Vlatka Jirouš-Rajković, Ivica Grbac, Stjepan Tkalec

An investigation into the protection of wood from UV-radiation and water

Istraživanje mogućnosti zaštite drva od UV-zračenja i vode

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SUMMARY • *The efficacy of various treatments for the protection of wood surface from ultraviolet (UV) radiation and water was investigated by using the measurements of the changes in adhesion on fir and oak samples after their exposure to natural climatic conditions and after accelerated weathering.*
The most efficacious of the six UV-protective treatments proved to be the treatment of the wood surface with the semi-transparent stain, followed by treatments with the transparent wood stain containing two types of photostabilizers. The stabilisation of the wood surface by chromium trioxide and ferric nitrate did not yield results which were expected according to the previous research.
Key words: *UV-radiation, photostabilizers, adhesion, chromium trioxide, ferric nitrate*

SAŽETAK • *Djelotvornost različitih tretmana zaštite površine drva od UV-zračenja i vode ispitivala se mjerenjem promjena adhezije na uzorcima jelovine i hrastovine nakon izlaganja prirodnim vremenskim utjecajima i nakon laboratorijskog izlaganja.*
Od 6 različitih tretmana zaštite drva od UV-zračenja najdjelotvornijim se pokazao tretman zaštite drva polu-transparentnom lazurom i zatim tretman zaštite transparentnom lazurom stabiliziranom sa dvije vrste fotostabilizatora. Stabilizacija površine drva krom (VI)-oksidom i željezo (III)-nitratom nije dala rezultate očekivane prema podacima dosadašnjih istraživanja.
Ključne riječi: *UV-zračenje, fotostabilizatori, adhezija, krom (VI)-oksid, željezo (III)-nitrat*

Authors are assistant, associate professor and professor, respectively, at the Faculty of Forestry of the University of Zagreb.
Autori su redom: asistent, izvanredni profesor i redovni profesor na Šumarskom fakultetu Sveučilišta u Zagrebu.

1. INTRODUCTION
1. Uvod

Ultraviolet (UV) radiation is only a small portion of the total incidents of global radiation (according to Kämpf it amounts to 5 - 6 %; depending on the geographic position and the season). However, this radiation is of great importance since its high energetic potential causes the breakdown of numerous chemical bonds.

Wood is an excellent light absorber (Hon et al. 1980) and therefore its surface, when exposed out of doors, undergoes physical and chemical changes which are caused by solar radiation. The reaction of light with the wood polymers distributed on their surface leads to a discoloration and degradation of the wood surface. Almost all wood chemical constituents (namely cellulose, hemicellulose, lignin and extractives) are UV-sensitive and prone to degradation which is attributed to the chromophoric groups within the polymers of the wood's cell wall. Fortunately UV light does not penetrate into the wood surface deeper than 75 μm (Hon and Ifju, 1978), which means that the reaction of wood with light is a surface reaction in which the emission of the free radicals plays a major role on the surface's degradation and discoloration (Hon et a. 1980).

The traditional methods of wood protection from UV-light include the application of protective coatings. The best protection is provided by pigmented coatings since the pigments preserve the polymer by absorption or by reflection of the UV-light. On the other hand, the pigments cover the colour and the structure of the wood. Transparent coatings are often requested in recent years because they do not change the natural appearance and colour of the wood. However, the resistance of these finishes to photodegradation is small because most of these materials are UV-sensitive and quickly lose their protective function. Besides, UV-light that penetrates through the coating may initiate a photochemical reaction on the wood surfaces. This results in a discoloration and loss of adhesion between the wood and the coating.

The modern protection of the transparent coatings against the negative effects of UV-light is mainly achieved by the application of UV-absorbers and HALS-compounds (Hindered Amine Light Stabilisers). The stabilising effect of UV-absorbers is based on their absorption of the damaging UV-energy and its transformation into a harmless heat form.

The efficiency of UV-absorbers depends on the film thickness and the distance from the wood surface (Böhnke and Hess, 1989). The chemicals which are most often incorporated into lacquers are oxalanilides, benzotriazoles and benzophenones. Besides UV absorbers the coatings are often modified with HALS (Hindered Amine Light Stabilisers) compounds whose main constituent is tetramethyl - piperidine system. Their stabilising effect is based on their ability to transform the free radicals, which develop in the binder during exposure, into harmless chemical forms. The action of HALS compounds does not depend on the film thickness, and that distinguishes them from the UV absorbers. HALS compounds are equally efficient on the film surface and in its depth. UV absorbers are the means for preventive protection of the coating from the UV-radiation, but HALS compounds become efficient only when the film is damaged and the formation of the free radicals is initiated.

