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Investigation into the changes of wood surface layer by measurement of pH-value

Istraživanje promjena površinskog sloja drva mjerenjem pH vrijednosti

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SUMMARY *• Wood pH has been studied with regard to its affecting some change on wood surface.*

The change on wood surface was analyzed after the following:

- chemical treatment;

- aging in room climate;

- exposure to the sun, rain and surrounding atmosphere;

- exposure to ultraviolet radation.

Each treatment was followed by measurements of the pH and the adhesion of the NC varnish. The procedure of pH measurement on the wood surface with a combined surface electrode was devised.

A 25 mm circel was drawn on the wood surface with NC varnish to prevent water spreading along the fibers. Into the circle 0,75 ml of water was applied, the electrode plunged in. After 5 minutes, the pH was measured. Within this time, no negative effects of carbon dioxide on the water pH were established.

The research was done on fir, beech, oak and poplar. After chemical treatment, the pH on the wood surface varied depending on the chemical used but some general conclusions about the effects of pH on the following adhesion may be drawn.

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Summer sunlight quickly reduces the adhesion of varnish on beechwood, increasing the pH of the wood surface.

Sunlight, and in combination with the rain in February, lasting 10 days, does not affect adhesion significantly. Instead, the surrounding atmosphere seems to have a greater influence in this time period.

Varnish adhesion may be enhanced with a certain dose of UV-light. It is likely that maximum adhesion is achieved by the highest pH.

Wood pH should be regarded as an indicator of chemical changes rather than cause of change.

Key words: *wood surface, surface pH, surface activation*

SAŽETAK • *pH vrijednost zanimljiva je zbog mnogih gledišta, a u ovom radu istražene su mogućnosti ustanovljavanja promjena na površini drva pomoću mjerenja promjena pH vrijednosti površine drva.*

Analizirane su promjene na površini nakon njenog tretmana:

- kemikalijama,

- starenja u sobnoj klimi,

- utjecajem sunca, kiše i okolne atmosfere

- utjecajem ultravioletnog zračenja.

Razrađen je postupak mjerenja pH površine drva kombiniranom površinskom elektrodom. Vrijednost pH površine drva dobar je indikator stanja površine.

Sunčevo svjetlo ljeti vrlo brzo djeluje na povećanje pH vrijednosti površine drva i time umanjuje adheziju laka na bukovini. Sunčevo svjetlo uz djelovanje kiše u veljači, u trajanju od deset dana, nije bitno utjeclao na adheziju. Umjesto svjetla izgleda da je okolna atmosfera imala značajniji utjecaj u tom razdoblju. Adhezija laka se može i povećati s određenom dozom UV-svjetla. Vjerojatno je da se najbolja adhezija postiže pri najvećim vrijednostima pH.

1. INTRODUCTION

Wood pH value is interesting from many aspects, such as

- corrosion of metals attached to wood;
- wood protection;
- glued bonds and joints;
- surface treatment of wood;
- the condition of wood surface reflecting the properties of various woods; the procedures it has gone through from tree felling to the given moment; drying; mechanical treatment; aging under particular conditions.

Wood surface, or top layer, is the interface with the surrounding medium. All external impacts begin from its top layer, i.e. through it. All changes on the wood are seen on its surface. Therefore the importance of studying the wood surface and the changes occurring on it should be noted.

Learning more about wood surface and its changes will help us to protect wood in a more efficient way, i.e. its modifications.

The state and changes in wood surfaces may be studied on thin sheets, models of surface layers, or on the top layer of thicker samples. The surface can be observed, microscoped, measured as to its behaviour when wetted with liquids. We can measure its pH, the degree to which adhesives stick to the surface, and the changes of mechanical properties at the surface or the model of top layer, as well as the chemical changes in the surface layer. Although some highly sophisticated methods may be mentioned here (e.g. magnetic resonance), in these particular cases they would come across great difficulties.

We have tried to investigate the possibilities of measuring wood surface changes by measuring the pH of the top layer.

