*Hrvoje Turkulin* [1], *Martin Arnold* [2], *Hilary Derbyshire* [3], *Jürgen Sell* [2]

# SEM study of the weathering effects on painted wood

## SEM ispitivanje djelovanja atmosferilija na površinski obrađeno drvo

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**SUMMARY** • *For the purpose of evaluating the performance and durability of modern wood coatings with low organic solvent content, natural and artificial exposure trials of various specimens were performed and subsequently the conditions of the coating, of the substrate and of their link was assessed by scanning electron microscopy (SEM). Two types of European softwood species were used as a substrate, namely pine and spruce, and they were used either as coated panels or as microtomed wood sections ('thin strips'), which were exposed behind a detached film of a coating. Solvent borne (sb) coatings were compared with modern water-borne (wb) coatings. Semitransparent stains were compared with opaque white paints. Pine and spruce did not show significant differences in their failure modes, film-holding properties or UV light resistance under semi-transparent coatings. However, spruce was shown to undergo somewhat smaller structural changes with weathering.*
*The paints did not penetrate the cell wall but firmly adhered to the S3 layer of the lumina. The solvent-borne coatings (both paint and stain) penetrated deeper into the wood surface than the water-borne coatings.*
*The opaque paints fully protect the wood from the effect of light through a 14-month period of natural exposure and maintain the coherent protective coating. The water-borne paint exhibits more brittle characteristics on the fractured transverse surface than the solvent-borne paint.*
*The stains vary in their protective effectiveness. The thick water-borne stain shows a tough, sound failure mode, good adhesion but very poor penetration into wood surface. The thin coating of the solvent-borne stain is degraded by light, and the interface with the wood is affected, resulting in the development of brittleness of both wood and coating and leading to*

[1] Faculty of Forestry, Zagreb University, Croatia. Dr H. Turkulin is an assistant lecturer. - Šumarski fakultet Sveučilišta u Zagrebu. Dr H. Turkulin je viši asistent.
[2] EMPA, Wood Department, Dübendorf, Switzerland. Authors are a research technologist (M. Arnold) and a Head of the Department (Dr J. Sell). - EMPA, Drvni odsjek, Dübendorf, Švicarska. Autori su istraživač (M. Arnold) i voditelj odsjeka (Dr J. Sell).
[3] Building Research Establishment Ltd (BRE), Centre for Timber Technology and Construction, Watford, Great Britain. Dr H. Derbyshire is a research physicist, Head of the Coatings science section. - BRE, Centar za drvnu tehnologiju i konstrukcije, Watford, Velika Britanija. Dr H. Derbyshire je predstojnica Sekcije za površinsku obradu.

*adhesion failures preceding the detachment of the film.*
*Thin strips with detached films of coatings realistically represent the surface of coated wood specimens, and are easy to handle, to detach and subsequently to investigate both mechanically and microscopically. The combination of strength measurements and the microscopic evidence proved particularly effective for the interpretation of the changes occurring at the very surface of wood components i.e. at the wood-coating interface. The microscopic observations confirmed that the progress of wood photodegradation can be successfully detected by the combination of the state of deterioration of anatomical elements on radial surfaces and by fractographic evidence on cross sections.*
***Key words:*** *SEM, photodegradation, durability, wood finishing, water-borne coatings, solvent-borne coatings*

**SAŽETAK** • *Zadaća istraživanja je bila procjena postojanosti i ponašanja u upotrebi modernih premaza za drvo s niskim sadržajem organskih otapala. U tu su svrhu provedena izlaganja različitih uzoraka prirodnim klimatskim uvjetima i izlaganja u laboratorijskom uređaju, nakon čega su metodom elektronske mikroskopije ispitana svojstva premaza, drvne podloge i njihove međusobne veze. Korištene su dvije vrste europskih četinjača - borovina i smrekovina - a uzorci su bili izrađeni u obliku obojenih daščica ili mikrotomskih odsječaka ("tankih listića") koji su bili izloženi ispod slobodnog filma premaza. Moderni vodotopivi premazi su uspoređeni s organskim premazima, a poluprozirne lazure su uspoređene s neprozirnim bijelim naličima.*
*Borovina i smrekovina ne razlikuju se bitno glede njihovih vrsti loma, adhezijskih svojstava ili otpornosti na ultraljubičasto (UV) svjetlo pod slojem poluprozirnog premaza. Ipak se moglo vidjeti da smrekovina s izlaganjem nešto brže iskazuje strukturne promjene nego borovina.*
*Nalići ne prodiru u staničnu stijenku nego čvrsto prianjaju uz S3 podsloj na površinama lumena. Premazi s organskim otapalima (i nalići i lazure) su prodrli nešto dublje u površinu drva nego vodotopivi premazi.*
*Pigmentirani nalići u potpunosti štite drvo od svjetla tijekom cijelog 14 -mjesečnog razdoblja prirodnog izlaganja i zadržavaju koherentni zaštitni sloj. Vodotopivi nalići naglašenije iskazuju značajke krtosti na poprečnim lomnim plohama nego što je to slučaj s organskim premazima.*
*Lazure se razlikuju u njihovoj zaštitnoj učinkovitosti. Način loma debelog sloja vodotopive lazure iskazuje žilavost i neoštećenost, dobro prianjanje ali vrlo slabu penetraciju u drvnu površinu. Tanki premaz organske lazure je djelomično oštećen svjetlom, a to djelovanje se očituje i na međusloju premaza i drva uslijed čega nastaje povećanje krtosti i drva i premaza. To dovodi do slabljenja adhezije koje prethodi odlupljivanju filma.*
*Tanki listići pokriveni slobodnim filmovima premaza uspješno predstavljaju površinu premazanih drvenih elemenata, a jednostavni su pri rukovanju, pri odvajanju od premaza i pri daljnjim mehaničkim i mikroskopskim ispitivanjima. Kombinacija mjerenja promjena čvrstoće i mikroskopskih uvida se pokazala vrlo učinkovitom u razmatranju promjena koje se odvijaju na samoj površini drvnih elemenata tj. u međusloju drva i premaza. Mikroskopska promatranja su potvrdila da se odvijanje svjetlosne razgradnje drva može uspješno pratiti kombiniranim uvidom u stanje oštećenosti anatomskih elemenata na radijalnim površinama drva i fraktografskom analizom poprečnih presjeka drva.*
***Ključne riječi:*** *SEM, svjetlosna razgradnja, postojanost, površinska obrada drva, vodotopivi premazi, organski premazi.*

## 1. INTRODUCTION AND OBJECTIVES
## 1. Uvod i cilj istraživanja

For the purpose of evaluating the performance and durability of modern wood coatings with low organic solvent content, natural and artificial exposure trials of various specimens were performed and subsequently the conditions of the coating, of the substrate and of their link was assessed by scanning electron microscopy (SEM). Two types of European softwood species were used as a substrate, namely pine and spruce, and they were used either as coated panels or as microtomed wood sections ('thin strips'), which were exposed behind a detached film of a coating. Solvent borne (sb) coatings were compared with modern water-borne (wb) coatings.

This study is dealing with the properties of the wood-coating interface. The particular scope of this study was to investigate the effectiveness of selected wood coatings in protecting the interface from the deleterious effect of ultraviolet (UV) light and to assess the penetration and adhesion of these coatings, initially and after exposure. The objectives of the study therefore were:

1.To define the changes in the micro structure and the modes of failure of uncoated pine and spruce thin strips exposed to natural and artificial weathering.

-What are the characteristic features of the weathering process as identified with the SEM?

-Are there any differences between the two species pine and spruce?

2.To investigate how the presence of a surface coating affects the weathering process.

-What changes are observed in the micro structure and the modes of failure in pine and spruce weathered behind a surface coating?

-Are there any discernible differences in the micro structural changes for weathering behind paints and stains?

3.To define the changes in the physical and mechanical properties of the surfaces of painted wood panels after natural exposure.

-What are the penetration, adhesion and cohesion of the coatings at the wood - coating interface?

-Are there any changes at the wood-coating interface observed for weathered panels? Are there any changes to be associated with the effect of UV light?

4.To study the conformity between the observations on coated panels and the thin strip method.

This study is a part of the EU/AIR-project 'Performance and durability of wooden window joinery painted with new types of paints with low organic solvent content' (AIR3-CT94-2463, DG XII). The preparation, exposure and tensile testing of the thin strips were carried out at The Centre for Timber Technology and Construction, Building Research Establishment Ltd, Watford (UK). The preparation and exposure of the panels, as well as the SEM work, were performed at the Wood Department of the Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf, Switzerland. The work was carried out within a programme of co-operation between EMPA and the Faculty of Forestry, Zagreb University, Croatia.

## 2. MATERIALS AND METHODS
## 2. Materijal i metode

### Wood species

Two softwood species were used in the study: Scots pine sapwood (*Pinus sylvestris* L.) and European (Norway) spruce (*Picea abies* Karst.). The exposed panels had an average wood density of 0.54 g/cm$^3$ and 0.44 g/cm$^3$ at 12.5 % moisture content for pine and spruce respectively. The wood was straight grained, without visible defects, with average ring width and latewood portion.

### Coatings

Four coatings were selected out of the 11 model paints of the project representing four different types of products regarding solvent type and appearance. Details about the selected coatings are listed in Table 1. The thin strips were not coated but exposed in close contact with a detached film of the coating (previously cast on a glass plate). All four coatings were used on panels, whereas the strips were exposed only behind the films of the solvent-borne opaque paint and semi-transparent stain.

