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Nanolevel surface treatment applied to veneered products

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***Abstract*—New researches or discoveries are regularly published in the field of nanotechnologies, revealing information about the new materials with unique properties and methods to achieve this. Wood veneer is often used in different real estate segments for interior decoration applications. It's ideal for residential projects as well as in hotel projects and offices; the result is a unique look and feel for the interior. Even more, veneer is processed to create also a variety of products such as veneer parquet, flexible veneer sheets, wood veneer boards, wood veneer wallpaper, etc. A disadvantage can be mentioned, veneered surfaces could to a greater or lesser degree change color, particular upon exposure to natural and artificial light. The level of color change depends on such factors as the species chosen, the coating type used and intensity and period of the exposure to light. In addition, conventional finishes have a tendency to yellow with age that can have negative effects on the original color of the selected timber. To minimize previously mentioned effects new finishes have to be developed. Invisible nanolevel coating based on the sol-gel process for veneer finish is offered in this paper. The sol–gel technique is an industrial process for colloidal nanoparticles generation from liquid phase, where the deeper development has been performed in last years for the production of advanced coatings. It is well adapted for oxide nanoparticles and composites synthesis. The main advantages of sol-gel techniques are comparable low processing temperatures offering unique opportunities for access to the organic and inorganic materials. In the paper there will be discussed the sol synthesis and application technology as well protective properties of coating. Leaf trees wood has a lot of good economic, technological, physical and mechanical properties, but under influences of external environment (rain, sun, wind, the rapid change in temperature) it fails to maintain and preserve all complex of properties , so it is essential to develop nano-coatings, capable natural material make durable and sustainable usage in outdoor spaces with increased moisture content.**

***Index Terms*— Wood veneer, advanced coatings, wood coatings, sol-gel technique.**

I. INTRODUCTION

The wood has a lot of good economic, technological, physical and mechanical properties. However, due to the influence of environment- rain, sun, wind, temperature and humidity changes- the wood fails to keep and maintain this complex of all the properties. It is very important to develop such nano-coatings, which could make the wood more durable and sustainable in outdoor and indoor conditions with increased moisture content.

A. Birch wood microscopy

Birch (Betula pendula) veneer is the finest use of timber, because it is real timber.

The benefits of its use are:

- the natural variations of timber means each project is individual as choice from the vast array of species, colors and textures are available; even from the same species veneers differ in grain, color, texture and markings;
- wood veneer is pleasant and friendly to the touch;
- veneered surfaces add prestige and style to the furniture and joinery;
- veneer can be molded to fit any shape and adhered to a different substrates to give all the versatility of solid timber; various types of substrates can be used for the production of veneered panels and furniture, such as solid timber, particle boards, medium density fiber boards, plywood, block boards, and hardboards;
- veneer is sustainable use of forest resources and highly efficient use of timber as from one cubic meter of log could produce around 1000 square meters of veneer; [1]

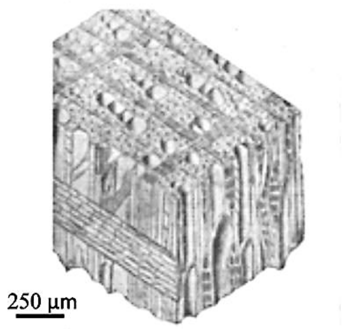

Fig. 1. Anatomical features of birch [2]

The main sources of veneers are hardwoods with the more complicated anatomy compared to softwoods and as consequence more complicated wood structure.

Veneer quality is a factor in construction and industrial plywood based on visually observable characteristics. Knots, decay, splits, insect holes, surface roughness, number of surface repairs, and other defects are considered. Veneer species and characteristics are also a major factor in categorization of hardwood and decorative plywood.

However, when observing the microstructure of a hardwood sample in practice it is normally easy to see the vessels, fibres and parenchyma cells, since the tracheids are very few in number.

