

RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
Institute of Polymer Materials

Errj Sansonetti

Doctoral Student of the Doctoral Study Programme “Chemical Technology”

**INNOVATIVE ALKYD EMULSION
COMPOSITION ENHANCED WITH NANOSIZE
IRON OXIDES FOR THE PROTECTION OF
THERMALLY TREATED WOOD IN OUTDOOR
CONDITIONS**

Summary of the Doctoral Thesis

Scientific supervisors:

Dr. chem.
BRUNO ANDERSONS

Assoc. Professor Dr. sc. ing.
JĀNIS KAJAKS

RTU Press
Riga 2021

Sansonetti, E. Innovative Alkyd Emulsion Composition Enhanced With Nanosize Iron Oxides for the Protection of Thermally Treated Wood in Outdoor Conditions. Summary of the Doctoral Thesis. Riga: RTU Press, 2021. 36 p.

Published in accordance with the decision of the Promotion Council “RTU P-01” of 23 November 2020, Protocol No. 04030-9.1/14.



The Doctoral Thesis has been drafted at the Latvian State Institute of Wood Chemistry between 2012 and 2020, within the framework of the following National Research Program (NRP) and the European Regional Development Fund (ERDF) funded projects:

- European Regional Development Fund project “Innovative wood and its processing materials with upgraded service properties” (2011–2013);
- European Regional Development Fund project “Plywood from thermally treated veneers with improved resistance properties” (2014–2015);
- National Research Programme 2014.10-4/VPP-6/6 “Forest and earth entrails resources: research and sustainable utilization – new products and technologies” (ResProd)” Project No. 3 “Biomaterials and products from forest resources with versatile applicability” (2014–2017);
- European Regional Development Fund project “Wood with improved life of service, combining thermal modification and impregnation” (2017–2020).

<https://doi.org/10.7250/9789934226069>

ISBN 978-9934-22-605-2 (print)

ISBN 978-9934-22-606-9 (pdf)

DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for a remote defense at the open meeting of RTU Promotion Council on 24 March 2021 at 14:00 online. <https://rtucloud1.zoom.us/j/9352086644>.

OFFICIAL REVIEWERS

Docent *Dr. chem.* Ingars Reinholds
University of Latvia, Latvia

Lead Researcher *Dr. habil. sc. ing.* Jānis Grabis
Riga Technical University, Latvia

Professor *Dr. habil. ing.* Piotr Czub
Cracow University of Technology, Poland

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Errj Sansonetti

Date:

The Doctoral Thesis has been written in English. It consists of Introduction; 3 chapters; Conclusions; 49 figures; 13 Tables; 10 appendices; the total number of pages is 101, including appendices. The Bibliography contains 197 titles.

ACKNOWLEDGEMENT

I express my gratitude to my scientific advisors Dr. chem. Bruno Andersons and Dr. sc. ing. Jānis Kajaks for their support, recommendations and patience throughout all the stages of my Doctoral Thesis.

I am very thankful for the help and assistance provided by colleagues of the Laboratory of Biodegradation and Protection of Wood, in particular, Dr. chem. Ingeborga Andersone and Dr. sc. ing. Dace Cīrule, for their important and generous help in the organization of work and for sharing their deep knowledge in this field, to improve my results.

I also express my gratitude to other colleagues at LSIWC for their support, technical assistance and positive words shared with me to reach this important goal.

I want to thank also LSIWC for providing a friendly, favorable and supporting environment and all the necessary instruments to carry out this work.

Per aspera ad astra.

Errj Sansonetti

ABBREVIATIONS

A – alkyd
CA – contact angle
CIELab – International Commission on Illumination (*Commission internationale de l'éclairage*) color space
DBLO – double boiled linseed oil
DEab – color difference (CIELab color space)
DSC – differential scanning calorimetry
FA – fatty acids
FTIR – Fourier transform infrared
HAP – hazardous air pollutants
LO – linseed oil
LOAR – long oil alkyd resin
LSIWC – Latvian State Institute of Wood Chemistry
MOAR – medium oil alkyd resin
o/w – oil in water
RTU – Riga Technical University
S – solvent
SD – standard deviation
SE – surface energy
SEM – scanning electron microscope
ST – surface tension
 T_g – glass transition temperature
TM – thermal modification
TTW – thermally treated wood
UV – ultraviolet
VOC – volatile organic compounds
W – water

