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Comparison of Some Physical and Mechanical Properties of Waterborne Acrylic Coating Systems Containing Commercial UV Absorbers and Tree Bark Extracts

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Abstract

Aim of study: The aim of this study was to compare solid content, dry film thickness, and adhesion strength of different tree bark extract based and a commercial UV absorber.

Materials and methods: Waterborne acrylic-based coating systems containing 5 different tree bark extracts (maritime pine, Calabrian pine, black pine, alder, fir) and a commercial UV absorber (Tinuvin 400 DW) were applied to 2 different wood species; Scots pine (*Pinus sylvestris* L.) and beech (*Fagus orientalis* L.). The dry-film thicknesses of the coatings were measured with light microscopy. The adhesion strength of the coatings was determined to investigate the bonding ability of the coatings with wood surfaces. The solid contents of the coatings were also determined.

Main results: Permeability is an important parameter for dry-film thickness and adhesion strength. Wood species also influenced the dry-film thickness as well as adhesion strength. The dry-film thicknesses of the coatings containing bark extracts were higher than those with commercial UV absorbers. Similarly, the solid content of the coating containing maritime pine bark extract was found to be the highest.

Highlights: The dry-film thickness and adhesion strength of waterborne acrylic coatings on wood substrate seem to be affected by addition of tree bark extracts.

Keywords: Acrylic Coating, Adhesion Strength, Dry Film Thickness, Tree Bark Extract, Pull-Off Test

Ticari UV Absorber ve Ağaç Kabuk Ektraktı İçeren Su Bazlı

Akrilik Yüzey Koruyucu Sistemlerin Bazı Fiziksel ve Mekanik Özelliklerinin Karşılaştırılması

Öz

Çalışmanın amacı: Bu çalışmanın amacı su bazlı yüzey koruyucu sistemlerin bazı fiziksel ve mekanik özelliklerinin incelenmesidir.

Materyal ve yöntem: 5 farklı ağaç türü (göknar, kızılçam, karaçam, kızılağaç, sahil çamı) ve UV absorber (Tinuvin 400 DW) içeren su bazlı akrilik reçine yüzey koruyucu sistemleri 2 farklı ağaç türüne; sarıçam (*Pinus sylvestris* L.) ve kayın (*Fagus orientalis* L.) uygulanmıştır. Kuru film kalınlıkları ışık mikroskobu ile ölçülmüştür. Yüzey koruyucuların yüzey ile bağlanma yeteneklerini incelemek amacıyla yapışma direnci belirlenmiştir. Ayrıca yüzey koruyucuların katı madde miktarları da belirlenmiştir.

Sonuçlar: Geçirgenlik, kuru film kalınlığı ve adezyon direnci için önemli bir parametredir. Aynı zamanda odun türü de kuru film kalınlığı ve adezyon direncini etkilemektedir. Kabuk ekstraktı içeren yüzey koruyucuların kuru film kalınlıkları ticari UV absorver içerenlerden daha yüksek bulunmuştur. Benzer şekilde, en yüksek katı madde miktarı sahil çamı ekstraktı içeren yüzey koruyucuda bulunmuştur.

Önemli vurgular: Su bazlı akrilik yüzey maddelerinin kuru film kalınlığı ve adezyon direncinin ahşap malzemeler üzerinde önemli etkileri vardır.

Anahtar Kelimeler: Akrilik Yüzey Maddesi, Yapışma Direnci, Kuru Film Kalınlığı, Ağaç Kabuk Ekstraktı, Çekme Testi

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Introduction

The physical and chemical changes occur on wood surfaces that are exposed to outdoor conditions (Kılıç & Hafızoğlu, 2007). Light (UV, IR), humidity (rain, snow) and mechanical forces (wind, sand, soot) alter the wood surface adversely and result in cracks, surface roughness, as well as discoloration (Feist & Hon, 1984; Williams, 2005). Biological and physical factors already cause modifications in the main components of wood, especially cellulose, hemicellulose and lignin. On the other hand, extractives are influenced relatively less during the photodegradation process. However, their concentration, color and odor change affects the non-mechanical properties of wood (Feist, 1990; Pandey, 2005).