The hardwood axial system is composed of vessel elements in various sizes and arrangements, and of axial parenchyma in various patterns and abundance (Fig. 1). As in softwoods, rays comprise the radial system and are composed of ray parenchyma cells, but hardwoods show greater variety in cell

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sizes and shapes. Vessel elements are stacked one on top of the other to form vessels. On the transverse section, vessels appear as large openings and are often referred to as pores (Fig. 1). Vessel diameters may be small (<30 μm) or quite large (>300 μm), but typically range from 50 to 200 μm. They are much shorter than tracheid's and range from 100 to 1,200 μm [2].

If all the vessels are the same size and more or less scattered throughout the growth ring, the wood is diffuse- porous. If the early wood vessels are much larger than the latewood vessels, the wood is ring-porous. Diffuse-porous species woods sample and birch have two main types of growth rings and one intermediate form. In diffuse-porous woods, vessels either do not markedly differ in size and distribution from the early wood to the latewood, or the change in size and distribution is gradual and no clear distinction between early wood and latewood can be found (Fig. 1). Vessels can also be arranged in a tangential or oblique arrangement in a radial arrangement, in clusters, or in many combinations of these types. In addition, individual vessels may occur alone (solitary arrangement) or in pairs (Fig. 1), or radial multiples of up to five or more vessels in a row. Where vessel elements come in contact with each other tangentially, intervessel or intervascular bordered pits ranging in size from 2 to >16 μm in height are formed (Fig. 2).

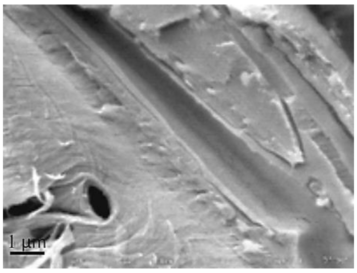

Fig. 2. Exposed channel of hardwood showing pit [3]

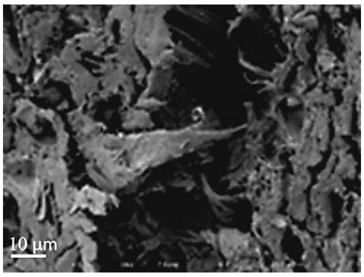

Fig. 3. Hardwood microstructure [3]

Fibres in hardwoods function almost exclusively as mechanical supporting cells. They are 0.2 to 1.2 mm in length, usually two to ten times longer than vessel elements. The thickness of the fibre cell wall is the major factor governing density and mechanical strength of hardwood. Species with thin-walled fibres have low density and strength; species with thick-walled fibres have high density and strength. Pits between fibres are generally inconspicuous and may be simple or bordered.

Hardwoods have a wide variety of axial parenchyma patterns. Paratracheal parenchyma is associated with the vessels, and further divided into vasicentric (surrounding the vessels), aliform (surrounding the vessel and with wing-like extensions), and confluent (several connecting patches of paratracheal parenchyma sometimes forming a band).

Apotracheal parenchyma is not associated with the vessels and is divided into diffuse (scattered), diffuse-in-aggregate short bands and banded, whether at the beginning or end of the growth ring or within a growth ring. Each specie has a particular pattern of axial parenchyma, which is more or less consistent from specimen to specimen, and these cell patterns are important in wood identification. The rays in hardwoods are structurally more diverse than those found in softwoods. Most species have rays that are more than one cell wide. In oak and hard maple, the rays are two-sized, uniseriate and more than eight cells wide. Such hardwood anatomy specifics and differences between species lead to a very complicated and uneven veneer surface microstructure (Fig. 3). Small holes are typically created when the wood cells shrink during the drying process at the mill. Cracks can also occur when a veneer loses too much moisture (or loses moisture too quickly). When this happens, internal stresses become so strong that the wood cells shrink, lose elasticity, and then separate from each other. These types of splits are more challenging to repair. The success rate for repairing this type of crack depends on several factors. It is difficult to select the highest quality logs, because many internal defects such as gum veins, rot and insect damages are difficult to detect from the log outside. Probably the most critical aspect of preparation for finishing is the moisture content of veneered products. Equilibrium moisture content of veneer are approximately from 10 to 12 %. High moisture content is difficult to detect visually so prevention is a key.