Besides the UV portion of the solar spectrum, its violet/blue portion significantly contributes to the degradation of wood (Derbyshire and Miller, 1981). That means that two competitive demands are made for the optical characteristics of the clear coatings since these finishing materials exhibit high levels of transmittancy in the visible part of the spectrum in order to sustain the natural look of wood. This is the main reason for certain reservations about the efficacy of the transparent finishes in the outdoor applications unless the wood surface is photo-stabilised. During the last two decades numerous research tasks have been focused on the improvement of the stability of wood against light. It has been established (Black, Mraz 1974; Feist 1977; Feist and Ellis 1978; Feist 1979) that some inorganic chemicals, when applied to the wood surface as diluted aqueous solutions, ensure the following: They:

1) Retard the wood surface degradation by the action of UV-radiation

2) Improve the durability of the UV-transmittent polymer coatings

3) Extend the service life of varnishes and stains

4) Enable the dimensional stability of the wood surface

5) Assure resistance against fungal deterioration

6) Serve as natural wood finishes even without additional treatments

7) They fix the water soluble components within the wood material and thus diminish the colour changes which may occur with the application of a top coating.

The most efficient treatments are those which contain chromium trioxide, copper chromate or ammonia solutions of these chemicals. The treatments with chromium trioxide are efficacious on both soft and hard wood surfaces (Feist ,1987). Chang et al. (1982), found out that UV-degradation may be retarded by the treatment of wood with chromium trioxide and ferric chloride. These authors assume that cellulose and lignin react with chromium or feric ions and thus compose a complex system which may take part in the photochemical reactions by emitting energy from the wood surface or by shifting the absorbing zone towards the shorter wavelengths. It is also possible that inorganic salts which are efficient quenchers of peroxides may prevent the formation of peroxides on the wood surface.

It has been established that some penetrating liquids containing polyethylene glycol and other organic compounds enhance the colour stability of the irradiated wood (Hon, Chang and Feist, 1985). Williams (1983) showed that the stabilisation of the wood surface with benzophenone UV absorber, which is chemically bonded to the wood surface, reduces the erosion of wood which is not varnished and serves as a priming treatment that improves the protective role of the transparent varnish and enhances the stability of the colour.

The scope of this work was to investigatie the efficiency of salts in wood surface stabilisation and the possibilities of the protection of wood from weathering by the application of stabilized water-based wood stains.

The combination of the effects of UV-radiation and water leads, initially, to the degradation of the shorter lignin molecules, which turn brownish and become soluble in water. Macromolecules of cellulose become sub-

Table 1. *Sample codes and description of the treatments.* • *Oznake uzoraka i opis tretmana*

Sample code *Oznaka uzorka (tretmana)*	Description of the treatment and material used *Opis tretmana i materijala*
L	Impregnating primer, applied by dipping Wood stain without a photostabiliser, air sprayed *Impregnacija nanešena uranjanjem* *Lazura bez fotostabilizatora ,nanos štrcanjem*
F1L	Impregnating primer, applied by dipping Wood stain with a photostabiliser F1 (TiO_2), air sprayed *Impregnacija nanešena uranjanjem* *Lazura sa fotostabilizatorom F1(1,5% TiO_2), nanos štrcanjem*
F2L	Impregnating primer, applied by dipping Wood stain with a photostabiliser F2 (1% Tinuvine 1130 + 1 % HALS Tinuvine 292), air sprayed *Impregnacija nanešena uranjanjem* *Lazura sa fotostabilizatorom F2(1%Tinuvin 1130 +1% HALS Tinuvin 292), nanos štrcanjem*
L2	Impregnating primer, applied by dipping Pigmented (semi-transparent) wood stain *Impregnacija nanešena uranjanjem* *Lazura sa pigmnentom (polu-transparentna lazura)*
CrL	Wood surface stabilised by the application of chromium trioxide Wood stain without a photostabiliser, air sprayed *Stabilizacija drva krom (VI)-oksidom nanešenim na površinu* *Lazura bez fotostabilizatora ,nanos štrcanjem*
FeL	Wood surface stabilised by the application of ferric nitrate Wood stain without a photostabiliser, air sprayed *Stabilizacija drva željezo (III)-nitratom nanešenim na površinu* *Lazura bez fotostabilizatora ,nanos štrcanjem*

sequently also degraded, and they form a soft and greyish surface under the clear film which looses its adhesion. Hence if the coating itself is very transmittent to UV light, the radiation degrades the surface underneath the film, and the first consequence is the loss of adhesion. The measurement of the adhesion between the wood and the coating was used in this work to assess the efficiency of various treatments in protecting the wood surface from weathering.