### Preparation and exposure of the panels

The panels of dimensions 300 (longitudinal) x 100 x 20 mm were semi-quarter sawn with an approximate angle of the growth rings to the surface of 45$^o$. All the surfaces of the panels were smooth planed, and the front faces were additionally sanded (grit size 120) prior to the coating application with a belt sander using minimal belt pressure. The coating was uniformly applied to all the surfaces, including the end grain. The panels

*Table 1.* *Details of the selected coating systems.* • *Neka svojstva ispitivanih sustava premaza*

| Coating | Coating system *Sustav premaza* | | | | | Film thickness [μm] *Debljina filma* [μm] | |
|---|---|---|---|---|---|---|---|
| No. *Premaz br.* | Type *Vrsta* | Appearance *Izgled* | Blue stain preserv. *Zaštita protiv plavetnila* | Primer *Temelj* | Topcoat *Završni sloj* | detached films (wet) *mokra* *(slobodni film)* | Panels (dry) *suha* *(obojene daščice)* |
| 3 | wb acrylate paint *vt akrilni nalič* | opaque (white) *neprozirni (bijeli)* | yes *da* | acrylate A, PVC 25% *Akrilat A* | PVC 25% | acrylate A, PVC 15% *Akrilat A* | PVC 15% |
| 7 | wb acrylate stain *vt akrilna lazura* | semi-transparent (red-brown) *poluprozirna (crvenosmeđa)* | yes *da* | acrylate C *Akrilat C* | acrylate C *Akrilat C* | | 200 |
| 10 | sb alkyd paint *oot alkidni nalič* | opaque (white) *neprozirni (bijeli)* | no *ne* | 2x sb alkyd *2x oot alkid* | | 80 | 60 |
| 11 | sb alkyd stain *oot alkidna lazura* | semi-transparent (red-brown) *poluprozirna (crvenosmeđa)* | no *ne* | 3x sb alkyd *3x oot alkid* | | 50 | 50 |

**wb** =water borne **vt** = *vodotopljiv,* **sb** = solvent borne - **oot** = *na osnovi organskih otapala*

were exposed inclined at 45° facing south at the EMPA exposure site in Dübendorf, Switzerland, from November 1995 until January 1997. The site is inland, semi-urban, located at 47° north, 450 m above sea level, and the climate is continental - prealpine, medium wet with an annual sum of precipitation of >1000 mm and approx. 1700 hours of sunshine per year. The upper portions of the panels (approx. 5 cm from the top edge) were covered from light and precipitation with metal profiles, and no precipitation reached the rear surfaces of the panels.

**Preparation and exposure of the thin strips**

The procedure for preparation of the microtomed thin strips was fully reported before (Derbyshire et al. 1981, 1995 and 1996), only a brief description is given here. Blocks of dimensions 100 x 10 x 20-30 mm in the longitudinal, radial and tangential directions respectively were vacuum impregnated with distilled water at ambient temperature until fully saturated. Thin strips were then microtomed from the radial face of the block using a conventional sliding microtome. The nominal thickness of the strips was 80 μm. The strips were allowed to dry naturally overnight and then were checked for uniformity of thickness using an electronic thickness gauge which gave an accuracy ± 0.1 μm. Normal scattering of thickness was within a range of ± 5 μm of the mean value. Strips were stored in the dark under standard laboratory conditions of 20 ± 1 °C, 65 ± 5 % relative humidity except during exposure and testing.

For natural weathering the strips were mounted on aluminium frames and covered with detached films of the coatings in close contact with the strips. The back sides of the strips were free and approx. 5 mm distanced from the aluminium mounting panel. The frames were exposed inclined at 45° facing south at the BRE exposure site (South-East England, 52° north, 70 m above sea level) between August and November 1995. The site is inland, semi-urban, and the climate is continental-maritime, medium wet, with annual sum of precipitation of approx. 600 mm and about 1500 hours of sunshine per year.

Artificial weathering was carried out in a QUV device (Q-Panel Co.) fitted with UVA-340 fluorescent lamps. The spectral output of these lamps is concentrated in the ultraviolet region of the spectrum between 300 and 400 nm with peak output at 340 nm. Thin strips were fixed to aluminium frames and covered with detached films of the coat-

*Table 2: Tensile strength of thin wood strips after natural and artificial exposure. • Vlačna čvrstoća tankih listića nakon prirodnog i laboratorijskog izlaganja klimatskim uvjetima*

| Coating *Premaz* No. Br. | Coating *Premaz* Type *Vrsta* | Exposure, duration *Način izlaganja, trajanje* | Species *Vrsta drva* | Dry strength retention [%] *Postotak zadržane početne vrijednosti čvrstoće (%)* Testing span - *raspon ispitivanja* 0 mm | 10 mm |
|---|---|---|---|---|---|
| | uncoated *nezaštićeno* | natural, 12 weeks *prirodno 12 tjedana* | pine - *borovina* | 44 | 19 |
| | | | spruce - *smrekovina* | 50 | 23 |
| 11 | sb stain - *oot lazura* | | pine *borovina* | 88 | 74 |
| | | | spruce - *smrekovina* | 104 | 96 |
| 10 | sb paint *oot nalič* | | pine *borovina* | 96 | 82 |
| | | | spruce - *smrekovina* | 104 | 96 |
| 11 | sb stain - *oot lazura* | QUV, 14 weeks *14 tjedana* | pine *borovina* | 82 | 55 |
| | | | spruce - *smrekovina* | 97 | 75 |
| 10 | sb paint *oot nalič* | QUV, 30 weeks *30 tjedana* | pine borovina | 86 | 66 |
| | | | spruce - *smrekovina* | 94 | 81 |

ings in close contact with the strips. The back sides of the frames were covered with aluminium plates to ensure controlled conditions within the chamber. The QUV was operated with continuous cycles of 4 hours of UV light (with 30 % relative humidity and 60°C) followed by 4 hours of condensation (100 % relative humidity, approx. 40 °C, lamps off). The strips were withdrawn at intervals, conditioned at standard conditions and tested for tensile strength. The testing was performed at 10 mm and at zero span, where the jaws are initially in contact. Finite span testing gives information principally about the level of degradation of the binding matrix and inter-fibre bonding, while the zero span results reflect the level of degradation of the cellulosic microfibriles. The results of the tensile testing (percentage retention of initial strength) are listed in Table 2.

### Preparation of the microscopic specimens

After exposure the thin strips were separated from the coating film and tested in tension. The tested strips were stored for further examination in self-adhesive photo album sheets and some were later randomly chosen for SEM examination. In preparation for the microscopic analysis the strips were vacuum dried at ambient temperature and sputtered with a layer of platinum. Using the usual preparation method, it is estimated that the layer of platinum was approx. 15 nm thick (Zimmermann et al. 1994). The specimens were mechanically fastened to the mounting blocks so that the fractured edges were exposed for observation. The field-emission scanning electron microscope (FE-SEM) used was a JEOL JSM 6300 F situated at the EMPA.

Fractured transverse surfaces from the exposed panels were gained with a bending test. Bending specimens were made by sawing the panels into 300 (longitudinal) x 10 x 10 mm sticks. These were conditioned at 23 ± 2°C, 50% relative humidity and tested in 3-point bending (constant speed 5 mm / min) so that the coated surface was in the tension zone. The tension zones of the tested specimens were separated and only the fractured transverse surfaces of these specimens were analysed. The small specimens were vacuum dried at 40 ± 2 °C, and sputtered with platinum for microscopic analysis.

Samples designated as 'unexposed' were taken from the rear sides of the exposed panels. They were therefore exposed under the same climatic conditions as 'exposed' samples, but without direct access to sunlight or preciptation. The comparison between exposed and unexposed samples thus reflects differences due solely to the influence of solar radiation and precipitation; other factors, such as the effect of thermal changes during weathering, would have been common to both sets of samples.

## 3. RESULTS
## 3. Rezultati

The main observations are compiled and commented in the plates with FE-SEM micrographs in the annex. A more detailed discussion follows in the next section.

*Fig. 1 - 4:*
*Fractured transverse surfaces of* **unexposed** *thin wood strips (dry-tested, 10 mm span):* **Pine earlywood** *(Fig. 1),* **pine latewood** *(Fig. 2),* **spruce earlywood** *(Fig. 3),* **and spruce latewood** *(Fig. 4).* • *Slike 1 - 4:Poprečne lomne površine* ***neizloženih*** *tankih listića (ispitanih suho na 10 mm rasponu):* ***bjeljika borovine*** *(sl. 1),* ***srževina borovine*** *(sl. 2),* ***rano drvo smrekovine*** *(sl. 3) i* ***kasno drvo smrekovine*** *(sl. 4).*