Different methods have been preferred to restrain the changes on wood surfaces during the service life in the outdoors and also increase durability of wooden materials (Williams, 2005). These methods (paint, varnish, polish, water repellent, etc.) have been applied prevent contact between water and UV light and the wood surface. Moreover, other than these, alternative products have been offered to market in recent years (Ozgenç, Hiziroglu & Yildiz, 2012; Decker, Masson & Schwalm, 2004; Evans & Chowdhury, 2010).

Tree bark extracts have been evaluated for their organic UV absorbance values due to their high antioxidant effects. Kocaefe and Saha (2012) compared the effects of acrylic polyurethane-based coatings containing bark extract, lignin stabilizer, UV absorber and hindered amine light stabilizer (HALS). The bark extracts and lignin stabilizer were found to provide the highest photo-stabilization effect on heat-treated wood surfaces. Saha, Kocaefe, Boluk and Pichette (2011) reported that bark extract and lignin stabilizers (alone or in combination) in acrylic polyurethanebased coatings increased resistance against outdoor conditions. Bark extracts also enhance color stabilization of wood samples. The combination of 2-hydroxy-4(2,3epoxypropoxy)-benzophenone (HEPBP) as UV absorbent and epoxy functional soybean oil increased color stabilization in outdoor conditions compared to only UV absorbent (HEPBP). Moreover, combination of UV

absorbent (HEPBP) and epoxy functional soybean oil provided protection against degradation factors in outdoor conditions (Philip & Mohammed, 2010; Olsson et al., 2012;). Saha, Kocaefe, Krause, Boluk & Pichette, (2013) investigated the weathering performance of polyurethane-based coatings containing three different UV stabilizers. It was reported that coatings containing bark extracts with or without lignin stabilizers hindered photo-degradation. In another study, wood surface was pre-treated with mimosa mollissima) (Acacia and quebracho (Schniopsis lorentzii) bark extracts before applying polyurethane, cellulosic and waterbased varnishes (Yalcin & Ceylan, 2017). It was reported that pretreatment with bark extracts decreased the adhesion strength of coatings.

Dry-film thickness and adhesion strength influence the weathering performance of acrylic-based coatings. This study investigates the adhesion strength of waterborne acrylic-based coatings containing tree bark extracts and commercial UV absorbents (Tinuvin 400 DW). For this purpose, five different tree species (maritime pine, calabrian pine, black pine, alder, fir) were selected and their bark extracts were obtained with alcohol-benzene. The coating systems were applied to two different wood species; Scots pine (Pinus sylvestris L.) and beech (Fagus orientalis L.). The dry-film thickness of the coatings was examined by light microscopy. The results were compared to adhesion strength values to evaluate the effects of the bark extracts. The solid content of coatings was also determined.

Material and Methods

Wood Materials

In this study, defect-free samples of scots pine (*Pinus sylvestris L.*) and oriental beech (*Fagus orientalis L.*) tree species were selected. The wood samples were prepared with dimensions of 150 mm (longitudinal) by 70 mm (tangential) by 20 mm (radial) for artificial weathering.

Tree Barks

The barks were peeled off from the 20-30year-old alder (*Alnus glutinosa*), calabrian pine (*Pinus brutia*), maritime pine (*Pinus* *pinaster*), black pine (*Pinus nigra*) and fir (*Abies nordmanniana* L.) trees that were cut down in the Black Sea Region in northern Turkey. The preparation and chopping processes of the tree barks were implemented according to the TAPPI T 257 cm-12 and TAPPI T 264 cm-07 standards of extraction. Tree barks were air-dried at room temperature (23 °C, 65% relative humidity) and then grinded by using a laboratory scale Willey mill to obtain 40 to 60-mesh wood powder.

Bark Extraction

The bark powders were extracted in a Soxhlet extractor to obtain extractives. The bark powder (25 g for each) was soaked in 300 mL of ethyl alcohol: benzene mixture (1:2 v/v). The solvents from each extract were removed by using a rotary evaporator at 50 °C and stored in sealed flasks at 4 °C until use.

Preparation of Coating Systems

Six different wood coating systems were obtained using acrylic resin, binder, diluent, antifoam, pure water, bark extract or UV absorber (Table 1). "Tinuvin® 400-DW ", which is used as a commercial UV absorber, is a product of BASF. Tinuvin® 400-DW is an aqueous white to light beige liquid dispersion of a 2-hydroxy-phenyl-s-triazine (HPT) UV absorber (UVA) (https://www.ulprospector.com/en/na/Coatin gs/Detail/479/741631/Tinuvin-400-DW-N).