2. MATERIAL AND METHODS
2. Materijal i metode

Two types of samples with radial surfaces were used for the experiment: fir wood specimens (density 404 kg/m^3 at 12 % M.C.) and oak specimens (density 681 kg /m^3 at 12 % M.C.) were prepared as plates with dimensions of 100 X 200 X 10 mm for natural exposure, and with dimensions of 75 X 100 X 5 mm for accelerated weathering. All the specimens were prepared by fine planing, sanded (grit size 150) and conditioned before finishing. The moisture content of the specimens application of the coating was 9%. The survey of the specimen types is presented in Table 1.

The specimens with the CrL and FeL codes were stabilised with the aqueous solutions of the chromium trioxide and ferric nitrate, respectively, before the application of the stain. The aqueous solutions of these salts were prepared so that they contained 2.5 % of the chromium or iron. Therefore 26.3 g of chromium trioxide was diluted in 500 ml of distilled water, while the ferrous solution was prepared by dissolving 94 g of the ferric nitrate ($Fe(NO_3)_3$ x 9 H_2O). The spreading rate was 0.1 ml per 6.45 cm^2, and that amount of liquid was dispersed over the entire surface using a brush for the larger samples, and a glass stick for smaller samples. After two hours of drying at room temperature (21 ^oC) the samples were put for 10 min into the oven at 135 ^oC so that the chromium and iron were fixed better to the wood (according to Feist and Ellis, 1978). The samples were conditioned for a week at 21 $\pm$ 2 ^oC and 60 $\pm$ 5 % relative humidity. Just before the stain application the samples were briefly rinsed with distilled water and reconditioned.

Samples of the L type were finished with the top-coat, film forming, transparent water-based wood stain*. The binder of this stain is a modified acrylic co-polymer emulsion with 45 % solid content, pH value of 8.7 and with a minimum film forming temperature of 0^oC. The binder was combined with the polyurethane dispersion in order to improve the surface resistance, and to reduce the effect of "blocking" (mutual sticking of the products in the stack). This also should improve the weather resistance.

The F1L samples were coated with the same stain which was modified with the 1.5 % of the ultra-fine colloid dispersion of the TiO_2. The F2L samples were finished with the same stain enriched with 1% of the Tinuvine 1130 UV-absorber and 1 % of the HALS Tinuvine 292 (weight proportions in respect to the final formulation).

L2 is the code which marks the specimens finished with the semitransparent *EKOL DS 2040* stain. This stain contains pigments of iron oxide instead of photostabilisers. Before the stain application all the samples (except those stabilised with salts) were impregnated with *Ecol* primer which contains an alkyd-acrylic copolymer dispersion as a binder.

The primer was applied by dipping for 10 seconds. After that the samples were dried overnight and gently hand-sanded with a "scotch brite" sponge. The stain was air-sprayed with a 2.5 μm nozzle which gave a wet film thickness of 300 $\pm$ 10 μm. After drying the stain for 24 hours at room temperature, the samples were additionally conditioned for a week at a temperature of 21 $\pm$ 2^oC and relative humidity of 60 $\pm$ 5%, and finally exposed.

2.1 Accelerated weathering

Accelerated weathering was performed in the QUV weathering tester. A 24-hour cycle consisted of 8 hours of UV-radiation with the UVA-340 lamps at 60 ^oC, followed by 4 hours of condensation at 50 ^oC; the exchange of 8 hours of radiation and 4 hours of condensation was then repeated. The samples were withdrawn after 1 week, 4 weeks, 8 weeks, 12 weeks and 16 weeks of accelerated weathering.

2.2 Natural weathering

Natural weathering was performed on the roof of the building. The specimens were fully exposed at 45^o facing south for six months between 01.02.1997 and 01.08.1997. The adhesion measurements were made at the end of each month.

2.3 Adhesion testing

The adhesion of the film-forming stains on the wood was measured by the pull-off method (according to ASTM D 4541-95)

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*All finishes used in this work are standard product of COLOR MEDVODE.
AllSvi materijali za površinsku obradu korišteni u ovom radu proizvodi su tvrtke COLOR MEDVODE.