*Fig . 1*

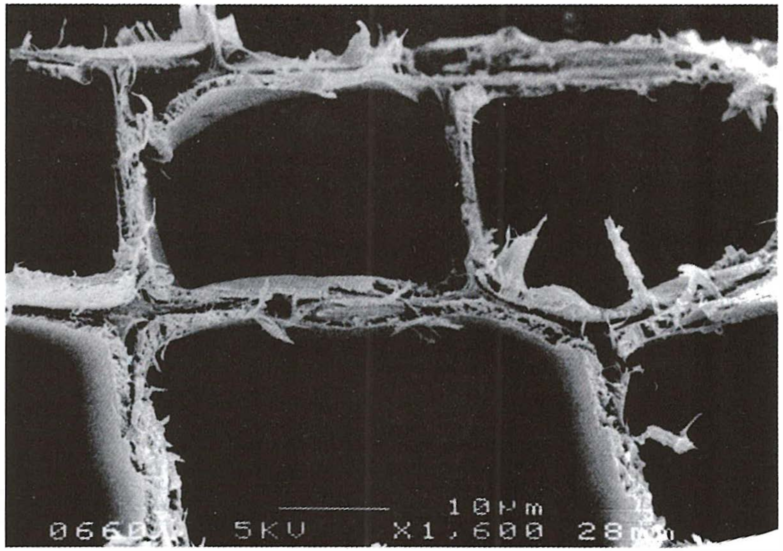


*Fig . 3*

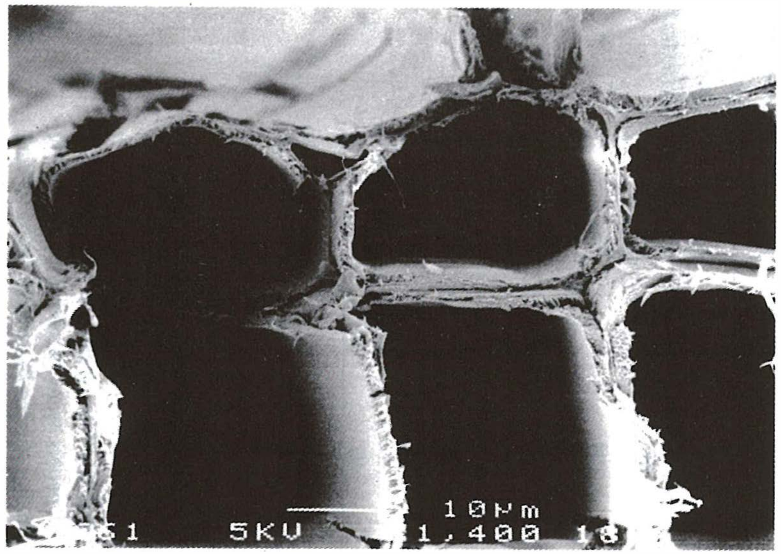


*Fig . 2*

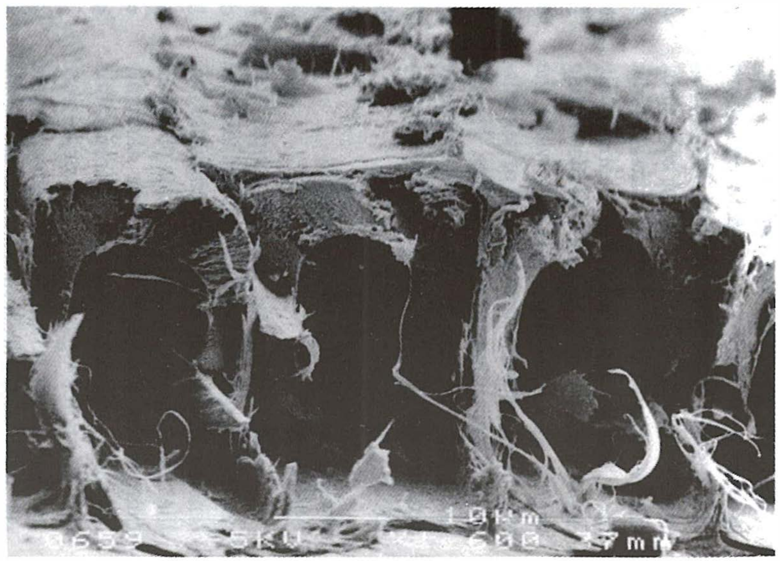

*Fig . 4*

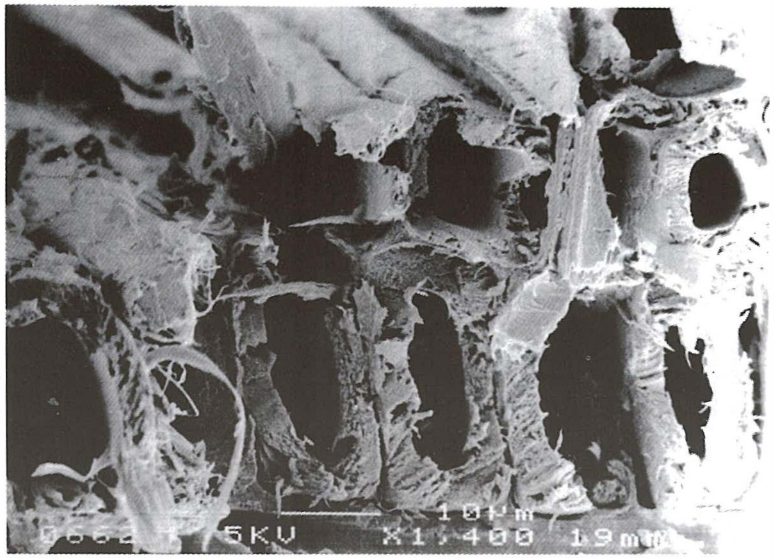

Fig . 5

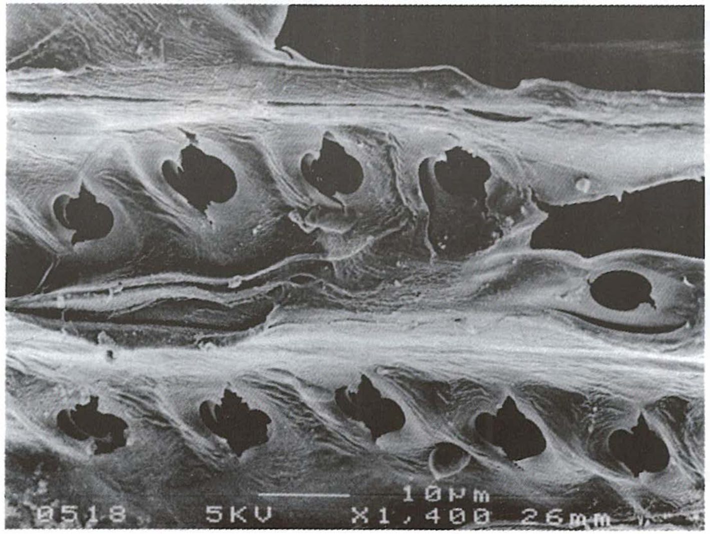


Fig . 7

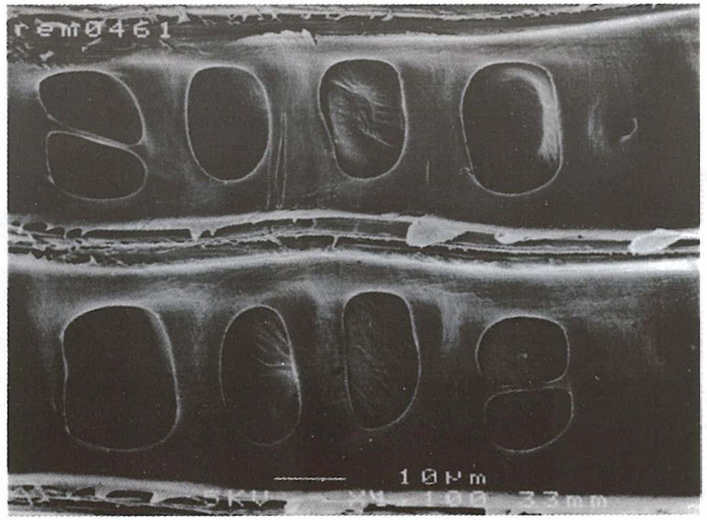


Fig . 6

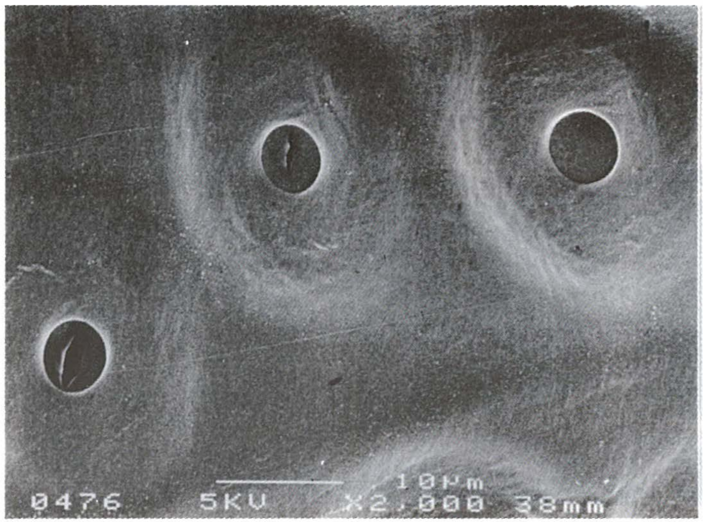


Fig . 8

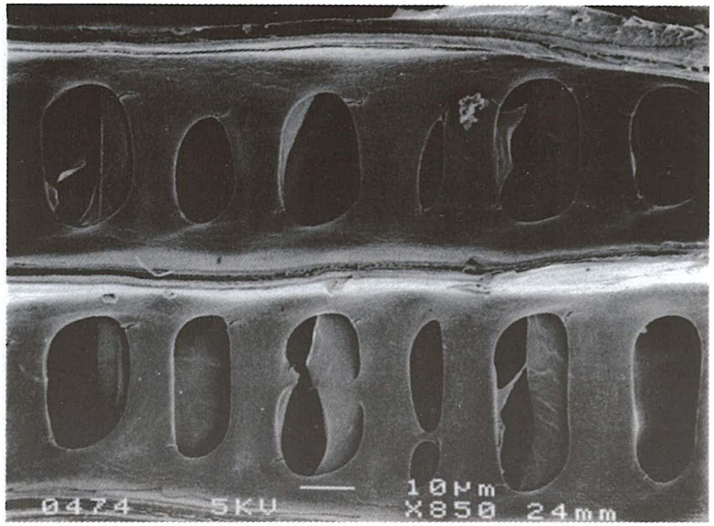


***Fig. 5 - 8:***
*Radial surfaces of thin pine strips exposed naturally for 12 weeks* **without a coating** *(Fig. 5) and behind a detached film of the* **solvent-borne stain** *(Fig. 6 - 8):* **Occasional damage on bordered pits** *(Fig. 6) or on* **fenestriform pitting** *(without damage in Fig. 7 and slightly damaged in Fig. 8) is recorded on the rear faces of the strips which is probably caused by the UV light reflected from the mounting panel* • *Slike 5 - 8: Radijalne površine tankih listića borovine koja je bila prirodno izložena 12 mjeseci* ***bez zaštitnog filma*** *(sl. 5) i iza slobodnog filma* ***organske lazure*** *(sl. 6 - 8):* ***mjestimična oštećenja ograđenih jažica*** *(sl. 6) ili* ***fenestriformnog ojažičenja*** *(bez oštećenja na sl. 7 i sa neznatnim oštećenjem na sl. 8) se mogu vidjeti na stražnjim plohama listića što je vjerojatno prouzročeno UV svjetlom koje se odbijalo od nosive plohe.*

***Fig. 9 - 12:***

*Fractured transverse surfaces of thin strips exposed naturally for 12 weeks: Pine earlywood behind a detached film of a* **stain** *(Fig. 9) and spruce latewood behind a detached film of an* **opaque paint** *(Fig. 10) show* **no changes in the mode of failure** *in comparison with unexposed strips (Fig. 1 - 4).* **Unprotected** *pine earlywood (Fig. 11) and pine latewood (Fig. 12) show development of* **biological growth** *(Fig. 11) and* **brittleness** *(Fig. 12).* • *Slike 9 - 12: Poprečne lomne površine tankih listića koji su bili prirodno izloženi 12 tjedana: rano drvo borovine iza slobodnog filma* ***lazure*** *(sl. 9) i kasno drvo smrekovine iza slobodnog filma* ***neprozirnog naliča*** *(sl. 10)* ***ne pokazuju nikakve promjene u načinu loma*** *u usporedbi s neizloženim listićima (sl. 1 - 4).* ***Nezaštićeno*** *rano drvo borovine (sl. 11) i kasno drvo borovine (sl. 12) pokazuju razvoj* ***mikrobiološke zaraze*** *(sl. 11) i* ***pojavu krtosti*** *(sl. 12).*

