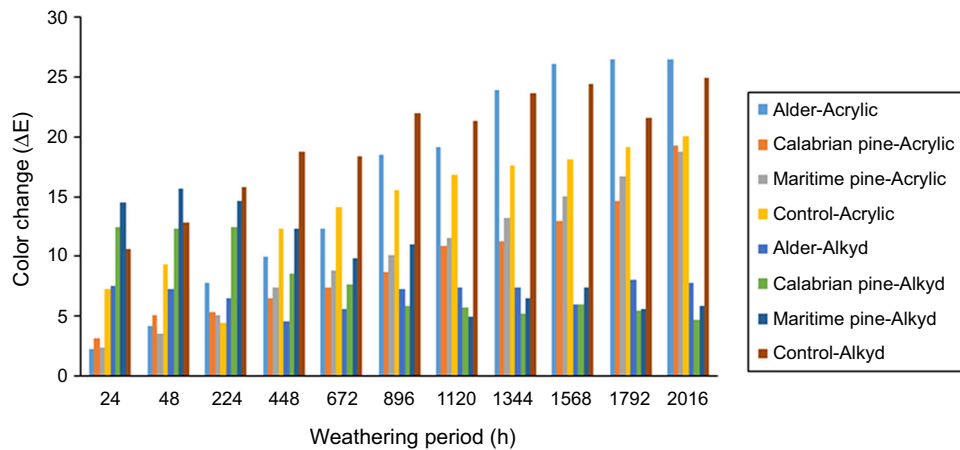


Fig. 5: Color change of wood surfaces applied with acrylic- and alkyd-based coating systems

Table 5: Comparison of color change values after 2016 h QUV test with Mann–Whitney *U* test

Scots pine	N	Mean rank	Rank sum	<i>U</i>	<i>p</i>
B-Acrylic	12	18.50	222	0.00	0.00
B-Alkyd	12	6.50	78		
C-Acrylic	12	18.50	222	0.00	0.00
C-Alkyd	12	6.50	78		
D-Acrylic	12	18.50	222	0.00	0.00
D-Alkyd	12	6.50	78		
F-Acrylic	12	6.50	78	0.00	0.00
F-Alkyd	12	18.50	222		

pared by using Mann–Whitney *U* test (Table 6). As a result of this analysis, there was no significant difference between the acrylic-based A and C coatings applied to the Scots pine and the control group (D) as $p > 0.05$. However, since $p < 0.05$, there was a significant difference between the color change parameters of the other test groups and control groups. The discolorations on the surface of pine after 2016 h of the QUV

test in the alkyd-based test groups were lower than the control groups, and those in the acrylic-based test groups were higher than the control groups.

However, the alkyd- and acrylic-based coatings used in the coating formulations are transparent so UV light can reach the wooden surface, and the alkyd and acrylic coatings applied to the wooden surface may cause polymer degradation.^{29,45} The alkyd and acrylic

Table 6: Comparison of color change values after 2016 h QUV exposure in acrylic- and alkyd-based coating systems applied to Scots pine in test and control groups with Mann–Whitney U test

Scots pine	N	Mean rank	Rank sum	U	p
A-Acrylic	12	18.50	222	0.00	0.00
D-Acrylic	12	6.50	78		
A-Alkyd	12	6.50	78	0.00	0.00
D-Alkyd	20	18.50	222		
B-Acrylic	12	11.00	132	54	0.295
D-Acrylic	12	14.00	168		
B-Alkyd	12	6.50	78	0.00	0.00
D-Alkyd	20	18.50	222		
C-Acrylic	12	11.75	141	63	0.601
D-Acrylic	12	13.25	159		
C-Alkyd	12	6.50	78	0.00	0.00
D-Alkyd	12	18.50	222		