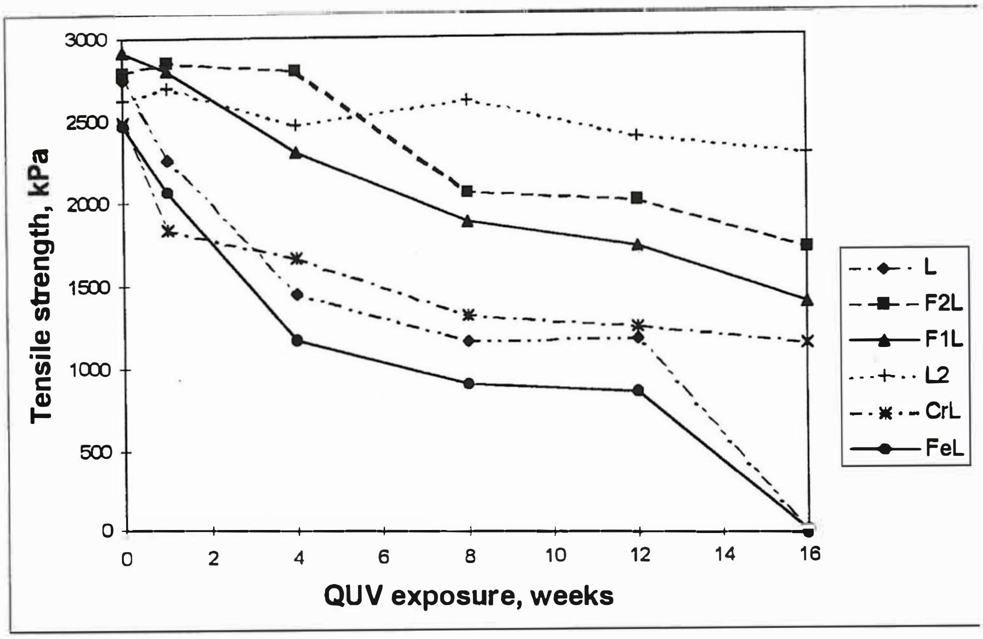


Fig. 1. *Change in adhesion during accelerated weathering of fir-wood • Promjena adhezije (vlačna čvrstoća, kPa) nakon ubrzanog izlaganja (tjedni QUV-a) uzoraka jelovine*

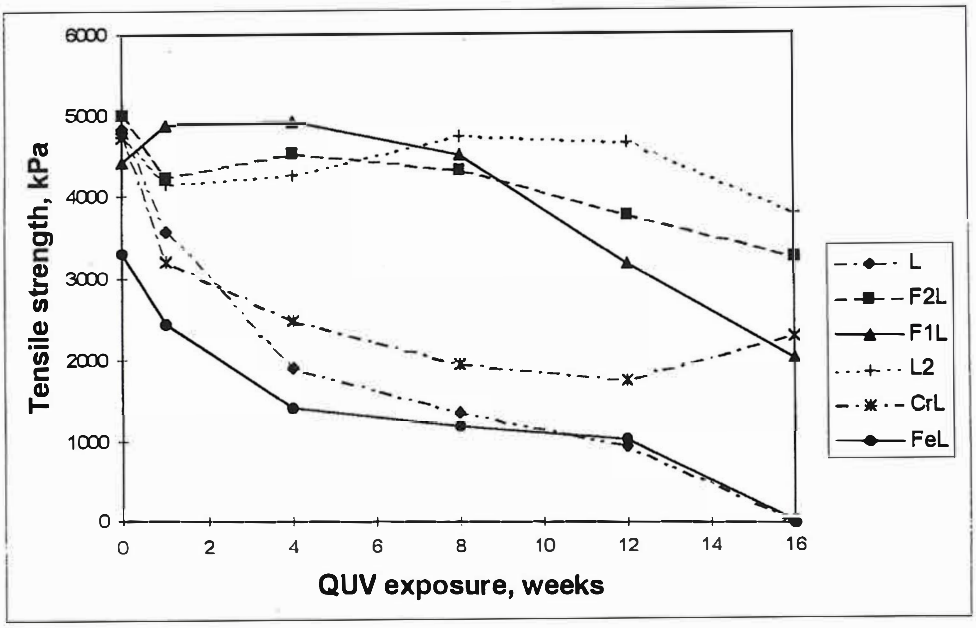


Fig. 2. *Change in adhesion during accelerated weathering of oak-wood • Promjena adhezije (vlačna čvrstoća, kPa) nakon ubrzanog izlaganja (tjedni QUV-a) uzoraka hrastovine*