2. PREVIOUS RESEARCH

A number of authors have dealt with the wood pH measurement. As it is impossible to measure the pH of dry wood, the measurements are usually performed on the sap extracted from green wood. The pH can then be measured directly, or the wood can be cut into small pieces and ectracted with water. After some time the pH of the liquid is measured.

As the acidity or alkalinity is reduced by the addition of water (pH is 7), and such measurements do not yield accurate results, Sandermann (4) and other researchers chopped small pieces of wood and added water with adjusted acidity of varying pH values. In the case when the pH had not changed by mixing the chopped wood with the liquid, the took the liquid acidity for that of the wood. Here we can also consider the buffer value for different wood species.

Wood pH may also be measured with electrodes. Special flat electrodes have been designed for the measurement of wood surface pH. Some researches suggest measuring wood surface soaked in water, which requires a longer time period and therefore we can hardly speak of the pH surface layer. Most researches measured the surface pH after they had applied some distilled water to it.

3. RESEARCH METHOD

In our research we have used a combined flat electrode Type Pl 7/DIN A 94 with a 12 mm top diameter, and a pH meter ISKRA MA 5722.

0.75 ml of distilled water (24°C±2) was applied inside a white 25 mm wide circle marked by NC varnish, to prevent spreading along the fibers (Figure 1).

The varnish itself did not affect the changes established by the tests. The duration of the water/wood interaction was 5 minutes, the time period chosen by most researchers. As wood has mostly acid reaction, the pH decreased abruptly at the beginning, then more slowly. Decreasing pH could be detected even after 15 minutes, though the question is whether the influence of the deeper wood layers needs to be considered.

Figure 2 shows the measurement of untreated beechwood and the one treated with Na OH 0.5 M whose surface was eventually rinsed with distilled water. The measurements were done on five places on each sample. During the first three minutes the water pH changed relatively rapidly, and after five minutes the value became stable. After a longer time period, we should consider the influence of the wood under the surface, which could be seen on the sample treated with NaOH, where the pH decreased after five minutes. Also, in spite of the same treatment and vicinity of the measuring place on the sample, the pH values varied on different measuring places.

The steady fall and rise of the measured values prove that the measuring itself is quite acurate.

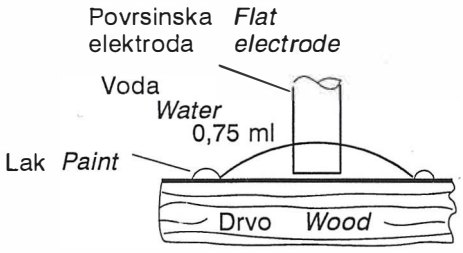

Figure 1
Sheme of pH-measurement on wood surface • Shema mjerenja pH - vrijednosti na površini drva.

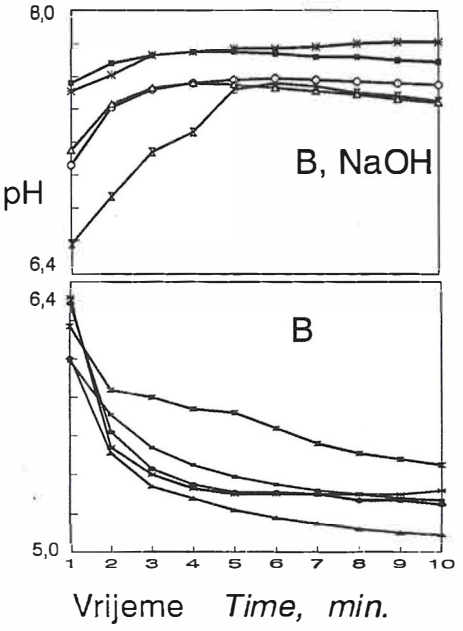

Figure 2
Results of pH measuring on wood surface • Rezultati mjerenja pH na površini drva.

After longer exposure to air, the change of the water pH may be caused by carbon-dioxide. However, the tests did not establish such influence within the time periods of 5 to 10 minutes.