coatings containing the bark extracts were darker in color than the control coatings because of their tannin content. Therefore, this can be explained by the phenolic and aromatic structures of tannins that absorb the entire UV range and some of the visible light.^{26,28} Aromatic-enriched surfaces absorb more UV light and cause dark wood surfaces. It is shown in Fig. 6 that the tannin content in coatings containing the bark extract decreased the dark color parameters and the total color change of the wood surfaces that probably absorbed more UV light.^{23,31} The positive value of Δb^* indicates increase in the yellowish color on the wood surface, while the negative value of it refers to a bluish color. As shown in Fig. 6, different from the case at the beginning of the artificial weathering test, the color of the samples turned from yellowish to bluish. The biggest change was seen in the alder bark extracts for the acrylic coating, while the control samples had the highest change for the alkyd coating. Moreover, a positive Δa^* value refers to a reddish color, and a negative value indicates a greenish color.⁵⁵ The general trend for the samples was turning from greenish to reddish in the first 1120 h. After that, the sample surfaces tended to become greenish. When the control samples were compared as a commercial product, it was seen that the bark extracts for the alkyd and acrylic coatings had the lowest Δa^* values. ΔL^* values provide clues about surface quality and lightness.⁶² Polymerization of lignin during a weathering test causes the wood surface to become dark.⁶³ ΔL^* values tended to be negative during the 2016 h weathering process. Therefore, the wood surface became rougher and darker during the artificial weathering test. It was found that the control samples had the highest deterioration, while the lowest deterioration was observed in the Calabrian pine for both the acrylic and alkyd coatings. Consequently, it may be deduced from these results that the tree bark extracts had a potential to be used as an alternative to commercial products like the control samples that were used in this study.

Surface roughness and macroscopic evaluations

The surface roughness of wood materials cannot be explained simply with the anatomical structure of wood since it is an anisotropic and heterogeneous material. Therefore, some factors such as earlywood and latewood content in the annual ring, natural growth characteristics (knot, fiber curl, etc.), annual ring wideness, drying temperature, shear direction, and angle must also be considered while evaluating surface roughness.⁶⁴

The surface roughness values of the waterborne-based acrylic and alkyd coating systems are given in Fig. 7, where it may be seen that there was no significant difference in the acrylic-based coatings after weathering. On the other hand, significant changes were observed in the alkyd coating after weathering.

Before and after the QUV test on the Scots pine surfaces, the paired samples t test was performed due to the normal distribution of the Rz parameters in the acrylic-based coating containing the bark extracts and the alkyd-based coating systems containing the commercial UV absorber (Table 7). In the comparisons made with the paired samples t test and the Wilcoxon signed-rank test, a significant difference was found between the Rz parameters before and after the QUV test on the Scots pine surfaces, where the acrylic- and alkyd-based test and control coating groups were applied. The high negative rank values of the acrylic- and alkyd-based coatings containing the commercial UV absorber applied on the Scots pine surfaces showed that the change in the Rz parameters before QUV was higher than the Rz values after QUV. The negative rank Rz value in the acrylic-based varnishes containing the bark extract applied to the surface of Scots pine was higher than Rz before QUV, while in the alkyd-based coating containing the bark extract, the Rz values before the positive rank QUV were lower than those after QUV.

As shown in Table 8, the roughness change rate parameters of the coating groups containing the bark extract and the commercial UV absorber after 2016 h