*Fig . 9*

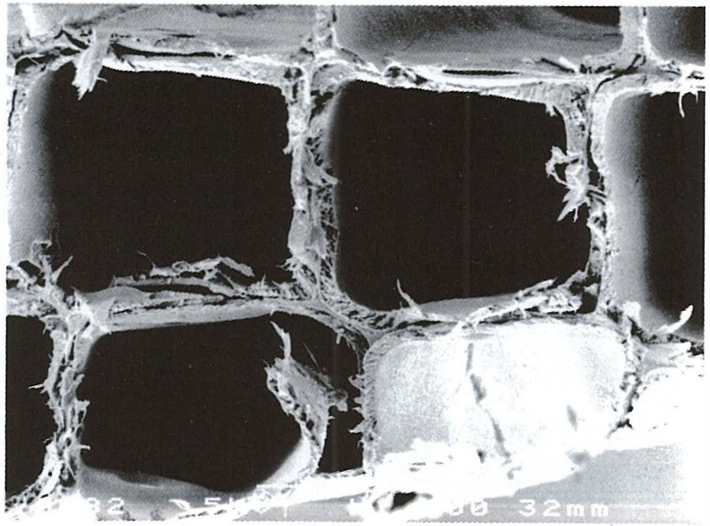

*Fig . 11*

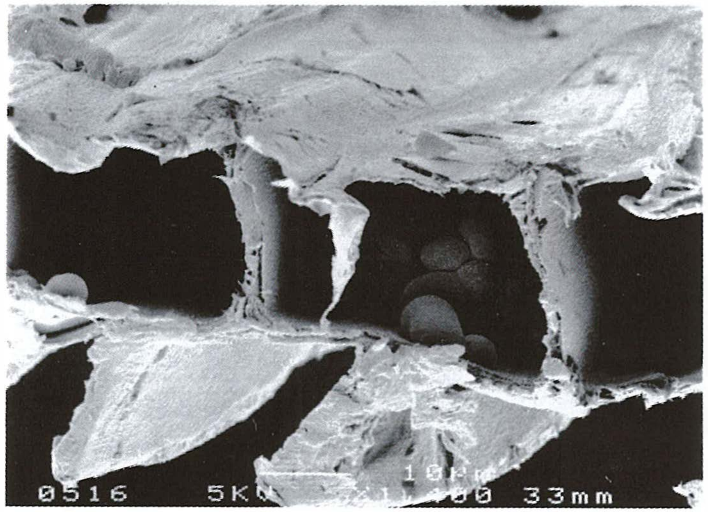


*Fig . 10*

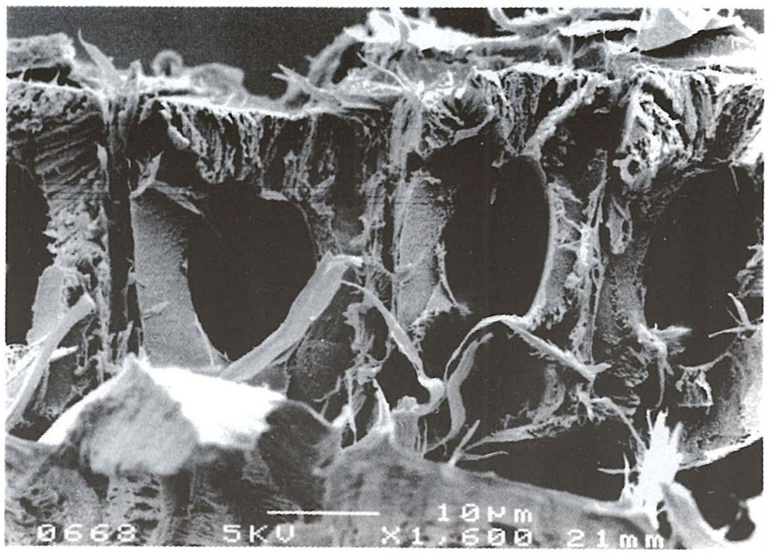


*Fig . 12*

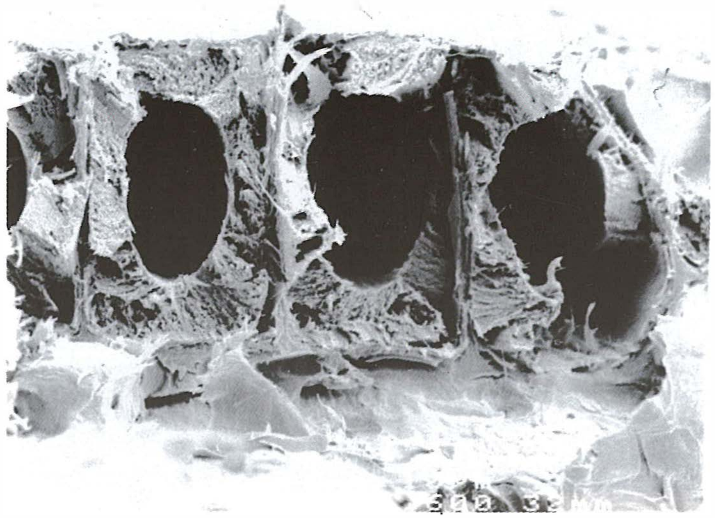

Fig . 13

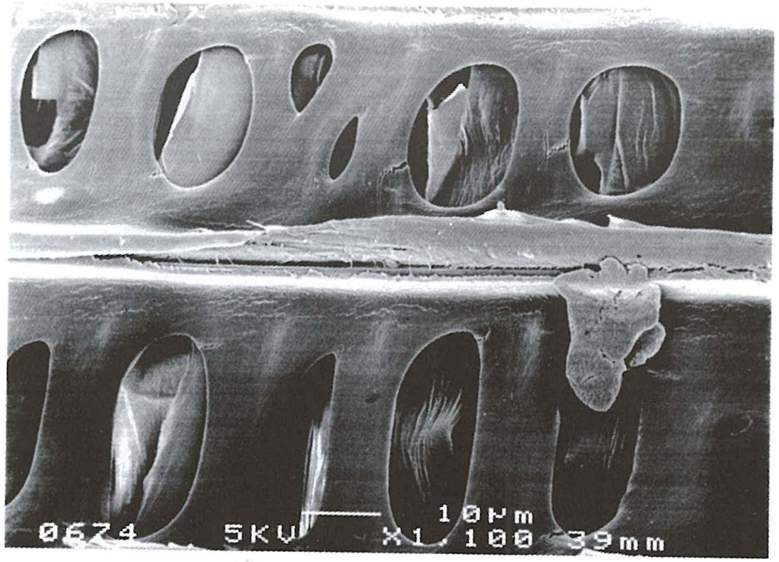


Fig . 15

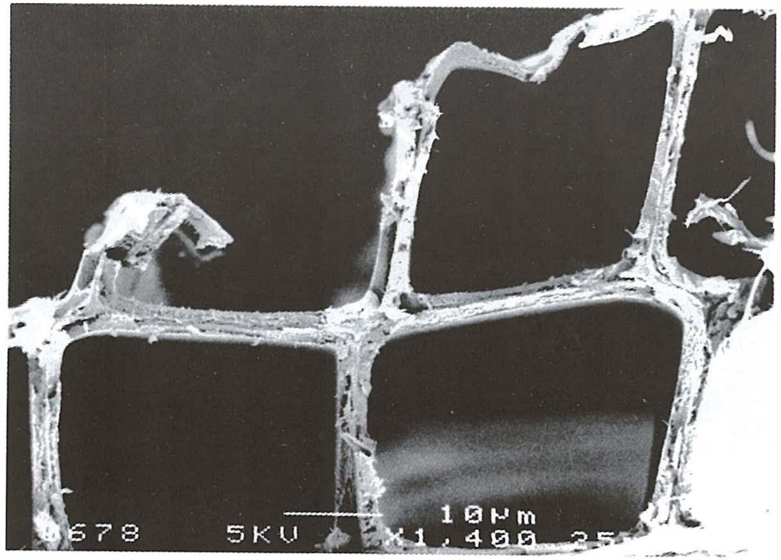


Fig . 14

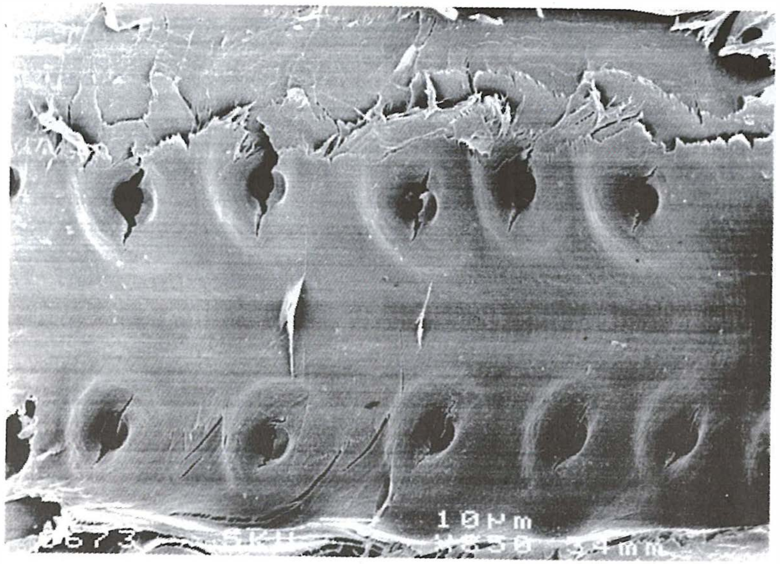

Fig . 16

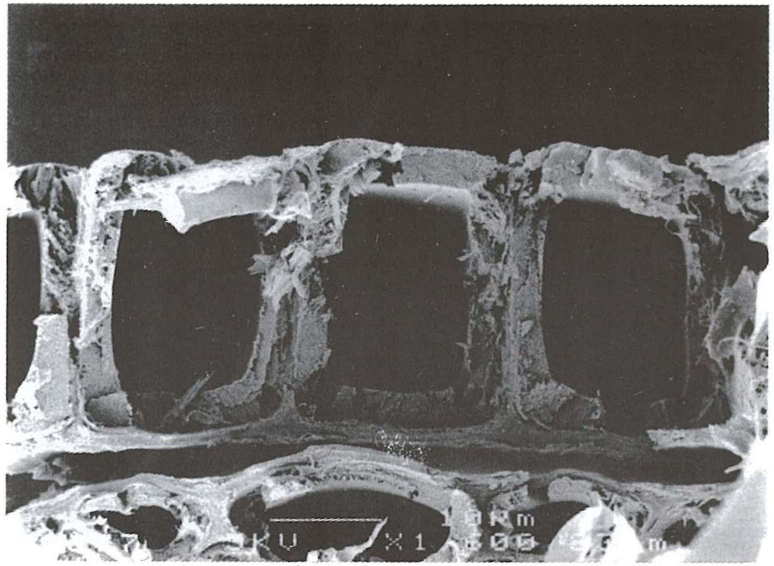

*Fig. 13 - 16:*
*Condition of thin strips exposed artificially in the QUV for 14 weeks behind a detached film of the* **solvent-borne stain**: *Fenestriform pitting (Fig. 13) and bordered pits of pine (Fig. 14) show characteristic* **damage from the effect of UV light**. *The tension-loaded cross sections of spruce earlywood (Fig. 15) and latewood (Fig. 16) exhibit typical* **brittle fracture** *due to light-induced delignification.* • *Slike 13 - 16: Stanje tankih listića koji su bili tijekom 14 tjedana izloženi u uređaju za laboratorijsko klimatsko izlaganje QUV. Listići su bili izloženi iza slobodnog filma* **lazure s organskim otapalima**: *Fenestriformne jažice polja ukrštavanja (sl. 13) ograđene jažice borovine (sl. 14) pokazuju karakteristična* **oštećenja uslijed djelovanja UV svjetla**. *Poprečne lomne površine vlačno potrganih listića ranog drva smrekovine (sl. 15) kasnog drva smrekovine (sl. 16) pokazuju tipični* **krti lom** *koji nastaje zbog svjetlom uvjetovane delignifikacije.*