The coatings containing the commercial UV absorber were regarded as a control and compared to the coatings containing bark extracts.

Variation code:

A: Water borne acrylic resin-based coating containing fir extract B: Water borne acrylic resin-based coating containing alder extract C: Water borne acrylic resin-based coating containing calabrian extract D: Water borne acrylic resin-based coating containing maritime pine extract



E: Water borne acrylic resin-based coating containing black pine_extract

F: Water borne acrylic resin-based	
coating containing UV absorber	_



Table 1	1. Acrylic	resin-b	based	surface
system	formulation	n comp	onent	s (%).

No	Components	Formulation containing bark extract	Formulation containing UV absorber
1	Acrylic resin	72.5	72.5
2	Diluted water	18.88	20.88
3	Coalescent	0.67	0.67
4	Defoamer	1.0	1.0
5	Thickener	0.6	0.6
6	Thickener	1.3	1.3
7	Bark extract	5.0	-
8	UV absorber	-	3.0
9	Ammonia	0.05	0.05

Application of coating systems on the wood surface

The water-based wood preservative Induline SW 900 was applied as a primer layer to the side and front of the $120x70x10 \text{ mm}^3$ wood samples for the artificial weathering test. The coating systems were applied in two layers using a brush with 24-hour intervals. The coated wood samples were conditioned for 2 weeks at 20°C and $65\pm5\%$ relative humidity.

Determination of Dry Film Thickness and Solid Contents

1-gr samples were taken from the acrylicbased coatings and dried at 103 °C. Solid content was calculated from the dry weight of the coatings. Three measurements were averaged for each type of coating. Dry film thickness was determined by a ZEISS Stemi 305 light microscope and a ZEISS Axiocam ERc 5s camera with 2X magnification based on the EN ISO 2808 (2007) standard.

Adhesion Test

Wood specimens, which had dimensions 120x70x10 of mm. were used for determination of adhesion strength. The wood specimens were measured. Experiments were carried out by taking two measurements from each sample according to the ASTM D 4541 standards. Steel cylinders with a diameter of 20 mm were attached to the center of the specimens with epoxy resin adhesive and left to condition for 24 hours at 20 \pm 2 $^{\circ}$ C and $65\% \pm 5$ relative humidity for curing the glue. Then, the samples were placed under the drawing cylinder of an adhesion resistance measurement instrument (Erichsen Adhesionmaster 525 MC), the steel cylinders were connected, and tests were carried out at a rate of 0.5 N/s.

The force value at break was measured on the sensitivity level of \pm 0.01 N, and the adhesion strength of the samples was calculated using the following equation:

$$\rho_a = \frac{F}{A}$$

 ρ_{a} : Adhesion strength (N/mm²); F: Force at failure (N); A: Application area (mm²)

Results and Discussions

Determination of dry-film thickness and microscopic analyzing

The dry-film thickness values of the acrylic-based coatings containing bark extracts (test) and commercial UV absorber (control) on the wood surfaces were determined by light microscopy as given in Table 2 (Grüll, Tscherne, Spitaler & Forsthuber, 2014). The dry-film thickness values of the coatings containing bark extracts were higher than those of the commercial UV absorber. Scots pine and beech wood have different specific gravity and anatomical structure. Therefore, it was found that the coating penetration was higher and dry film thickness was lower on the scots pine wood surfaces as seen in Fig. 1-2. It is well-known that scots pine wood is much more permeable than beech wood which results in much deeper coating penetration (Ozdemir & Hiziroglu, 2007; Ozdemir, Bozdogan & Mengeloglu, 2013; Ozgenc, 2017). Consequently, this situation could cause formation of a thin film on scots pine wood samples. The dry-film thickness values also verified this phenomenon. Meanwhile, dryfilm thickness also had an effect on the service lives of coatings which reduce during aging (Skale, Doleček & Slemnik, 2008). Previous studies reported that beech wood with or without coating is more durable due to its structural properties against weathering factors in comparison to scots pine (Ozgenc et al., 2012; Ozgenc, 2017).

Table 2. Dry film thickness on the scots pine
and beech surfaces coated with acrylic based
coatings (µm)

Coating code	Scots pine	Beech
А	45.36	71.24
В	43.73	80.47
С	44.58	70.59
D	52.81	68.37
E	53.73	87.96
F	37.23	65.37

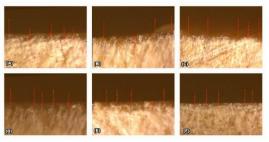


Figure 1. Microscopic image of scots pine surfaces coated with test and control acrylic systems.