using the PATTI-2A (Pneumatic Adhesion Tensile Testing Instrument). The method consists of gluing the cylindrical studs with epoxy resin onto the surface of the film. After the curing of adhesive for 24 hours, the studs were loaded with a lifting, continuously increasing force until the studs were pulled off or until the certain limit value of the force was achieved. The tensile strength of the film on the wood (adhesion of the film) was calculated from the ultimate force which led to the detachment of the stud from the surface. The design of the PATTI-2A instrument enabled the lifting of the stud virtually parallel to its axis. Adhesion was measured at six positions on the samples for natural exposure, and on 4 places on the samples for accelerated weathering.

3. RESULTS AND DISCUSSION
3. Rezultati i diskusija

Figures 1 and 2 present the results of the adhesion measurements during accelerated weathering. After 16 weeks of accelerated weathering the film peeling and complete loss of adhesive link between the film and the substrate was recorded on fir-wood and oak-wood samples, finished with transparent stain without a photostabiliser (samples marked *L*) and on the samples stabilised with ferric nitrate and coated with the same stain (samples marked *FeL*).This is why the value of the tensile strength of these samples is virtually zero.

The specimens that were stabilised with chromium trioxide and coated with the

Fig. 3.
Change in adhesion during natural weathering of fir-wood • Slika 3. Promjena adhezije (vlačna čvrstoća, kPa) nakon prirodnog izlaganja (u mjesecima) uzoraka jelovine

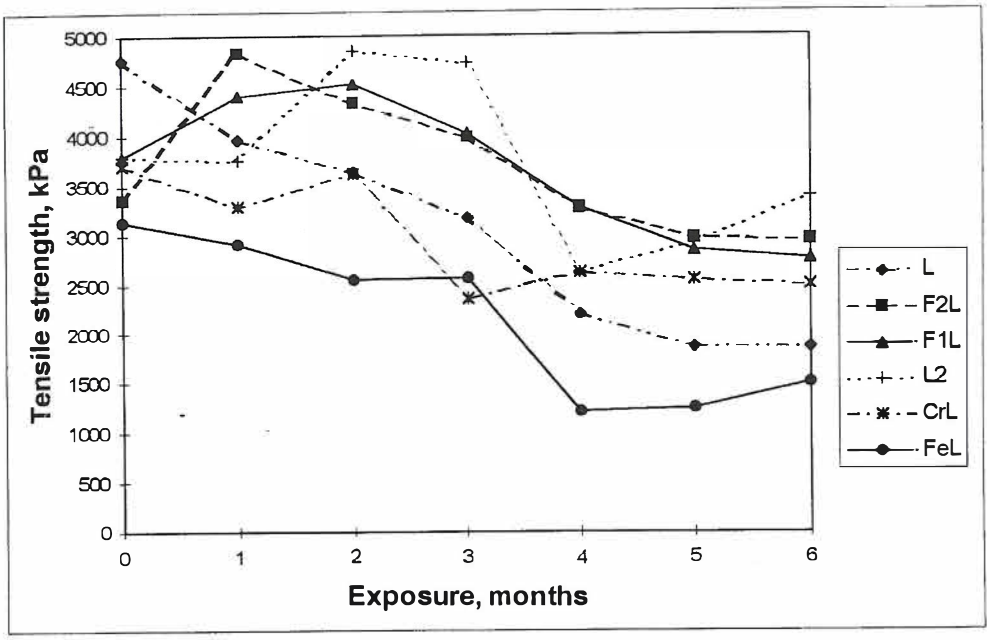
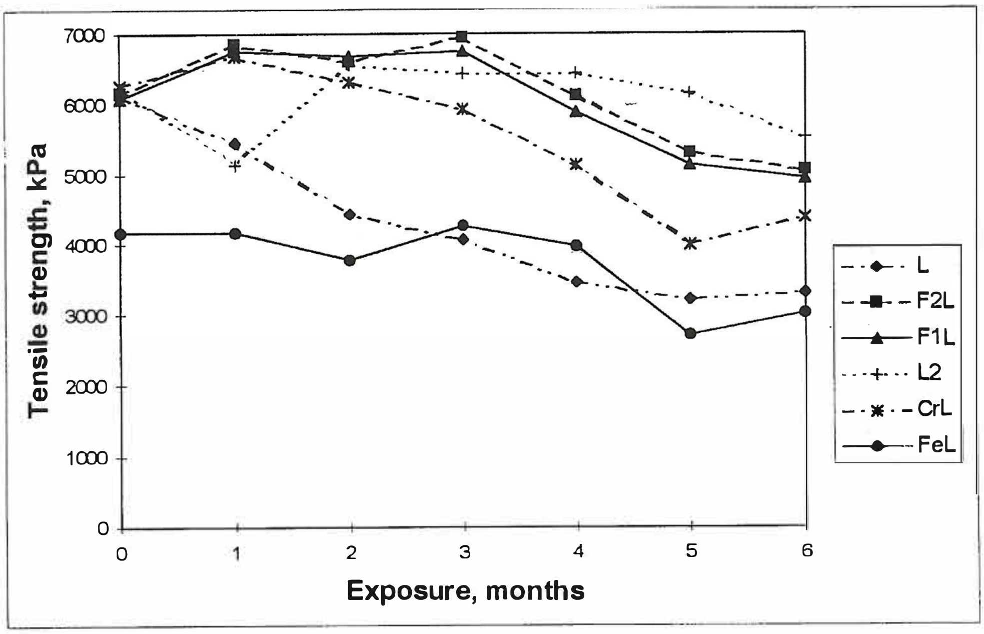