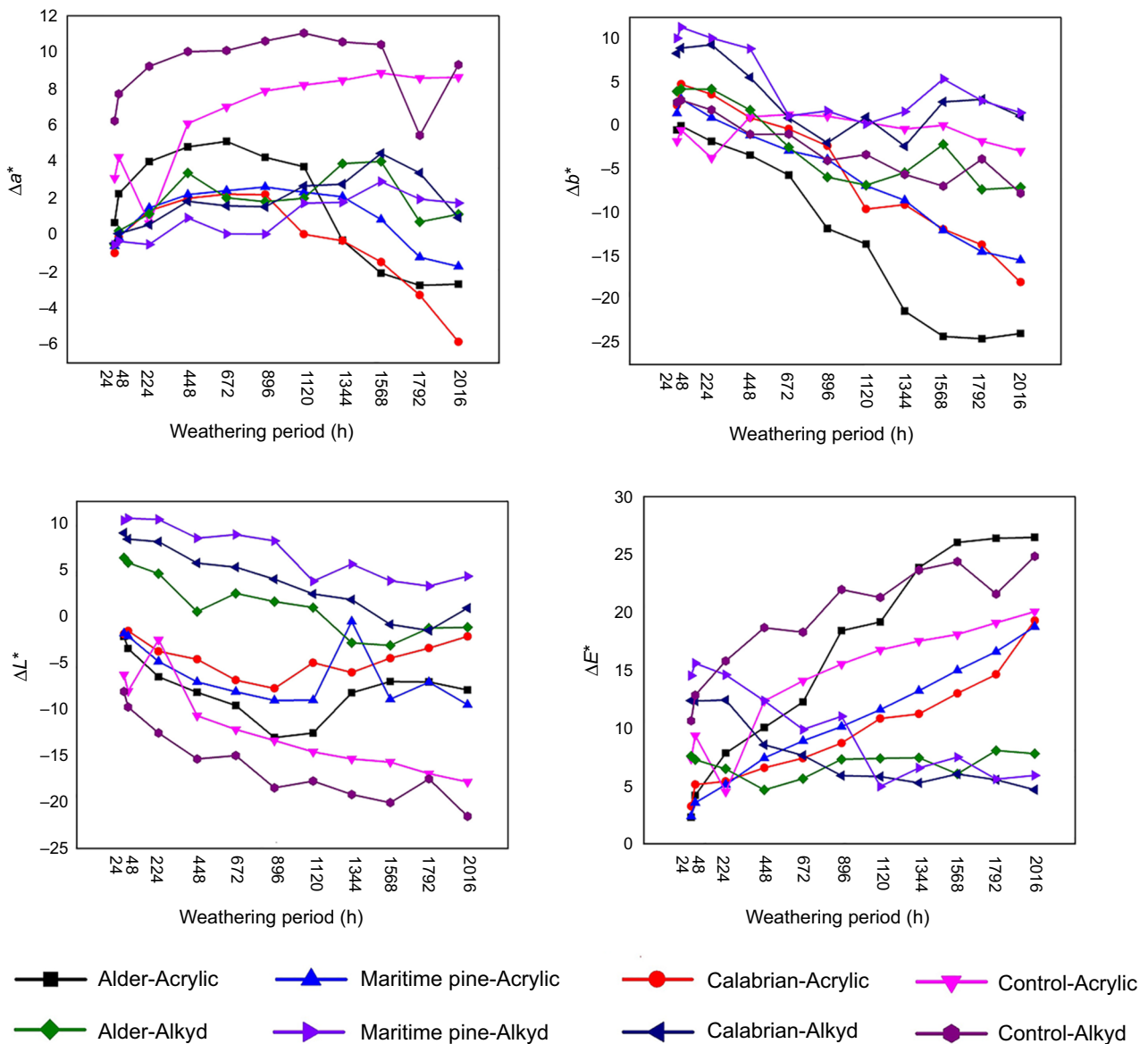


Fig. 6: Changes in color coordinates of wood surfaces applied with acrylic- and alkyd-based coating systems

of the QUV test were compared by using Mann-Whitney U test since they did not show a normal distribution. As a result of this comparison, a significant difference was found between the roughness change rates of all test and control groups as $p < 0.05$. The change rate of the roughness value in the coating groups containing alkyd- and acrylic-based bark extract applied on Scots pine surface after 2016 h QUV test was higher than those in the control groups containing the commercial UV absorber.

Extensive weathering conditions influence the wood surface, and some chemical changes take place in both coating structures and wood structures, which lead to a decrease in coating adhesion and cohesion.⁶⁵ Film

thickness decreases depending on the intensity of weathering conditions due to surface erosion during the exposure period.⁶⁶ Therefore, the wood surface deteriorates and leads to occurrence of hollows and hills on its surface. In this study, it was seen that the R_a values for coatings containing extracts for both coatings increased after weathering, while a decrease was observed in the control samples. Furthermore, the R_z values decreased for the control samples and acrylic-based coatings containing the bark extract. However, an increase was found for the alkyd-based coatings containing the bark extract. Chemical changes occurring in the polymer structure cause different changes