*Fig.17 - 20:*
*Fractured transverse surfaces of tension-loaded bending specimens from 'unexposed' coated pine panels:* **Water-borne opaque paint** *(Fig. 17),* **water-borne semi-transparent stain** *(Fig. 18),* **solvent-borne opaque paint** *(Fig. 19)* **and solvent-borne semi-transparent stain** *(Fig. 20).* • *Slike 17 - 20: Poprečne lomne površine vlačnih zona uzoraka potrganih savijanjem: ovo su "neizložene" plohe površinski obrađenih borovih daščica.* ***Vodotopljivi neprozirni nalič*** *(sl. 17),* ***vodotopljiva poluprozirna lazura*** *(sl. 18),* ***organski neprozirni nalič*** *(sl. 19) i* ***organska poluprozirna lazura*** *(sl. 20).*

*Fig . 17*

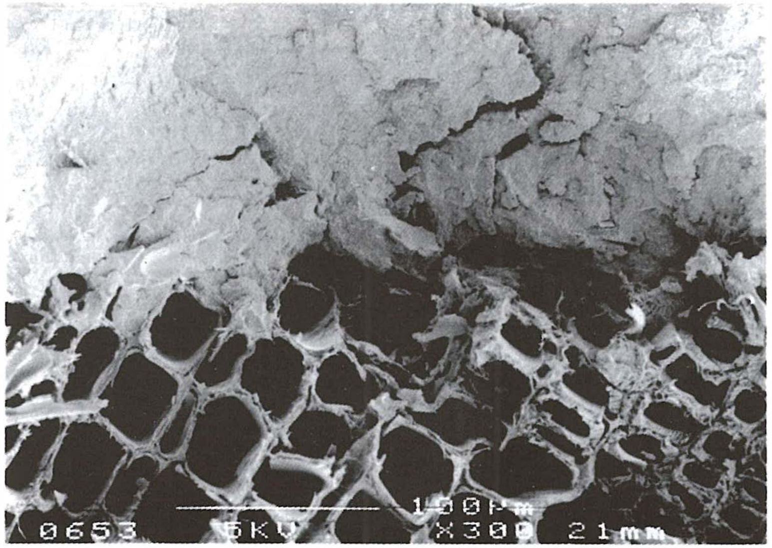


*Fig . 19*

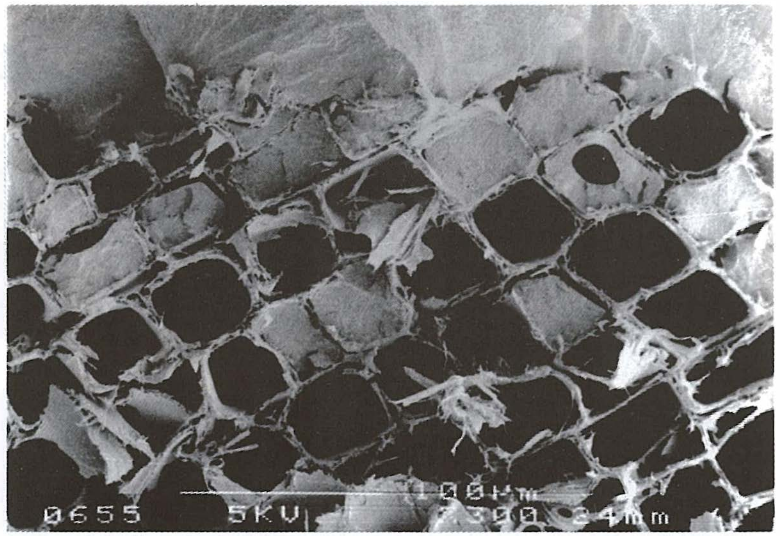


*Fig . 18*

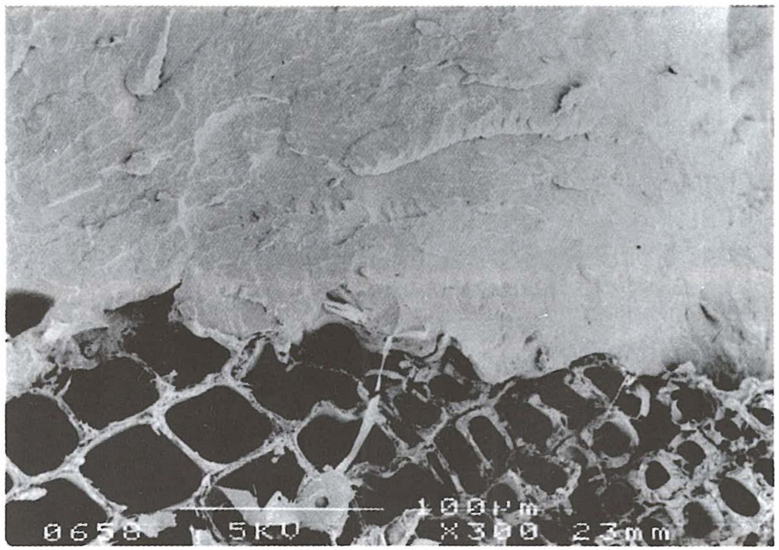

*Fig . 20*

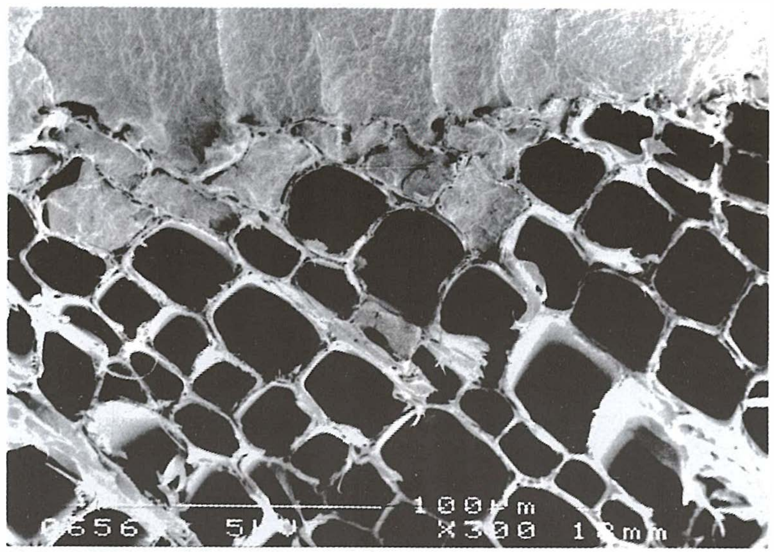

Fig . 21

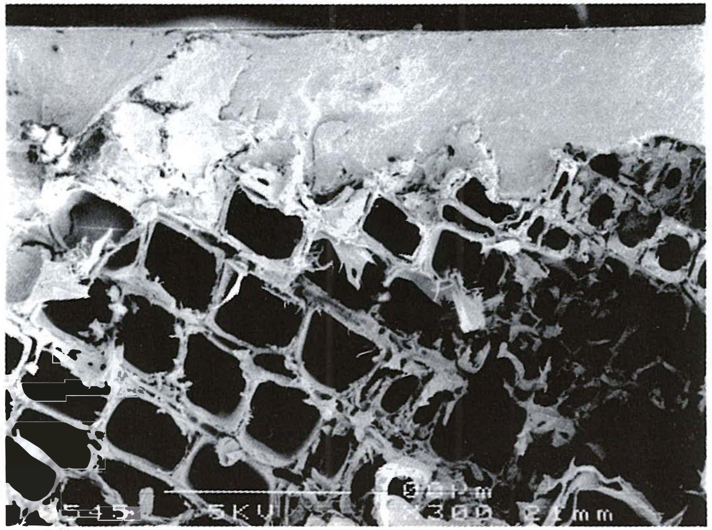

Fig . 23

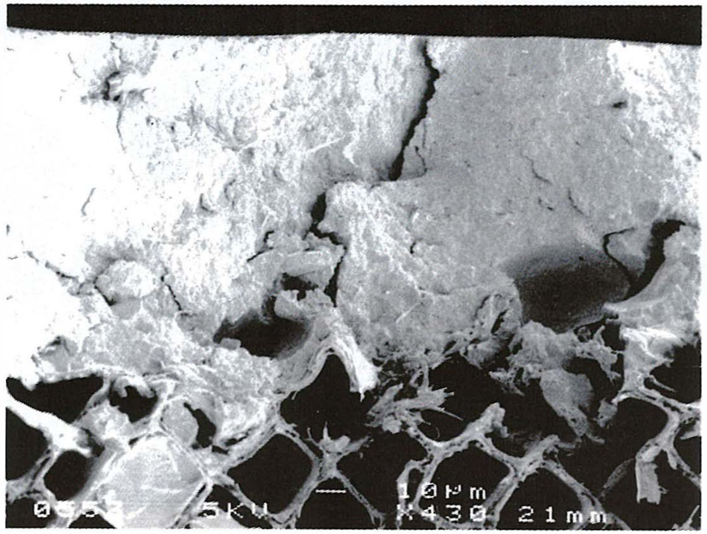


Fig . 22

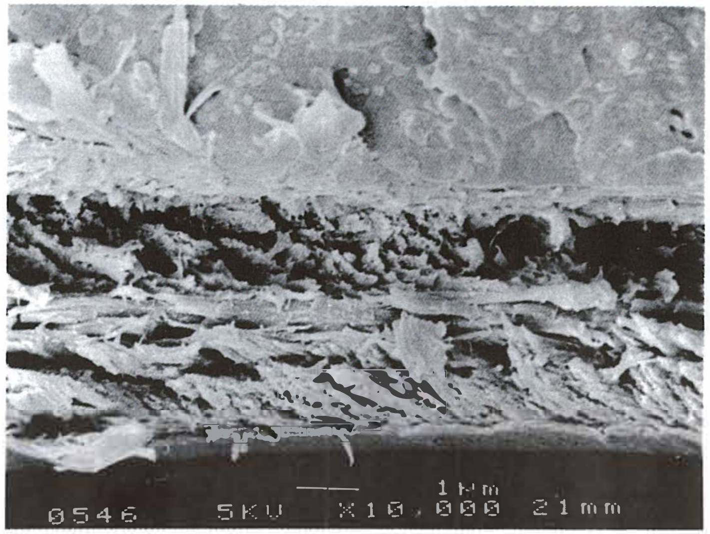


Fig . 24

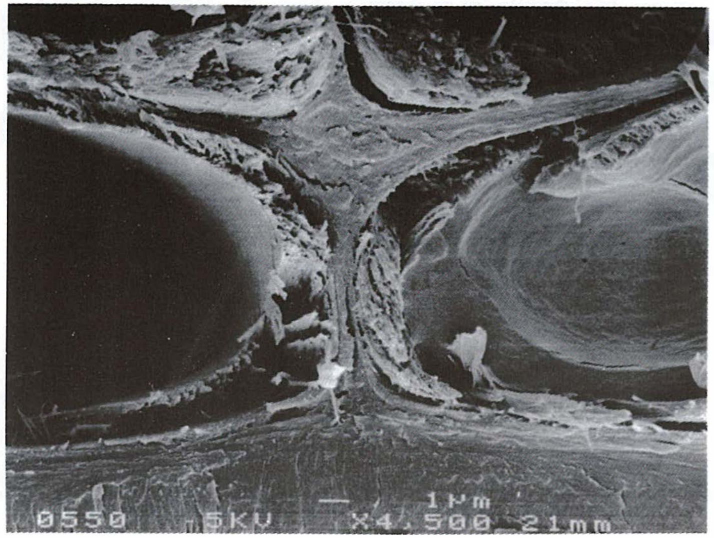


***Fig. 21 - 24:***

*Fractured transverse surfaces of tension-loaded bending specimens from pine panels coated with* **solvent-borne** *(Fig. 21 - 22) or* **water-borne opaque paint** *(Fig. 23 - 24) after 14 months of natural exposure: The higher magnification reveals* **good adhesion** *of both paints to the S3 layer but* **no penetration into the cell wall.**

• *Slike 21 - 24: Poprečne lomne površine vlačnih zona uzoraka potrganih savijanjem. Ovo su izravno izložene plohe borovih daščica obrađenih* ***organskim*** *(sl. 21 i 22) ili* ***vodotopljivim neprozirnim naličem*** *(sl. 23 i 24) nakon 14 mjeseci prirodnog izlaganja. Veća povećanja otkrivaju* ***dobru adheziju*** *oba premaza na S3 podsloj ali* ***nema penetracije premaza u staničnu stijenku.***

**Fig. 25 - 28:**
*Fractured transverse surfaces of tension-loaded bending specimens from pine panels coated with solvent-borne (Fig. 25 - 26) or water-borne* **stain** *(Fig. 27 - 28) after 14 months of natural exposure.* ● *Slike 25 - 28: Poprečne lomne površine vlačnih zona uzoraka potrganih savijanjem. Ovo su izravno izložene plohe borovih daščica obrađenih* **organskom** *(sl. 25 i 26) ili* **vodotopljivom lazurom** *(sl. 27 i 28) nakon 14 mjeseci prirodnog izlaganja*