Fig. 4.
Change in adhesion during natural weathering of oak-wood • Promjena adhezije (vlačna čvrstoća, kPa)nakon prirodnog izlaganja (u mjesecima)uzoraka hrastovine



stain (samples of the *CrL* type) as well as the samples finished with the stain that was enriched with the TiO_2 stabiliser (marked *F1L*) lost after 16 weeks of exposure more than 50 % of their initial strength, and consequently their adhesion was reduced by 50 % on both the oak-wood and fir-wood samples. The samples finished with the semi-transparent stain which was modified with two types of photostabilisers (samples marked *F1L*) exhibited after a 16 weeks exposure the smallest reduction in adhesion.

The natural exposure of 6 months is too short a period to cause drastic visual changes on the samples (save for the colour change), but the results of the monthly adhesion measurements show the changes, particularly on the fir-wood samples (fig. 3). According to these results the fir-wood samples finished with the stain without a photostabiliser (samples marked *L*) and the samples stabilised with ferric nitrate before the application of the stain (those marked *FeL*) after only 6 months of natural exposure exhibited a loss of adhesion that exceeded 50 %. The samples stabilised with the chromium(VI)-oxide and subsequently finished with the stain also showed a substantial loss of adhesion after only 6 months of exposure. The decrease in adhesion during natural exposure is much smaller for the oak-wood samples and the period of 6 months is far too short for this naturally durable species to exhibit significant changes (figure 4). Similarly as with the fir-wood samples, the greatest adhesion loss was recorded on the samples finished with the transparent stain without added photostabiliser (mark *L*). Of all the six protective treatments the most efficacious proved to be the treatment with the semi-transparent stain (mark *L2*) and the treatment with the transparent stain which was stabilised with either UV-absorber or HALS stabiliser (samples marked *F2*). Stabilising the stain with the titanium dioxide TiO_2 proved much less efficacious. It was interesting to see that the treatment of wood stabilisation with chromium trioxide and ferric nitrate did not yield the expected results. Adhesion of the tested stain applied on the oak-wood samples treated with the ferric nitrate was initially smaller than on the other samples, and after 16 weeks of accelerated weathering the film of stain showed peeling defects. The greatest reduction in adhesion was recorded (as was expected) on the samples finished with the transparent stain without the addition of a photostabiliser. The light easily penetrated through this stain and initiated the changes on the wood surface, and this eventually led to the loss of adhesion. It should be emphasised here that water, besides the UV radiation, also played an important role. Water was present during the accelerated weathering in the condensation cycles, and also contributed to the natural weathering.

4. CONCLUSION
4. Zaključak

The method of the measurement of changes in adhesion on wood samples during accelerated or natural weathering may yield indications about the efficacy of particular treatments in the protection of wood against UV-radiation and water. The most efficacious of the six UV-protective treatments proved to be the treatment of wood surface with the semi-transparent stain, followed by the treatments with the transparent wood stain containing two types of photostabilisers. The stabilisation of wood surface by chromium trioxide and ferric nitrate did not yield the expected results.

5. LITERATURE
5. Literatura

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