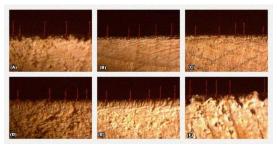


Figure 2. Microscopic image of beech surfaces coated with test and control acrylic systems.

Determination of Solid Content

The solid content of acrylic based coatings was given in Table 3.

Table	3.	Solid	content	of	acrylic	based
coating	gs (9	%)				

 0 ()	
Coating code	Solid content %
 А	38.11
В	32.09
С	41.18
D	42.09
E	39.27
 F	35.47

As seen, the solid content of coating was similar, except coating B and F. In general, bark extracts had higher solid content as compared to coating containing commercial UV absorber.

Adhesion Test

The adhesion of coating materials to wood and their ability to spread over the substrate primarily controlled surface are bv interactions between the surface forces at the interface (Kúdela & Liptáková, 2006). The adhesion strength of the acrylic-based coating systems containing bark extracts and commercial UV absorber on wood surfaces was shown in Table 4. The adhesion strength of the coatings on the beech wood surface was found to be higher in comparison to scots pine wood, which could have been affected by the thin dry-film thickness. According to previous studies, penetration of coatings into the wood is inversely proportional to dry-film thickness (Kim, 2018). Therefore, the increase in penetration resulted in a thin dry-film thickness, as seen in the scots pine wood samples in this study. These phenomena have affected adhesion strength between wood and coatings negatively (Bardage & Bjurman, 1998; Bulian & Graystone, 2009). Meanwhile, Yalcin and Ceylan (2017) reported that bark extractives decrease adhesion strength.

Table 4. Adhesion test values of coating systems (N/mm^2)

Coating	Acrylic-beech	Acrylic-Scots
type	Actylic-beech	pine
А	2.64	1.36
A	(0.46)	(0.19)
В	2.35	0.45
D	(0.24)	(0.17)
С	2.93	0.29
C	(0.32)	(0.09)
D	2.71	0.64
D	(0.88)	(0.16)
Е	2.71	0.19
	(0.45)	(0.09)
Б	1.71	0.64
F	(0.41)	(0.11)

Note: The standard deviation values are given in parenthesis.

The application of extracts before coating could change the wood's chemical structure which adversely effects the adhesion strength. On the contrary, in this study, bark extractives increased adhesion strength, which could have resulted from different application methods. The change in adhesion resistance is mainly due to interactions between polar components of the surface free energy of adjacent phases. The increase in the adhesion of the coating materials during the curing process was accompanied by a decrease in the interface free energy at the interface with wood (Kúdela &Liptáková, 2006). The change in adhesion strenght depends on the cohesion and adhesion effect between the wood surface and the varnish system. Therefore, factors such as polar structure of the coating system, moisture content of wood material, surface chemistry, application method of varnish (brush, spraying etc.) change the adhesion strenght (Gindl, Reiterer, Sinn & Stanzl-Tschegg, 2004). In both wood types, the acrylic-based coatings containing fir bark extract (A) provided the highest adhesion strength values. The coatings containing commercial UV absorber had even lower adhesion strength values for both wood species.

Conclusion

The dry-film thickness and adhesion strength of coatings have an important role in the service life of wooden materials. The importance of dry-film thickness and adhesion strength was particularly highlighted in this study. Many factors influenced drythickness, including film species, permeability and density. It was clearly seen that high permeability reduces adhesion strength as well as dry-film thickness. Scots pine penetrated by more coatings resulted in a thin dry-film thickness. Therefore, the adhesion strength of the coated scots pine wood samples was found to be lower than the coated beech wood samples. Moreover, bark extracts increased dry-film thickness which is important to obtain high adhesion strength. Eventually, these results indicated that bark extractives could be evaluated as natural UV absorbers instead of commercial UV absorbers because they are durable. environmentally friendly, easy to apply and economical. Therefore, waterborne acrylicbased coatings containing bark extractives could be applied on furniture, deck, pergolas, fences, children's play elements, pots, rails

and sidings. Moreover, utilization of tree barks which are normally recognized as forest waste, can be used for value addition.

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