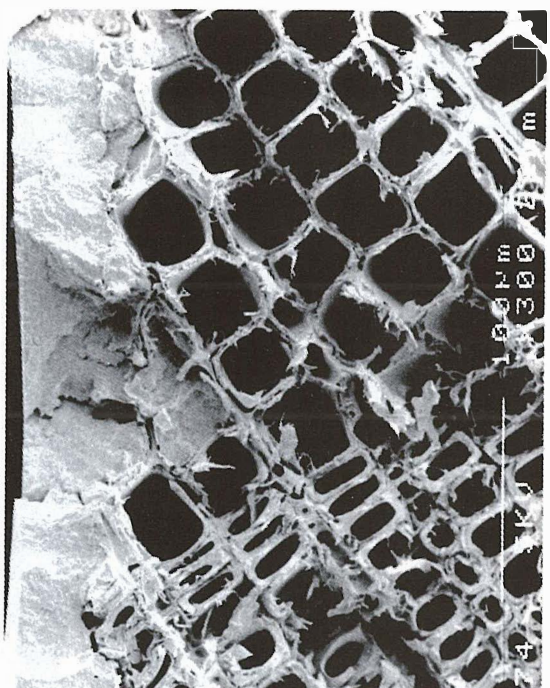

*Fig. 25*

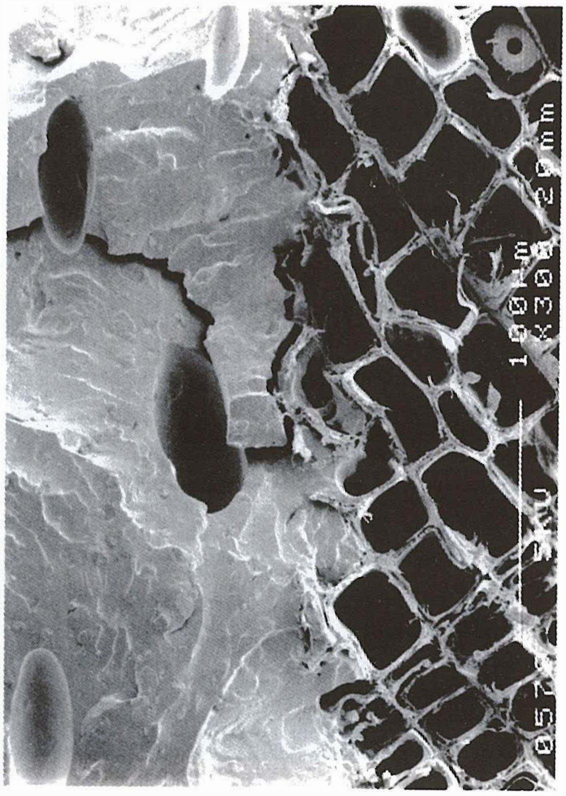

*Fig. 27*

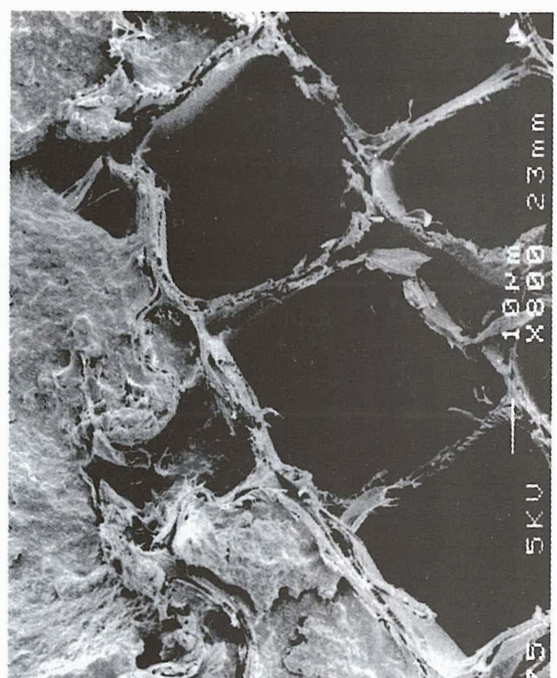

*Fig. 26*

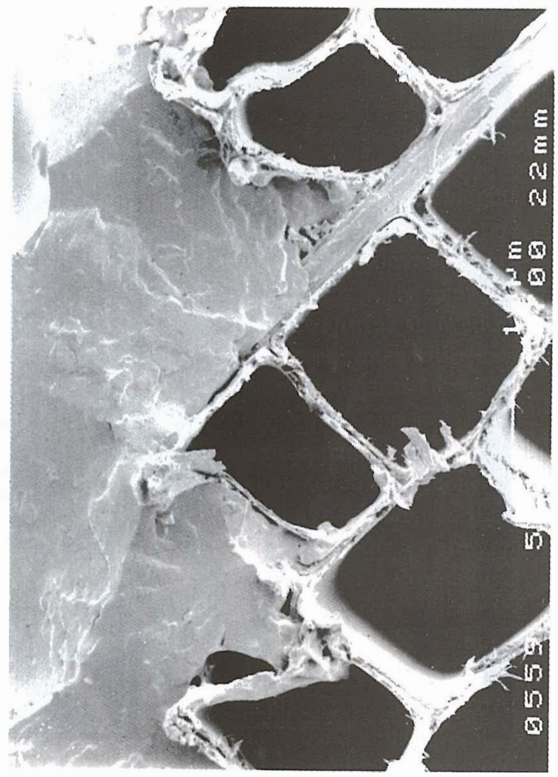

*Fig. 28*

Fig . 29

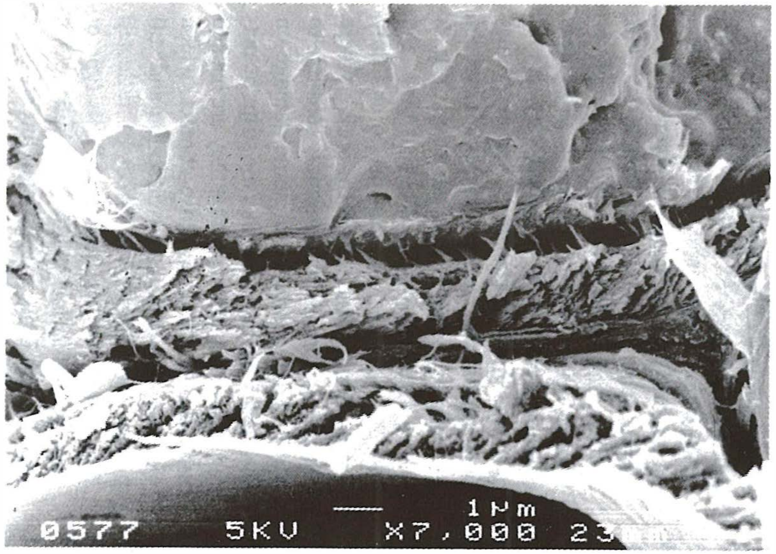

Fig . 31

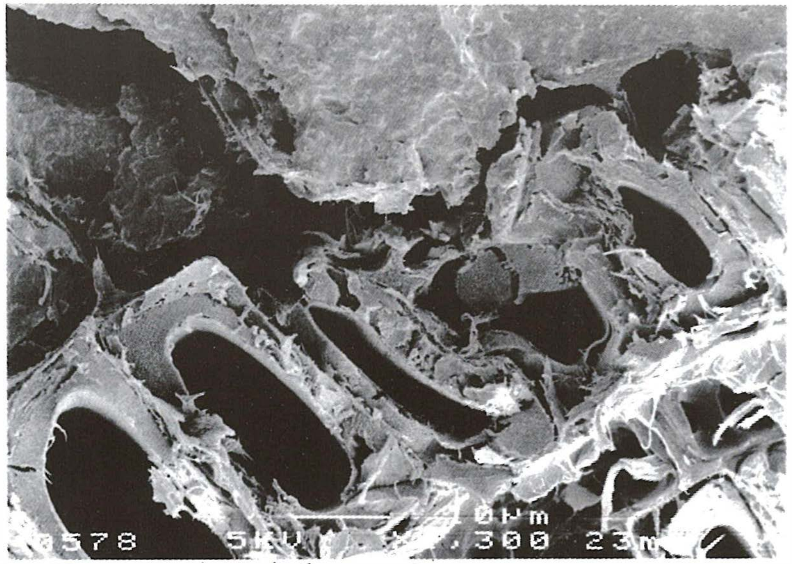

Fig . 30

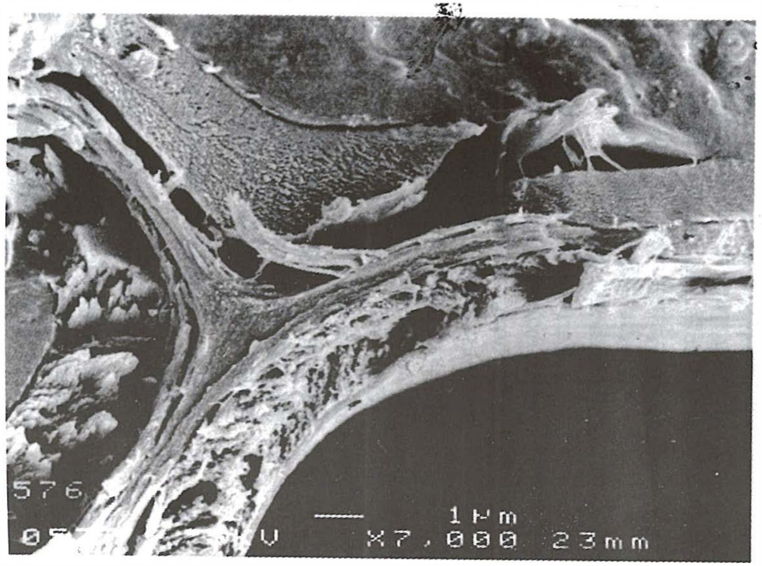

Fig . 32

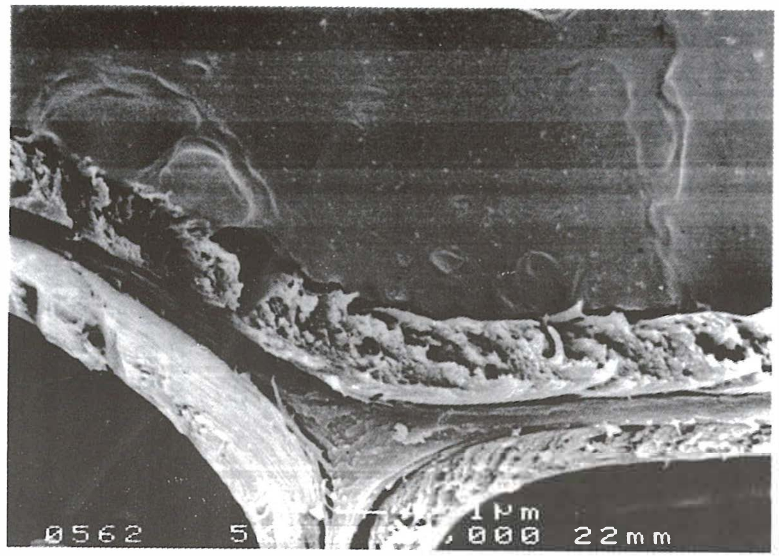

***Fig. 29 - 32:***

*A larger magnification of the cross sections from the pine panels coated with* **stains** *(Fig. 25 - 28) shows* **cases of delamination***: The solvent-borne stain was observed to fail through* **separation from the cell wall** *(Fig. 29) or by the* **cohesive failure** *of UV light-damaged wood (Fig. 30) or by a combination of the two (Fig. 31). The water-borne stain only very rarely exhibits lack of adhesion to the substrate (Fig. 32).* • *Slike 29 - 32: Veća povećanja poprečnih presjeka uzoraka od borovih daščica obrađenih* ***lazurom*** *(sl. 25 - 28)* ***iskazuju delaminaciju****: primjećuje se da lazura s organskim otapalima pokazuje grešku* ***odvajanja od stanične stijenke*** *(sl. 29) ili da nastaje* ***kohezijski lom drva*** *oštećenog djelovanjem UV svjetla (sl. 30). Mjestimično se može vidjeti kombinacija ovih dviju grešaka (sl. 31). Vodotopljiva lazura vrlo rijetko iskazuje smanjenje prijanjanja o supstrat (sl. 32).*

## 4. DISCUSSION
## 4. Rasprava

### Unexposed thin strips and the differences between the species

The extensive microscopic study encompassed both pine and spruce samples and also samples exposed to natural and artificial weathering. There were no notable effects that were specifically attributable to species, the failure modes of pine and spruce were closely similar, especially when comparisons were made between the earlywood regions of the two species. Paajanen (1994) has also reported the lack of observable differences in the structural changes of pine and spruce after two years of natural weathering. General impression remains, however, that the lateral surfaces of spruce showed less damage due to weathering, the bordered pits were seldom damaged to an extent to which the aspirated pits of pine were affected by weathering.

The comparison of pairs of figures on the first micrograph plate (Fig. 1 & 3 and Fig. 2 & 4) shows that in 10 mm span testing the mode of failure for the two species is essentially the same. The fracture in the latewood spreads faster and leaves the thick-walled tracheid cross sections partly smooth, and as the speed of the crack propagation decreases, the failure deformation increases. With a decreasing speed in crack propagation the latewood cells are fractured in an interlocked mode, with bundles of fibrils pulled out and often with visible radial organisation of fibrils in the S2 layer.

Earlywood always fails with the greater extensibility than latewood, therefore its fractured transverse surfaces almost never exhibit smooth areas which would reveal the places of rapid crack spreading (Fig. 1 & 3). The earlywood failure mode is mainly interlocked, sometimes even frayed in appearance, showing the tough character of the material. The agglomerations of fibrils in radial direction regarding the tracheid axis is a regular feature of earlywood crack surfaces.