The changes on the wood surface were measured by means of the changes in the adhesion of the varnish to wood. Of the many methods for measuring the holding properties, none meet all the requirements, particularly not in the case of the varnish upon wood. The basic procedures in these methods are:

- removing the coating with a special knife;
- using inertia for removing the coat (by shooting a sample out of a "gun");
- cutting in the coat down to the wood with a knife to activate shear stress,
- thrust upon the varnished surface with a ball causing the destruction and detachment of the coating;
- gluing consoles on the coating and removing them to cause stress concentration;
- gluing stups and removing them by peeling;
- gluing stubs on the varnished surface, then pulling them off by a force perpendicular to the surface, or by torsion.

In our research we chose the pull-off test for adhesion (DIN - EN 24624).

It has already been reported (Sickfeld and Hosp 1979), that even at perfectly perpendicular pulling force on the well glued stub the surface stress is unequally distributed. Therefore we reported only the ultimate (breaking) force without calculating the maximum strength. The perpendicular application of the force was obtained in the Wolpert double-joint mechanical tester, while the test was done according to Figure 3. In all the tests we used the nitro-cellulose varnish.

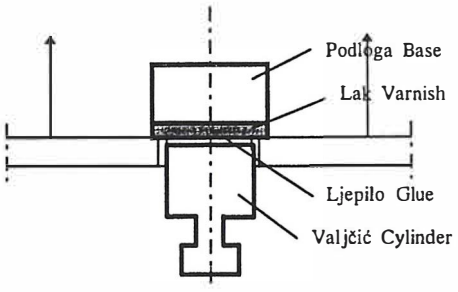

Figure 3
Scheme of adhesion testing • Shema mjerenja adhezije premaza na drvu.

4. TEST SAMPLES

The tests were carried out on beechwood, poplar, oak and fir. More tests were made with beechwood. The samples were of radial- tangential texture, 1000 mm long x 100 mm wide x 20 mm thick. Moisture content was about 10%, and the samples were conditioned to this moisture content before each test.

5. RESEARCH RESULTS

5.1. Modification of surface with chemicals

In the research of Buglaj (1) and others, the chemical modification of wood was applied for better adhesion. The results were varying. In our research, we prepared the surfaces with

- sodium hydroxide (10%),
- hydrogen peroxide (15%),
- nitric acid (0.5 M),
- ammonium hydroxide (6%).

The following changes may occur when these chemicals are applied:

Acid reaction of the most wood species is caused by the free acids and acid groups that split easily, e.g. mostly acetic acid and acetyl groups.

Wood is very resistant to chemicals, and there is no solvent that can dissolve wood tissue without chemically affecting its individual constituents at the same time. This stability is explained by a complex structure of the mutually linked high polymeric compounds. The solvent or chemical reagent that can disolve one major constituent of wood cannot disolve another.

Wood material is resistant to the effects of diluted mineral acids at room temperature, though concentrated acids quickly affect wood by causing the decomposition of polysaccharides.

Solutions of strong alkalis dissolve considerable quantities of wood material even at room temperature. Strong alkalis affect less resistant polysaccharides and a certain part of the lignin. Alkalis also dissolve most part of the extractive. Accordingly, the alcaline extract is of a complex chemical composition.

Wood reacts to strong oxidants such as hydrogen peroxide and concentrated nitric acid. The resulting oxidation of lignin and carbohydrates causes the formation of carboxyl and carbonyl groups. The diluted solutions of strongs oxidants have a limited activity.

In the above tests, we first treated the surface with chemicals and after that rinsed the wood surface with distilled water to remove the rest of chemicals that did not react.

The results did not justyfy procedure under test conditions.

After chemical treatment, 24-hour drying, and pH measurement, the samples were varnished. The holding properties of the varnish on variously treated wood were measured seven days after varnishing. The results of these experiments are shown in Figure 4. The pH of the wood surface was changed depending on the treatments.