B. Birch wood veneer surface modification

One of the different new approaches and possibly one of the most promising for surface modification of materials is the sol-gel technology. Probably this technology offer possibilities to tailor surface properties to a certain extent and to combine different functionalities in a single material was one of the most important developments in material sciences during the last decades. At the same time the application of sols treatment can be carried out with the techniques commonly used in finishing processes such as immersion or sprinkling following by thermal processing.

Colloid solutions of nano sized oxides particles in aqueous or organic solvents or in their mixtures (nanosols) today become more and more popular. Due to the high surface area of the small particles the nanosols are metastable and during coating process the particles will aggregate as well as condense, initiated by evaporation of solvent in result of thermal treatment. Process result in dense three-dimensional networks leading in coatings which exhibit new functions [4].

In comparison with many other materials such as ceramics or metals, wood products possess low thermal resistance. The conditions for the treatment and the sol composition have to be adapted to the particular demands of material. As chemical structure of such natural fibres as flax and hemp are close to the chemical structure of hardwoods, the sol synthesized for cotton and lignocellulosic fiber textiles surface modification are used. Obtained by this sol modified textile surfaces had presented excellent protection from ultraviolet radiation, antimicrobial activity and water repellency. All mentioned properties are important to improve protection of veneered surfaces in outdoor and indoor applications [5].

Some stains, notably dye stains can fade if subjected to long term ultra violet light; if wooden surface is not protected, destruction of lignin could be caused by UV radiation.

Under direct sunlight fading, bleaching or color changes of veneered surfaces may occur. Excessive hot sunshine may dry the veneer surface more quickly than substrate thereby causing appearance of small surface checks parallel to the grain and possible damage of the coating. Surface treated with the sol will become more protected due to the restricted water vapor transmittance.

It is well known that all chemical substances and alcohols should be removed immediately from all veneered surfaces to avoid their damages. Water repellency property doesn't allow liquid to penetrate into surface and make it easy-to-clean.

Antimicrobial properties are necessary in a wide range of uses such as furniture of public and hospital premises, kitchen, dining room and bathroom furniture, outdoor constructions and furniture etc.

II. MATERIALS AND METHODS

To make a modification of the veneer with the sol-gel coating, the preparation of plywood samples must be done. Birch veneer sheet were sanded on both sides with 100 grit and blown with compressed air to release the surface from dust. Prepared veneer sheets are cut in 50 mm x 50 mm sample pieces. To degrease the surface veneer samples are rinsed with diluted (30 ml distilled water to 100 ml acetone) acetone (EC no. 200-662-2, manufactured RILAK, Latvian). Degreased samples are washed in distilled water and dried in an oven at 90 °C.

A. *Sol-gel method*

The veneer samples were modified with silica sols and silica sol with the Zinc acetate dehydrate as precursor. Sols were synthesized using silica alkooxide tetraetylortosilicate, ethanol and water added to perform the hydrolysis and condensation, and hydrofluoric acid used as a catalyst. Zinc acetate dehydrate was used as the modifier of the sol-gel system. After the treatments, the samples were dried in an oven with the following thermal post-treatment, low temperature drying and thermal post-treatment were combined [5].

The another simple modification of veneer was applied veneer samples were soaked in acetic anhydride 80 % aqueous solution for 1,5 h at room temperature (24 ^{o}C), then pressed for 2 min in 50 °C and loaded till is completely dry not to damage.