### Thin strips after 12 weeks of natural weathering

Natural weathering of pine and spruce strips during 12 weeks caused heavy structural damage. The micrographs are not presented here (except Fig. 5) since there have been numerous former studies of structural damage due to weathering or due to the effect of light under various climatic conditions (Miniutti 1964, 1967, 1970 and 1973, Borgin 1971, Futò 1974, Chang et al. 1982, Kucera and Sell 1987, Evans 1989, Paajanen 1994, Yata and Tamura 1995). A weathered wood surface shows damage to anatomical elements, in particular the development of cracks of the tori and domes of bordered pits, cracks and loss of membranes of the ray pits and cracks which can be seen on the lumen surfaces, in general following the angle of the microfibrils in the S2 layer and originating at single pits.

All the main characteristic anatomical weathering changes mentioned above were observed and recorded in the course of this microscopic study. This confirms that the cellular structural changes of thin strips are essentially the same as in solid wood. In addition, since the examination of the naturally and artificially weathered strips showed no difference in the character or intensity of anatomical changes in the course of the weathering process, it may be concluded that artificial weathering can reliably substitute weathering out of doors.

The strips that have been exposed behind a detached film of a coating were generally well protected from the UV light within the exposure period. The faces of the strips adjacent to the film did not show either soiling or any damage to anatomical elements. Some damage occurred on the rear faces, probably due to the action of light reflected from the aluminium mounting panel. This type of damage (Fig. 6 - 8) could be otherwise normally observed after 2 to 4 days of full natural exposure. Along with yellowing of the strips it indicates that some delignification took place. Consistent lower values of 10 mm span tensile strength (Table 2) could be therefore attributed to the effect of reflected light. This is though a sporadical damage, which was observed very rarely, and was of small intensity. It happened that the neighbouring anatomical elements would be both undamaged and damaged (Fig. 6 shows aspirated bordered pits of pine, and Fig. 7 - 8 depict perfectly sound and only lightly damaged fenestriform pitting where the pit membranes are extremely sensitive to light). The occurrence of some damage on the back sides indicates that the strips be better exposed in such way that they are backed with veneer plates in close contact, which would enable the vapour diffusion and still hinder the undesirable effect of reflected light. However, the scarcity of this type of damage and its low intensity let believe that this did not induce significant alteration of the wood material. This is particularly so with spruce where the strips did not exhibit any strength loss over the exposure period.

Cross sections of tension-tested strips confirm that the level of degradation behind a film of stain or paint after 12 weeks of natural weathering is too small to be positively evident in the change of the mode of failure. Thus the fractured transverse surfaces in Fig. 9 - 10 look very much the same as those of unexposed strips in Fig. 1 - 4. It may be worth noticing that some degradation evidence could be seen near the rear faces of the strips due to reflected light. A characteristic detail can be seen in Fig. 9, where the radial agglomerations of fibrils seem to cease near the upper portion of the cross section, which is a zone at the reverse strip face. However, the occurrence of radial agglomerations in the central portion indicates that the delignification was not intensive enough to cause complete loss of the binding properties between the fibrils in the S2 layer of the cell wall.