TABLE OF CONTENTS

INTRODUCTION.....	7
Actuality of the Topic.....	7
Aims and Objectives.....	8
Scientific Significance and Novelty	9
Practical Significance	9
Main Thesis to Defend	9
Structure and Volume of the Thesis	9
Publications and Approbation of the Thesis.....	9
1. SUMMARY OF THE LITERATURE REVIEW	13
2. MATERIALS AND METHODS	15
3. MAIN RESULTS OF THE WORK.....	16
3.1. The Surface Energy and Hydrophobicity of Wood	16
3.2. Formulation of Water-Based Coating for Thermally Treated Wood.....	18
3.2.1. Selection of Surfactants and Their Suitable Concentration.....	18
3.2.2. Efficiency of Different Driers.....	19
3.2.3. Glass Transition Temperature of Coating Film.....	21
3.3. Weathering Performance of the Developed Coating Formulation	22
3.3.1. Hydrophobicity Characteristics of Coated Thermally Treated Wood Samples.....	22
3.3.2. Contact Angle before and after Artificial Weathering	23
3.3.3. Contact Angle before and after Outdoor Weathering.....	25
3.4. Color Stability of Coated Thermally Treated Wood Samples	26
3.4.1. Color Changes during Artificial Weathering.....	27
3.4.2. Color Changes during Outdoor Weathering.....	30
CONCLUSIONS.....	34
BIBLIOGRAPHY	35

INTRODUCTION

Actuality of the Topic

Wood has been used for centuries as a material in many different fields and for many purposes. The negative aspect of wood as a construction and decorative material is the low resistance against degradation.

Since the development of the wood processing industry, many methods have been developed to protect wood. At present, very actual are treatments and techniques that do not use harmful chemical compounds, according to the latest restrictive legislation regarding the use of biocides and other toxic compounds.

One of these methods is thermal modification (TM) of wood, an attractive alternative way to preserve wood, thanks to its improved properties in terms of dimensional stability, moisture content and biological resistance. After TM, wood becomes more hydrophobic due to modifications in its chemical composition and in the structure of the wood surface.

The increased hydrophobicity is correlated to a different wettability of thermally treated wood (TTW) compared to untreated one. Despite its improved properties, also TTW is subjected to degradation caused by UV radiation and water, which are responsible for the color changes of wood and other damages. To delay such processes and enhance the service life of wood, coatings are still necessary and widely used because they retard the water uptake protecting the wood surface, and the UV absorbers protect wood from photodegradation. Considering the above-mentioned changes in wood caused by TM, alternative paint formulations can be necessary and specifically designed for protection of TTW.

The paint and coating industry is directed towards the replacement of paints that use volatile organic compounds (VOC) such as hydrocarbons, which are harmful to the environment, with greener options, more environmentally friendly alternatives.

As a result, formulators and users of industrial coatings face significant challenges as they try to respond to their customers' demands for cost-effective, high performance paints and coatings while meeting increasingly stringent regulations.

Speaking of water-based paints, one of their limits is the gap in performance compared to traditional solvent-based paints, and formulating low VOC water-based coatings with equal or better properties than conventional systems is still a challenge.

The different wetting properties of wood after TM must be considered to improve the formulations of new water-based paints specifically prepared for TTW. It has been observed that after TM, the hydroxyl groups OH available for water adsorption are reduced, and consequently, the wood becomes more hydrophobic [1].

The wetting of wood by a coating can be determined directly by measuring the contact angle (CA) of coating on a wood surface. The shape and CA of the spreading coating droplet is influenced by capillary penetration under or at the front of the droplet. In general, there is a good correlation between the CA and the degree of penetration of the coating into the wood [2]. In the case of water-based emulsion paints, the formation of a gradient of surface tension (ST) during the application of coating occurs due to coalescence which takes place during the

separation of micelles from water after the application of coating on the wood surface. This situation leads to an increase in viscosity during the capillary penetration process [2]. The gradient of viscosity hinders the homogeneous distribution of coating and hence can lead to:

- an uneven film formation on the wood surface (rheology of coating);
- a reduced adhesion due to lower penetration of binders into wood.

The changes in viscosity can have impact on the final film properties. It must be considered that there could be a different behavior during the application of varnishes or paints, which are traditionally formulated for untreated wood, on TTW. In conclusion, water-based paints are a green alternative to solvent-based formulations, and the replacement of petroleum-based monomers by renewable resources is another green approach.

To improve the resistance against photodegradation, more economical UV absorbers – nano-sized iron oxide particles – can be used in the final paint formulation.