B. *Adhesion theory and wetting parameters*

Several adhesion mechanisms or theories have been proposed and applied in the adhesion science and technology field [6]. This work involves the wetting (or adsorption) theory, which by far is the most applied concept for evaluation of theoretical secondary (non-covalent) bonding, for example hydrogen bonding, i.e. interfacial forces relevant mainly for adhesion and gluing technology. Wetting phenomena can be defined as "macroscopic manifestations of molecular interactions between liquids and solids in direct contact at the interface between them [7]. Surface free energy, contact angles and work of adhesion are some parameters that define the wettability of materials.

Four basic types of birch wood veneer specimens with dimensions of 100x100x0.6 mm and 15x15x0.6 mm were prepared: reference samples of unmodified wood, and four types of modified wood samples, i.e. 1) modified with silica sol following by two different regimes of thermal post-treatment 120 ^{o}C and 140 ^{o}C; 2) modified with silica sol with Zn diacetate precursor following by thermal post-treatment at 120 ^{o}C and 140 ^{o}C.

Fig. 4 illustrates an equilibrium state of a drop of liquid surrounded by a gas at a solid surface. This is the fundamental basis for the Young's equation (1) and is expressed as:

$$\gamma_{LG} \cos\theta = \gamma_{SG} - \gamma_{SL} \qquad (1)$$

where θ is the liquid-solid-air contact angle, γLG and γSG are the surface free energy of the liquid (L) and the solid (S), respectively, exposed to a gas (G), and γSL is the solid-liquid interfacial free energy [5].

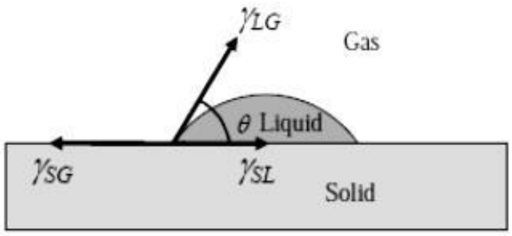

Fig. 4. Equilibrium state of a drop of liquid surrounded by a gas on a solid surface.

The sample is placed on an adjustable platform and a drop of distilled water is placed on it (~ 5 ml). The machine automatically records and photographs measurements and changes that take place with a drop of the sample surface (Fig. 5). There are taken five measurements of each type of sample.

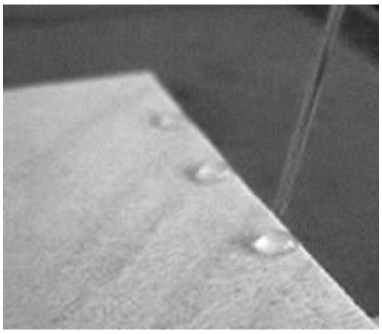

Fig. 5. Distilled water drops on the veneer sample

III. RESULTS AND DISCUSSION

A. *Wetting contact angle*

Surfaces of samples labeled "T" are not modified high wetting angle dispersion are determined by the specific surface structure of wood veneer. Some of the "T" range samples surface wetting behavior are similar to the silica sol modified samples reaction after a few seconds the average wetting contact angle decreases to 80° and continues to decline linearly to 70° in 10 s (Fig. 6 and Fig. 7). There is a large dispersion between the parallel measurements, covering plywood surface properties unevenness.