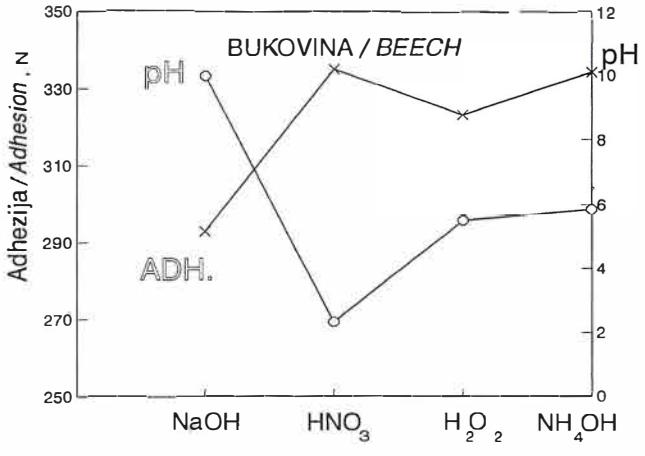

Figure 4
Effects of chemical treatment on pH-value and on adhesion • Utjecaj kemijskoga tretmana na pH - vrijednost i adheziju prevlake na drvu.

The poorest holding properties were recorded on wood treated with sodium hydroxide. Varnish on the other samples treated with other chemicals had similar holding properties. Similarly to the previous research and the scrape-test adhesion measurement, the data of ammonium hydroxide treatment showed high adhesion values.

5.2. Effects of surface aging in room climate

A lot of research has been done on the so-called free exposure (aging in the room climate) of the wood-surface between the mechanical processing and the application of varnish or adhesive. The research encompassed the measurements of the wetting and contact angle change. In most the results show that free exposure had adverse effects on the adhesion of the coating.

In our tests, the samples of beech, poplar, fir and oak were left in room conditions without any access of light. The results are shown in Figures 5 and 6.

All woods increased their surface pH values.

After free exposure, the varnish holding power of all woods was reduced. Figure 6 shows both changes. It would be a wrong conclusion to make immediate correlations between the holding power and the pH, as found in much of the previous research.

The pH values tell as about the state of the wood surface, while adhesion is the relation between the wood surface and the varnish. By generalizing this relation, the conclusion would be that the increased pH reduces the holding power. Figure 4 clearly shows that this general rule does not hold good.

5.3. Effects of the sun, rain and surrounding atmosphere

A beech sample, 1000x100x20 mm, wrapped in several layers of black paper to shield from light, and finally in polyethylene film, was exposed to the sun, southward at

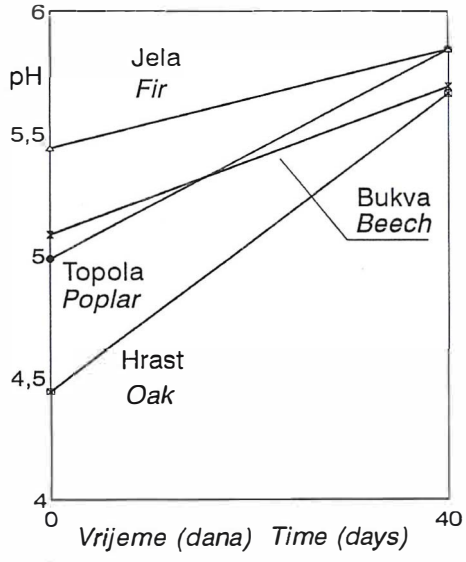

Figure 5
Aging in room climate • Promjena pH vrijednosti sa vremenom stajanja u sobnim uvjetima.