Aims and Objectives

Overall goal of the Thesis

The main goal of this work is to demonstrate that the replacement of organic solvents with water in alkyd paints can give a product with similar or better exploitation properties in terms of efficiency against weathering in outdoor conditions, used specifically for TTW, without the formation of a visible thick film on the wood surface. This alkyd paint is in the form of emulsion, and to avoid shrinkage and obtain an even and homogeneous distribution of resin on the TTW surface after the application of the coating and during drying of the film, modification of the composition of alkyd micellar aggregates is desirable, and part of the amount of alkyd resin must be replaced by another component, which can improve the wetting of the wood surface, considering the increased hydrophobic nature and the reduced polarity of the surface energy (SE) of TTW.

The suitable component must be searched among renewable resources, and it can be pure linseed oil (LO) or partially polymerized double boiled linseed oil (DBLO).

Tasks of the Thesis

The work's tasks can be summarized as it follows in these main points, firstly, to determine the alkyd emulsion composition and its properties, followed by testing its efficiency during weathering, to obtain information about the parameters which can improve its performance:

- 1) investigate the changes of the SE of wood caused by TM and the relation with wood wetting;
- 2) investigate the interaction between TTW and resins (alkyds, LO and DBLO);
- 3) create and optimize the composition of a water-based alkyd emulsion paint suitable for TTW, with high protection efficiency for a non-film forming coating (thickness <5 μm);
- 4) investigate and compare the performance of alkyd emulsion and solvent-based alkyd paint during the weathering of coated TTW.

Scientific Significance and Novelty

In this work, the wettability of TTW has been studied and explained in relation to the changes of its SE. A water-based paint formulation specifically designed for TTW has been obtained. It has been verified that such a paint can be obtained even without the use of organic solvents which are usually also added to water-based formulations. Very reduced or excluded use of VOC in the obtained formulation makes this water-based paint an environmentally friendly product. Moreover, part of the binders is replaced with DBLO, which is of natural origin; hence, the use of renewable resources reduces the consumption of synthetic resins obtained from the raw material derived from fossil fuel resources.

Practical Significance

The study is specifically done to obtain a paint formulation designed for use with TTW. The information obtained on the properties of wood after TM and during weathering is important to optimize the appropriate composition of the paint and to select the most suitable additives to enhance the protection against the factors which cause degradation.

Main Thesis to Defend

The composition of the obtained alkyd emulsion has a high efficiency in the protection of TTW and can be compared and replace the traditional solvent-based paints. The paint does not form a visible thick film on the surface of wood, but the aesthetic properties of wood are protected also in outdoor uses. For this purpose, the composition is specifically formulated for TTW and can differ from traditional paints designed for untreated wood.

Structure and Volume of the Thesis

The Doctoral Thesis consists of Introduction and three main chapters: Literature review, Materials and Methods, Results and Discussions. The main topics treated in the Literature review are about the main factors responsible for wood degradation and the possible methods to protect wood and enhance its service life, especially in outdoor conditions.

The Results and Discussions section reports the results of the investigation of the surface properties of TTW, the composition and the properties of the alkyd emulsion and the efficiency of the optimized alkyd emulsion composition during artificial and outdoor weathering tests of coated TTW samples.

The Doctoral Thesis has been written in English and has 101 pages. There are 49 figures, 13 Tables and 10 appendices. In the Thesis, 197 literature references are cited.

Publications and Approbation of the Thesis

The results of the present Doctoral Thesis have been discussed and presented in 11 scientific publications and 17 international scientific conferences. One patent of the Republic of Latvia is registered.