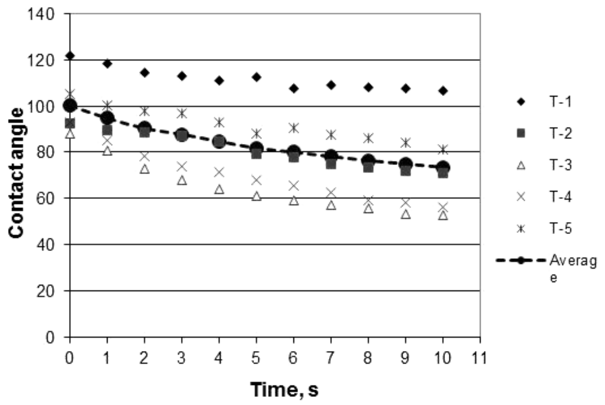

Fig. 6. Contact angle changes of the non-modified samples

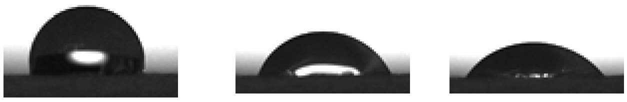

Fig. 7. Water drop shape changes of the non-modofied samples

Also, veneer samples of variant "E" (Fig.8) with prolonged soaking 1.5 hours at 24 °C acetic anhydride and subsequent drying at room temperature does not ensure stable damping obtuse angle, which only initially be close to 80 °. Already in the first few seconds the average value drops below 70 °, and continues to decrease non-linearly till 40° in 10 s interval (Fig. 8 and Fig.9). There is a large dispersion between the parallel measurements, covering the surface properties unevenness of veneer and uneven coating structure formation in processing and post-processing modes. "E" variant sample test results as a whole allows to conclude that appropriate treatment conditions and sol solution cannot provide a stable surface wetting reduction.

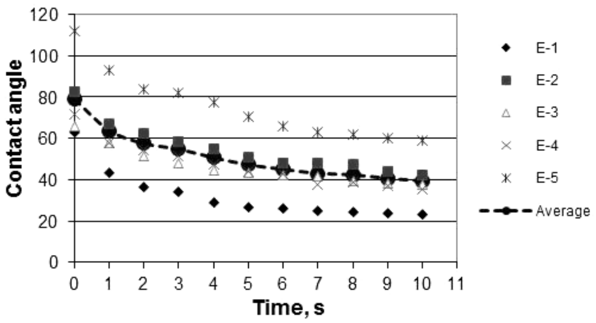

Fig. 8. Contact angle changes of the acetic anhydride modified samples

Fig. 9. Water drop shape changes of the acetic anhydride modified sample surface

In Fig. 10 and Fig. 12 are showed average values of wetting contact angle of samples treated with zinc acetate dehydrate (CAD) integrated in silica sol-gel system ("Z") in comparison with those processed with silica sol ("S") system. Indicators of variants Z4 and Z6 are much better than the corresponding values of untreated sample – contact angle is reduced to 91° and 95° in 10 seconds angle is reduced to 91° and 95° (Fig.11). Also variants S3 and S4 have better indicators than the untreated sample, respectively 89° and 80°.

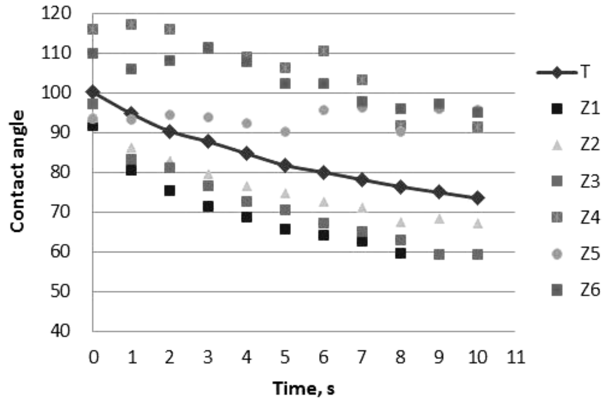

Fig. 10. Contact angle changes for samples with zinc acetate dihydrate integrated in Si sol-gel system compared and with raw sample

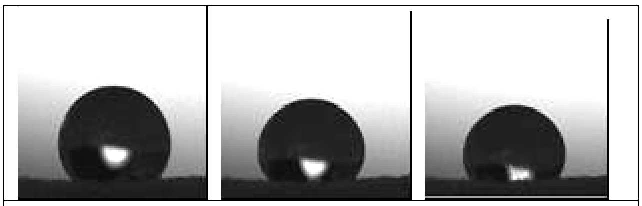

Fig. 11. Water drop shape changes of the zinc acetate dihydrate integrated in Si sol-gel system sample surface