In contrast to this, fully exposed strips (Fig. 11 - 12) show brittle characteristics. The radial agglomerations of fibrils can not be seen because the binding role of lignin is impaired. Obviously the mode of failure reflects the drastic reduction in tensile strength down to some 20% in 10 mm span (Table 2) with the development of brittleness being the main feature of intensive delignification. The fractured transverse surfaces look brash, and no tough bundles of fibrils pulled out in separation of material could be seen. This indicates also the cellulosic breakdown, evident in the substantial reduction of the zero span strength to less than 50% (Table 2).

In conclusion, it may be stated that the 12 weeks natural exposure in the August - November period was insufficient to cause substantial damage to the strips protected with detached films of a stain or a paint. This exposure also could not discriminate between the levels of damage on wood covered with paint or stain. The issue of the influence of the reflected light on the structural integrity of thin strips must be carefully considered.

#### Thin strips artificially weathered

The strips exposed in the QUV weathering tester had their rear side protected with aluminium plates and hence no reflected light could have reached them. The structural damage and strength losses can be hence attributed only to the effects of light and moisture which passed through the detached film of the coating.

The strength losses (Table 2) indicate some changes in the structural integrity of the strips exposed behind a film of stain. The strips exposed behind a film of opaque paint show some development of brittleness, but this change was not great enough to be recorded as a positive evidence of photodegradation. It is worth noticing that pine again exhibits greater changes than spruce in all cases. The fact that the strength losses were greater over finite span than in zero span testing indicates the development of delignification, rather than cellulose degradation.

The strips weathered behind a semi-transparent stain show some characteristic surface damage (Fig. 13 - 14) but mostly only on the pits and less frequently than expected. Spruce again shows less structural damage than pine, and generally only in terms of cracks in the tori of aspirated bordered pits. Pine 10 mm span dry strength loss is significant at this length of weathering (55 - 60%) and one would expect regular appearance of destruction of bordered pits and frequent occurrence of the pit membrane disintegration. However, that was not the case. Such damage was only occasionally observed, and the micrographs presented here are examples of the most severe cases of damage found. It appears that samples weathered behind a coating film show less structural damage, for a given degree of strength loss, than samples exposed directly to radiation. The development of brittleness appeared to be a better indicator of the intrinsic chemical changes, since it more closely mirrored the strength changes.

The fractured transverse surfaces of the strips exposed behind a stain show the signs of substantial degradation (Fig. 15 - 16). This condition corresponds well with the level of the strength loss. Parallel comparison of Fig. 15 with Fig. 1 & 3 for earlywood and Fig. 16 with Fig. 2 & 4 for latewood shows that the fractured surfaces of dry tested specimens exhibit distinct development of brittleness. The crack propagates through wood perpendicular to the load axis in a plane across the cells rather than step-wise and that is a sign of embrittlement caused by delignification. Bundles of torn-out fibrils are rare now and they look like flakes rather than frays. The development of brittleness is even more obvious in earlywood, where the frayed appearance is completely gone and no structural features in the S2 layer can be seen (compare Fig. 15 and Fig. 3). Pine surfaces were initially even more frayed than spruce (compare Fig. 3 and Fig. 1) but after weathering the earlywood of both species exhibit the very same brash appearance.

It can therefore be concluded that the penetration of light through a detached film of a stain caused the damage not only to the wood-coating interface, but to the underlying wood as well. The changes in the fracture mode reliably indicate the reasons for the reduction in strength, for the delignification, the first intensive degradative reaction, caused the reduction in lateral stress transfer and the development of brittleness.

### Coated panels after 14 months of natural exposure

Micrographs of the tension-loaded zones near the paint surface of coated panels readily reveal the different characteristics of the coatings and their weathering durability. The paint surface itself - as seen with the SEM - did not yield any information about the level of chalking, porosity or brittleness. No minor cracks were visible. It appeared that the fractured transverse surfaces of the coating films may be much more informative in gaining such information than the actual surface of the exposed paint film.

#### *Paints*

The two paints differ in their coating thickness on the pine substrate (Fig. 17 & 19, Table 1) but also in appearance of their fractured transverse surfaces. The thick-layered water-borne paint is characterised by brittleness in its brash look on the fractured transverse surface, a number of small cracks across it and the cracked and ground-looking layer near the wood surface (Fig. 17). The solvent-borne paint on the other hand fails in a tough mode and the fractured transverse surface is smooth (Fig. 19).

Neither paint penetrated deeply; only in the earlywood regions did any penetration occur beyond the surface layer of tracheids, as seen with the occasional paint filled lumen (Fig. 19). The direct paths for paint penetration were the rays and they are often filled to a depth of several rows of tracheids from the surface and occasionally also a few neighbouring tracheids are filled in this process. There are some regions where it is obvious that the penetration of solvent-borne coatings is better than is the case with water-borne materials (compare Fig. 19 and 20 with Fig. 17 and 18).

Regardless of the limited penetration the adhesion of the two paints to the wood substrate seems to be good (Fig. 17 & 19, 22 & 24). The paint films stick to the S3 layer and embed it (Fig. 22 & 24, Fig. 30) but do not appear to penetrate the cell wall; the cell wall fracture shows characteristic radial agglomerations and the general appearance of uncoated, unexposed wood (Fig. 22 & 24). The water-borne paint, however, seems to show signs of a weakening of the link with the wood at the interface (Fig. 23) where a series of cracks either in the wood or in the coating indicate the brittle character of the failure. This can not be seen with the solvent-borne paint (Fig. 19, 21 & 22). Since virtually no UV light passes through the film of the opaque coating, it was expected that no embrittlement, a sign of photodegradation of the wood, would be seen near the interface. Both species under both coatings show frayed, interlocked type of failure at the very interface (Fig. 29 & 31) which is a typical failure mode of unexposed wood. The consistent presence of radial agglomerations indicates that no delignification has yet taken place (Fig. 22 & 24).

The water-borne paint appears generally brittle, and on the unexposed (rear) side of the panels its interface with wood also shows a brash appearance (Fig. 17). Although on most of the coated surface the earlywood portions may reveal a sound interface, there are cases which show that water-borne paints can be initially unexpectedly brittle and further develop brittleness with exposure. This can result in frequent interface failures (Fig. 23).

#### *Stains*

The stains again differ in their physical appearance. They both cover the wood surface well and stick to it, but the penetration is unexpectedly poor and only occasionally a cell or two beneath the surface in earlywood zones are filled with coating (Fig. 18 & 20, 25 & 27). This appearance is very similar on both substrates, pine and spruce. Still no peeling of the coating or its detachment on the wider area of the interface can be seen after 14 months of natural exposure (Fig. 25 & 27).

The solvent-borne stain looks on both substrates quite brittle, and the thin coat shows numerous cracks (Fig. 25). A direct comparison of the fractured stain film at the directly exposed side and at the rear, 'unexposed' side (Fig. 20 & 25) shows that the coating was initially less brittle and that the light caused the increase in its brashness. A closer look on the earlywood portions (Fig. 20) reveals that the surface layer of the panel was prepared with some crushing of the cells. However, the number and character of cracks at the wood-coating interface differs on the exposed (Fig. 25 & 26) and the unexposed side (Fig. 20) thus indicating that the light affected the coating, the wood underneath it and the link between the two.

It can sometimes be noticed that the cell walls near the interface with the solvent-borne stain show a less frayed appearance with rare occurrence of radial fibril agglomerations (Fig. 26). That indicates some damage due to the effect of UV light transmitted trough the coating with a delignification as the first consequence of that process. This damage with two characteristic failure modes is easily seen on the earlywood tracheids in Fig. 29 (failure of the link between the coating and the S3 layer of the cell wall) and in Fig. 30 (separation of the cell walls or cell wall layers due to delignification). The combination of the two types of defects is present in Fig. 31, where the detachment of the coating takes place through both adhesive and cohesive breakdown. The embrittlement of the wood cells can also be seen in terms of their flat, brash fractured transverse surface (Fig. 31).

In contrast to that, the interface cells of the wood coated with the water-borne stain seem to be well protected from UV light, and here again both species show the same condition. The coating is thicker, tough, and the trapped air bubbles suggest a higher initial viscosity and consistency (Fig. 27) then was the case with the solvent-borne stain (Fig. 20). The comparison of the 'unexposed' water-borne stain (Fig. 18) and the directly exposed coating (Fig. 27) does not reveal any difference in the failure mode or in the adhesion properties of the stain film. The adhesion is good, and no failures at the interface can be seen which could be attributed to the photodegradation (Fig. 28). A rare exception is found and presented in Fig. 32; however it cannot be determined whether this coating - cell wall separation is a consequence of the weathering, the mechanical testing or the subsequent specimen preparation.

## 5. CONCLUSIONS
## 5. Zaključci

The microscopic inspection of the micro structural changes in naturally and artificially exposed panels and thin strips leads to the following conclusions:

1.The main early evidence of wood photodegradation are cracks in the pit membranes, mostly on the aspirated bordered pits of pine and spruce and on the fenestriform tracheid-ray pitting of pine. The tension-tested cross section surfaces show a change in their failure mode with progressive weathering, mainly seen in the loss of occurrence of radial fibril agglomerations, as the development of brittleness and in an increased delamination.

2.Pine and spruce do not show significant differences in their failure modes, film-holding properties or UV light resistance under (semi-transparent) coati ʒs. However, spruce was shown to undergo somewhat smaller structural changes with weathering.

3.The paints do not penetrate the cell wall but firmly adhere to the S3 layer of the lumina. The solvent-borne coatings (both paint and stain) penetrated deeper into the wood surface than the water-borne coatings.

4. The opaque paints fully protect the wood from the effect of light through a 14-month period of natural exposure and maintain the coherent protective coating.

5.The water-borne paint exhibits more brittle characteristics on the fractured transverse surface than the solvent-borne paint.

6.The stains vary in their protective effectiveness. The water-borne stain shows a tough, sound failure mode, good adhesion but very poor penetration into wood surface. The solvent-borne stain is degraded by light, and the interface with the wood is affected, resulting in the development of brittleness of both wood and coating and leading to adhesion failures preceding the detachment of the film.

Thin strips with detached films of coatings realistically represent the surface of coated wood specimens, and are easy to handle, to detach and subsequently to investigate both mechanically and microscopically. However, they should be protected from any access of light except through the coating in order to ensure reliable information about the effect of light on their structural integrity.

The combination of strength measurements and the microscopic evidence proved particularly effective for the interpretation of the changes occurring at the very surface of wood components i.e. at the wood-coating interface. The microscopic observations confirmed that the progress of wood photodegradation can be successfully detected by the combination of the state of deterioration of anatomical elements on radial surfaces and by fractographic evidence on cross sections.

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## 6. Literatura


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