Scientific publications

1. **Sansonetti, E.**, Cirule, D., Kuka, E., Andersone, I., Andersons, B. 2020, “Changes in ecological linseed oil paints during outdoor weathering of wood panels” *Key Engineering Materials*, 850, 316–321.
2. **Sansonetti, E.**, Cirule, D., Kuka, E., Andersone, I., Andersons, B. 2019, “Investigation of linseed oil based wood coatings: effect of artificial weathering” *Key Engineering Materials*, 800, 223–227.
3. Meija-Feldmane, A., **Sansonetti, E.**, Morozovs, A., Spulle, U. 2019, “Thermal modification as tool to increase hydrophobicity of veneers” *Engineering for Rural Development*, 18, 1059–1064.
4. Andersons, B., Andersone, I., Zudrags, K., **Sansonetti, E.** 2018, “Impregnated and covered birch plywood performance during external exposure” *Wood Material Science & Engineering*, 13(1), 21–27.
5. Grinins, J., Irbe, I., Andersons, B., Andersone, I., Meija-Feldmane, A., Janberga, A., Pavlovics, G., **Sansonetti, E.** 2016, “Thermo-hydro treated (THT) birch plywood with improved service properties” *International Wood Products Journal*, 7(4), 181–187.
6. Grinins, J., Andersons, B., Irbe, I., Andersone, I., Meija-Feldmane, A., Janberga, A., Pavlovics, G., **Sansonetti, E.** 2016, “Thermo-hydro treated (THT) birch veneers for plywood production with improved properties” *Holzforschung*, 70(8), 739–746.
7. **Sansonetti, E.**, Andersons, B., Andersone, I. 2016, “Novel alkyd-linseed oil emulsion formulations for wood coatings” *IOP Conference Series: Materials Science and Engineering*, 111(1) 012020.
8. Irbe, I., **Sansonetti, E.**, Zudrags, K., Andersone, I., Andersons, B. 2016, “Fungal resistance of different plywood types during outdoor exposure” 27th International Conference on Wood Science and Technology, ICWST 2016: *Implementation of Wood Science in Woodworking Sector – Proceedings*, 89–97.
9. Narkevica, I., Reinis, A., Bugovecka, L., **Sansonetti, E.**, Kroica, J., Ozolins J., 2016, “In vitro bioactivity and bacteriostasis effect of thermally treated and UV-light irradiated TiO₂ ceramics” *Key Engineering Materials*, 674, 121–126.
10. Biziks, V., Andersons, B., **Sansonetti, E.**, Andersone, I., Miltz, H., Grinins, J. 2015, “One stage thermo-hydro treatment (THT) of hardwoods: an analysis of form stability after five soaking-drying cycles” *Holzforschung*, 69(5), 563–571.
11. **Sansonetti, E.**, Andersons, B., Biziks, V., Grinins, J., Chirkova, J. 2013, “Investigation of surface properties of hydrothermally modified soft deciduous wood” *International Wood Products Journal*, 4(2), 122–127.

Conferences papers

1. **Sansonetti, E.**, Cirule, D., Andersons, B., Andersone, I., Kuka, E. 2019, “Changes in ecological linseed oil paints during outdoor weathering of wood panels” *Materials Science and Applied Chemistry*, Riga, Latvia, 24 October, 64.

2. Cirule, D., **Sansonetti, E.**, Kuka, E., Andersone, I., Andersons, B. 2017, "Surface finishing for improvement of thermally modified wood resistance to discoloration, Building with bio-based materials: best practice and performance specification" Final COST Action FP1303 International Scientific Conference, Zagreb, Croatia, 6–7 September, Book of abstracts. Eds: Vjekoslav Živković and Dennis Jones, 28–29.
3. **Sansonetti, E.**, Andersons, B., Andersone, I. 2016, "Formulation of an alkyd emulsion suitable as a wood paint" Proceedings of 12th Meeting of the Northern European Network for Wood Science and Engineering (WSE), Riga, Latvia, 12–13 September, 87–93.
4. **Sansonetti, E.**, Grinins, J., Andersons, B., Andersone, I. 2015, "Novel linseed oil-alkyd emulsion formulations for wood coatings" Proceedings of the 11th Meeting of the Northern European Network for Wood Sciences and Engineering (WSE), Poznan, Poland, 14–15 September, 118–124.
5. Grinins, J., Andersons, B., Irbe, I., Andersone, I., Meija-Feldmane, A., Janberga, A., Pavlovics, G., **Sansonetti, E.** 2015, "Thermo-hydro treated (THT) birch plywood with improved service properties" International Panel Products Symposium IPPS 2015, Llandudno, Wales, U.K., 7–9 October, 153–164.
6. **Sansonetti, E.**, Andersons, B., Andersone, I. 2015, "Novel alkyd-linseed oil emulsion formulations for wood coatings" Scientific Conference of the Forest Sector "Knowledge based forest sector", Riga, Latvia, 5–6 November.
7. **Sansonetti, E.**, Grinins, J., Andersons, B., Andersone, I. 2015, "Novel alkyd-linseed oil emulsion formulations for wood coatings" Baltic Polymer Symposium, Sigulda, Latvia, 16–18 September, 127.
8. Cirule, D., **Sansonetti, E.**, Meija-Feldmane, A., Andersone, I., Andersons, B. 2014, "Coatings improving resistance of thermally modified wood to discoloration" 10th Coatings Science International 2014, COSI2014, Noordwijk, The Netherlands, 23–27 June, 97–100.
9. **Sansonetti, E.**, Cirule, D., Grinins, J., Andersone, I., Andersons, B. 2014, "Efficiency of zinc oxide and pigments against UV degradation of hydrothermally treated wood samples" 7th European Conference on Wood Modification ECWM7, Lisbon LNEC, Portugal, 10–12 March 2014, 126–127.
10. **Sansonetti, E.**, Cirule, D., Andersons, B., Andersone, I. 2013, "Effect of outdoor exposure on coated modified wood samples" Proceedings of the 9th Meeting of the Northern European Network for Wood Science and Engineering (WSE), Hannover, Germany, 11–12 September, 197–201.
11. Grinins, J., Biziks, V., Andersons, B., Andersone, I., **Sansonetti, E.** 2013, "Effect of heat treatment on water related properties of hydrothermally modified hardwoods" Proceedings of the 9th Meeting of the Northern European Network for Wood Science and Engineering (WSE), Hannover, Germany, 11–12 September, 136–141.