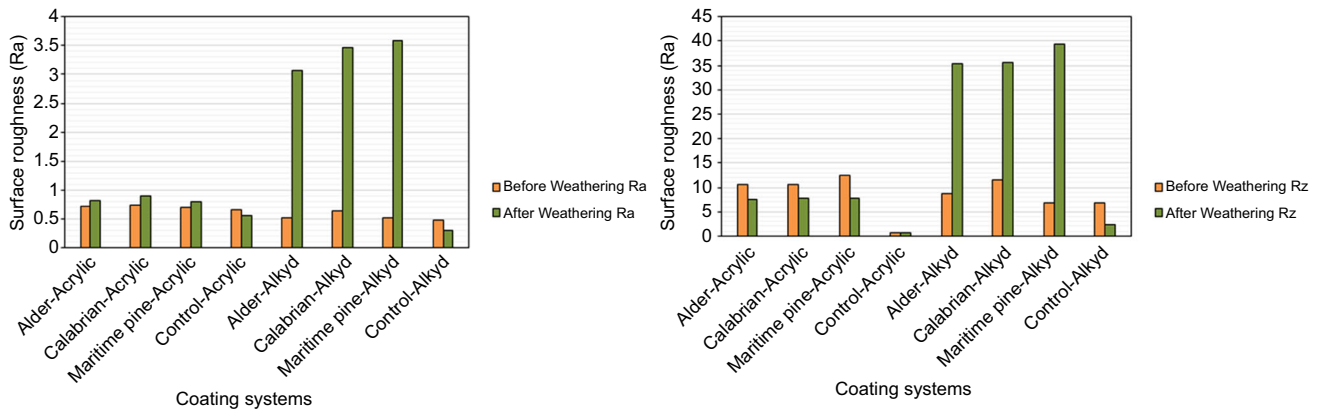


Fig. 7: Changes in surface roughness values of wood surfaces applied with acrylic- and alkyd-based coating systems

Table 7: Comparison of the Rz parameters before and after the QUV test on Scots pine surfaces of the test and control groups

	<i>N</i>	Mean rank	Rank sum	<i>Z</i>	<i>p</i>	
<i>A-Acrylic</i>						
Negative rank*	16	11.38	182.00	2.875	0.004	
Positive rank**	4	7.00	28.00			
Equal	0					
<i>A-Alkyd</i>						
Negative rank*	1	2.00	2.00	-3.845	0.00	
Positive rank**	19	10.95	208.00			
Equal	0					
<i>B-Acrylic</i>						
Negative rank*	17	10.76	183.00	-2.913	0.004	
Positive rank**	3	9.00	27.00			
Equal	0					
<i>B-Alkyd</i>						
Negative rank*	0	0.00	0.00	-3.920	0.00	
Positive rank**	20	10.50	210.00			
Equal	0					
<i>C-Acrylic</i>						
Negative rank*	19	10.95	208.00	-3.846	0.000	
Positive rank**	1	2.00	2.00			
Equal	0					
<i>C-Alkyd</i>						
Negative rank*	0	0.00	0.00	-3.920	0.00	
Positive rank**	20	10.50	210.00			
Equal	0					
<i>D-Acrylic</i>						
Negative rank*	20	10.50	210.00	-3.923	0.000	
Positive rank**	0	0.00	0.00			
Equal	0					
Measurement	<i>N</i>	\bar{X}	<i>S</i>	SD	<i>t</i>	<i>p</i>
<i>D-Alkyd</i>						
Before weathering	20	6.71	0.63	19	15.147	0.00
After weathering	20	2.30	0.97			

Table 8: Comparison of change rate of Ra roughness value of Scots pine surface of coating groups containing bark extract and commercial UV absorber after 2016 h QUV test

Scots pine	N	Mean rank	Rank sum	U	p
A-Acrylic	20	26.00	520	90.00	0.003
D-Acrylic	20	15.00	300		
A-Alkyd	20	30.50	610	0.00	0.00
D-Alkyd	20	10.50	210		
B-Acrylic	20	27.40	548	62	0.00
D-Acrylic	20	13.60	272		
B-Alkyd	20	30.50	610	0.00	0.00
D-Alkyd	20	10.50	210		
C-Acrylic	20	27.15	543	67	0.00
D-Acrylic	20	13.85	277		
C-Alkyd	20	30.50	610	0.00	0.00
D-Alkyd	20	10.50	210		

Table 9: Macroscopic evaluation of samples applied with alkyd- and acrylic-based coating systems

Resin type	Alder	Calabrian pine	Maritime pine	Control
Alkyd	4	6	5	8
Acrylic	2	3	3	8



Fig. 8: Appearance of samples applied with alkyd- and acrylic-based coating systems

on the surface,⁶⁵ which could result in variation for coating types.