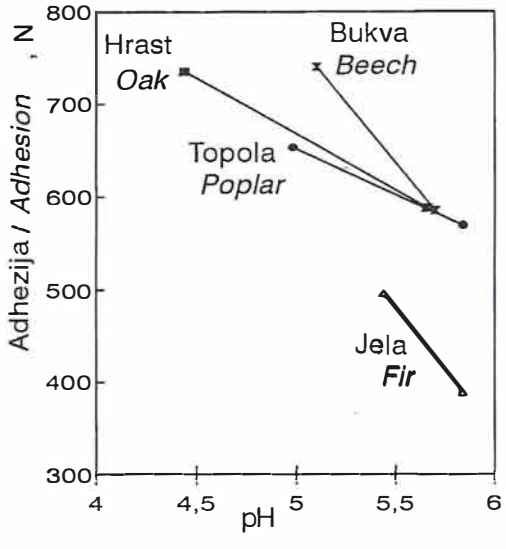

Figure 6
Aging in room climate (pH and adhesion) • Promjena adhezije s promjenom pH vrijednosti pri stajanju u sobnim uvjetima.

45° angle, in the summer months, so that both the paper and the film were removed part by part, in order to obtain the various durations of exposure to the sun. The last part, marked "zero days", was not unwrapped before the pH was measured and the varnish was applied. Other intervals were 1, 11, 31 and 91 days.

The results of this experiment are shown in Figure 7. After only one day exposure, the pH increased and the adhesion fell. The difference in adhesion between 1 and 91 days (the lowest adhesion), and 11 and 31 days (somewhat higher adhesion) is explained by the incidental deviations at the holding power measurement, and also by the activation of the wood surface by insolation.

To establish the effects of the sun, rain and the surrounding atmosphere, the samples of beech, oak, poplar and fir were exposed to the sun and surrounding atmosphere, and also to the sun, rain and surrounding atmosphere, at the end of February and the beginning of March. One sample group was protected from the rain, exposed to the south at a 45° angle. Another group was exposed to the sun, rain and atmosphere, with the same orientation.

After 5 days (2 sunny, two rainy, and 1 cloudy day) the samples were removed from the weathering station and put to climatization. After 10 days (4 sunny, 3.5 rainy and 2.5 cloudy) another group was taken off the weathering station. The pH change is shown in Figure 8.

The changes do not indicate any rule that may be explained by weak and short-term insolation in this time period. The surrounding atmosphere seems to have the highest impact, since the beech pH did not change;

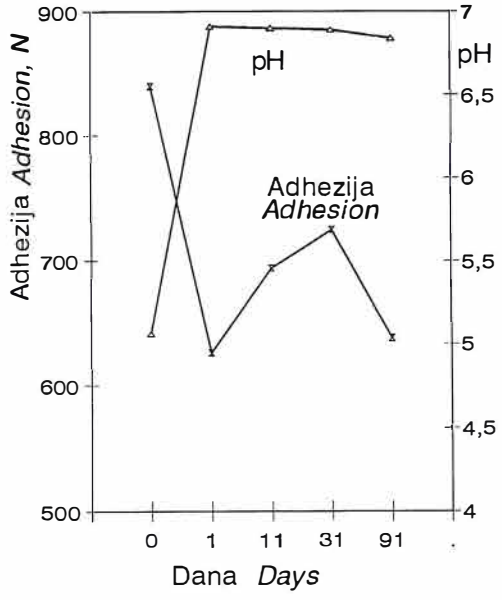

Figure 7
Effects of the sun in the summer • Utjecaj ljetnog sunca na promjenu pH i adheziju.