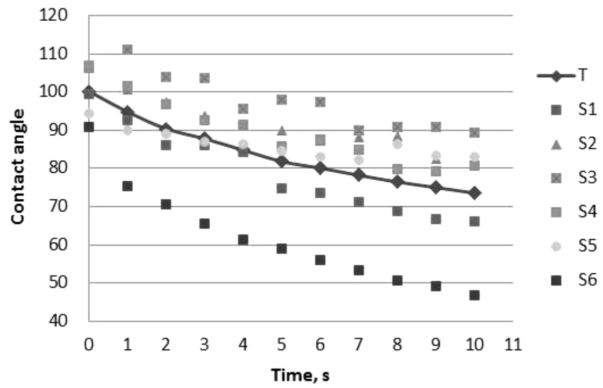

Fig. 12. Contact angle changes for samples with Si sol-gel system system compared with raw sample

B. Water absorption

The significant lack for wood is water absorption, which affects its physical and mechanical properties. Previously it found that modifying veneer samples with sol-gel technology obtained coatings can reduce the surface wetting. To determine the water absorption capacity of modified samples they are immersed in water (at room temperature) to 168 hours. After 168 hours all samples reached equilibrium values.

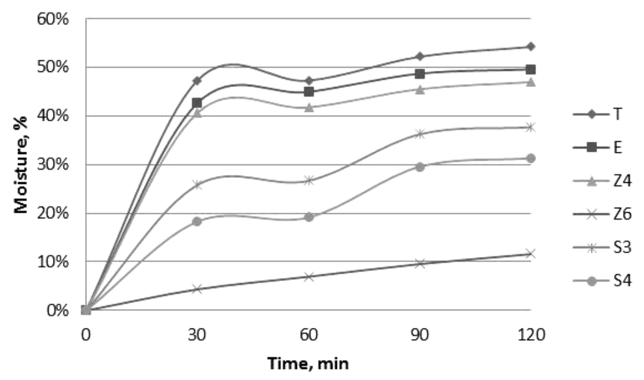

Fig. 13. Water absorption comparison

In Fig. 13 traceable moisture absorption capacity changes with in Si sol-gel system integrated CAD and with Si sol-gel system in the first 2 hours. Increasing mass changes occur after 30 minutes. Very steep is variant Z4 weight increase that reaches 40 % after 30 minutes, while the mass of Z6 increased by only 5 % and after 90 min soaking by 10 %. But it is 78% less than for untreated sample and 76% less than for sample treated with acetic acid anhydride. The best results with silica sol-gel system processed samples show samples of variants S3 and S4, where S4 change mass by 16 % less than S3, but 2.7 times higher than Z6. Overall, the weight changes of samples treated in Si sol-gel system integrated CAD and Si sol-gel system are on average 39 % lower than for raw sample and by 34 % lower than for sample treated with acetic acid.

IV. Conclusion

Birch veneer modification with acetic anhydride for reduction of surface wetting and moisture absorption capacity was not confirmed in experiments and is not considered usable.

Birch veneer modification with Si sol-gel integrated CAD and appropriate technological parameters for 30 minutes holding of 30 minutes lasting thermal post-treatment at a temperature of 140 ° C enables a significant reduction in the surface wetting and moisture absorption capacity, at the same time providing a good link with the glazes and the bottom paint, but reduces adhesion to the glue used in experiment.

Modification with the silica sol-gel with CAD precursor regarded as a targeted treatment that provides substantial birch veneer moisture absorption and surface wetting reduction. In order to ensure the sufficient adhesive strength, the processing must be carried out by spraying the modifying sol to the protected surface.

Although the veneer treatment with silica sol is less effective for surface wetting decrease, moisture absorption tests show the ability of this treatment to significantly reduce moisture absorption, especially if the samples are exposed to the short-term exposure.

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