The surface views of the samples coated with the tree bark extracts and UV absorber exposed to weathering are shown in Fig. 7, and the results of the macroscopic evaluation are given in Table 9. Surface appearance and macroscopic evaluation showed that degradation was much more intense for the acrylic-based coatings than the alkyd-based coatings.

As shown in Fig. 8, as the exposure time increased in the outdoor test, the acrylic coating containing the alder and Calabrian pine extracts was separated from the wood surface as a result of reduced adhesion and

cohesion resistance. However, there was no deformation in the acrylic coating containing the maritime pine extracts. In addition to high amounts of color change, surface degradation such as cracks and tensions occurred on the wood.⁶⁷ The tree bark extracts, on the other hand, provided much more protection for the alkyd-based coatings. Moreover, the coatings containing UV absorbance further resisted against extensive weathering conditions for both coatings during the exposure time. The tree bark extracts provided protection comparable to the UV absorber in the first 1000 h. After that, their resistance against weathering decreased gradually. As a result, the wood surface

changed its color and deteriorated during the exposure time.

Conclusions

In this study, tree bark extracts were compared to a commercial UV absorber in terms of their ability to restrain weathering. High phenol contents indicate high UV absorbing ability, and high antioxidant capacity moderates the detrimental effects of weathering. Therefore, the color change of the acrylic- and alkyd-based coatings on the wood surface was restricted by the extracts, as was the case with the UV absorber. The differences in the absorbance values of the IR bands were determined with ATR–FTIR spectroscopy analysis of the coating systems containing the bark extracts and the commercial UV absorber. This shows the difference in characterization of each coating. In general, carbonyl absorption of related peak heights of the alkyd- and acrylic-based coating systems in the IR bands was found to be higher in the coatings containing commercial UV absorbers. For durability in outdoor conditions, the coating containing the commercial UV absorber received the highest score as a result of macroscopic evaluation at the end of 2016 h. The ATR–FTIR spectroscopy analysis for coating characterizations revealed the results of the artificial weathering test.

In general, when the results of this study were evaluated, the surface protective effect of the alkyd-based coating containing the bark extract was found to be higher than the acrylic-based coatings during the 2016-h QUV test. In the acrylic-based coatings, the control group was found to have higher resistance to outdoor conditions than the coatings containing the bark extract. However, in the alkyd-based coatings, the durability of the coatings containing the bark extract against the artificial weathering process was higher than the control coating. In particular, the weathering durability of the alkyd- and acrylic-based coatings containing the Calabrian pine bark extract with a low antioxidant effect compared to the other barks was found to be quite good. In comparison with the control coatings, the coatings containing the maritime pine and alder barks with high antioxidant effect had a low protective effect on the surfaces of the Scots pine wood. During the first 1000 h of the QUV test, in comparison with the control coatings, it was observed that the varnish groups containing the shell extract had a high surface resistance. After the 1000th hour of the QUV test, a rapid deformation was observed in the coatings containing the bark extract. The degradation of the acrylic-based coating containing the Calabrian bark extract on the wood surface after the 2016th hour was found to be similar to the commercial UV absorber. The alkyd-based coatings containing the alder and maritime pine bark extracts provided excellent protection on the wood surface.

Extensive weathering conditions induced chemical changes in the coating structure, which influenced the surface roughness values. However, the control samples provided more stable values in comparison to the extracts. According to the results obtained out of the macroscopic evaluation, it was seen that the bark extracts acted as natural photostabilizers. However, the acrylic coating did not show the same performance as the alkyd coating. This might have stemmed from the incompatibility of the extracts with the coating. Consequently, the bark extracts which had high antioxidant capacity and high phenol content provided photostabilization and protected the wood surface against extensive weathering conditions, which means that the extracts in the coating systems had a potential to compete with the commercial UV absorber.

According to these results, instead of the commercial UV absorber, it may be stated that the bark extract content in resin-based coatings can be used frequently, especially in the exterior of wooden plateau houses because of its weather resistance, environment-friendly nature, easy applicability, and economical characteristics. In addition to these, resin-based coatings containing shell extract may be used in areas such as balconies, garden furniture, floor coverings, pergolas, garden fences, children playgrounds and wooden flower pots. The resin-based bark extract is environmentally friendly due to its organic content. Furthermore, with this study, tree barks known as waste may be utilized in organic coating systems.

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