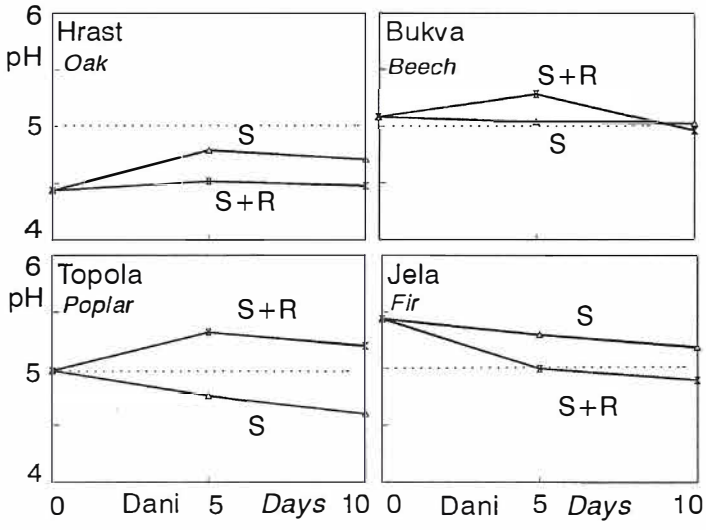

Figure 8
Effects of the sun, rain and atmosphere • Utjacaji sunca, kiše i atmosferskog zraka na promjenu pH - vrijednosti.

- the initial value was about 5. The pH of oak and fir increased or fell nearing the value of 5. This also proves that when samples are exposed, it is not enough to measure time and establish the change, but the surrounding atmosphere, which may have a critical impact, should also be measured.

5.4. Effects of ultraviolet radiation

A prolonged exposure to ultraviolet radiation has adverse effects on the surface. It leads to the destruction of anatomic wood components and loss of substance. However, some researchers found that ultraviolet exposures through a limited time period may activate the surface and improve adhesion (1).

Beech samples were exposed to an ultraviolet light source with impulse radiation lasting in turns 0, 15, 30, 45, 60, 120, and 1000 seconds, followed by pH measurement, varnishing and measurements of adhesion.

The results are shown in Figure 9. At first the pH and adhesion rose, then they fell. Figure 9 also shows the results of Buglaj's research. Although different wood kinds (birch and beech) and varnish types (nitrocellulose and polyester) were tested, similar results were achieved. The conclusion may be, that a particular amount of ultraviolet light may activate wood surface and increase its varnish-holding power. The change on the wood surface is also connected to the pH change, a link that may be helpful. However, it would be wrong to consider the pH change as the cause, and the adhesion change as the consequence.

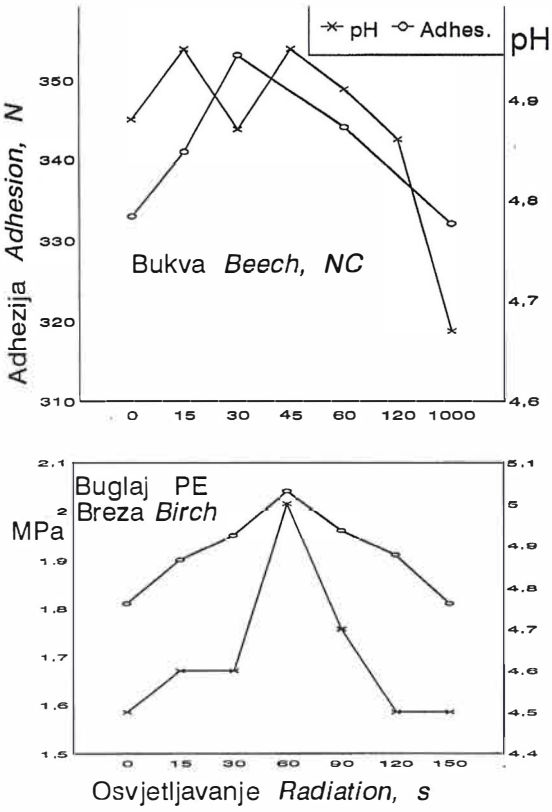

Figure 9
Effects of ultraviolet radiation • Utjecaj ultraljubičastog zračenja na promjene pH i adhezije.

5. CONCLUSION

1. Accurate measurements of the wood surface pH may be done with a special electrode.

2. In order to prevent the spreading of water along the fibers, the optimal water quantity to use with the electrode is 0.75 ml poured into the circles drawn with varnish upon the wood surface. The best measuring time is 5 minutes, as the impact of carbon dioxide from the air has not been found within this time period. The pH value may be a good sign of the state, i.e. the changes on wood surface.

3. The pH of the wood surface should be considered as the sign of change rather than its cause.

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