12. Berzina-Cimdina, L., Narkevica, I., Ozolins, J., Kleperis, J., **Sansonetti, E.** 2013, “Bulk and surface properties of nonstoichiometric TiO₂-x ceramic” Proceedings of the 21st Annual International Conference on Composites or Nano Engineering (ICCE-21), Tenerife, Spain, 21–27 July, 1–2.
13. Andersons, B., Andersone, I., Irbe, I., Chirkova, J., Biziks, V., Grinins, J., **Sansonetti, E.** 2013, “New products from deciduous wood by one-stage hydrothermal modification” International Science Conference on Hardwood Processing (ISCHP2013), 2013, Florence, Italy, 7–9 October, 220–226.
14. **Sansonetti, E.**, Cirule, D., Grinins, J., Andersone, I., Andersons, B. 2013, “Colour changes of hydrothermally modified coated wood after artificial and outdoor exposure” Joint focus workshop of COST Action FP1006 & FP0904, Rogla, Slovenia, 16–18 October, 261–267.
15. Chirkova, J., Andersone, I., **Sansonetti, E.**, Grinins, J., Andersons, B. 2012, “Estimation of the wood surface energy by Hansen solubility parameters” 12th European Workshop on Lignocellulosics and Pulp EWLP, Espoo, Finland, 27–30 August, 216–219.
16. Grinins, J., Biziks, V., Andersons, B., Andersone, I., **Sansonetti, E.** 2012, “Influence of the hydro-thermal treatment on chemical composition, physical and mechanical properties of ash-tree wood” “Hardwood Science and Technology”, the 5th Conference on Hardwood Research and Utilisation in Europe 2012, Sopron, Hungary, 10–12 September, 241–250.
17. **Sansonetti, E.**, Kapaca, E., Cirule, D. 2012, “Comparison and evaluation of several industrial and experimental coatings: effects of artificial weathering” Proceedings of 8th Meeting of the Northern European Network for Wood Science and Engineering (WSE), Kaunas, Lithuania, 13–14 September, 35–41.

Patent

Sansonetti, E., Cīrule, D., Kuka, E., Andersons, B., Andersone, I., Patent of the Republic of Latvia P-18-66 “A protective coating for thermally treated wood”. Application date: 13.07.2018.

1. SUMMARY OF THE LITERATURE REVIEW

Wood, like other biological materials, is susceptible to changes and transformations in the structure and composition, which lead to its degradation. These processes occur rapidly when wood is exposed outdoors, and in this case, all the transformations which take place are defined as “weathering”. This is a widely studied subject, since the comprehension of the involved processes and reactions is necessary to delay them and to increase the durability of wood as a substrate and to extend its service life. It can be said that the understanding and knowledge about weathering is well established. The weathering factors responsible for the changes in wood surfaces are solar radiation (mainly UV), moisture (dew, rain, snow and humidity), temperature and oxygen. The effects on wood are the results of a synergic combination of all these factors.

Among all the factors, solar radiation is recognized as the most damaging component of the outdoor environment and initiates a wide variety of chemical changes at wood surfaces [3]. The UV fraction of solar radiation is recognized as the main factor responsible for the degradation of wood components, in particular, of lignin more than others, and it gives origin to a wide series of photochemical reactions at the wood top layer [4]. It has been well known for a long time that weathering of wood is a surface phenomenon, and many studies have been conducted to determine the depth of wood degradation caused by UV radiation [5]. Different reaction products have been reported that depend on the wavelength of the UV radiation. It has been reported that also the violet fraction of the visible light can give photodegradation: due to its longer wavelength it can penetrate deeper into the wood surface extending photodegradation beyond the zone affected by UV radiation [5]. The protection of wood can be done with different approaches and methods. The actual trend is towards more environmentally friendly approaches in order to reduce pollution and use less toxic compounds.

The TM of wood has gained a lot of interest in the last 2 decades, when it became necessary to find alternative and ecological methods to improve wood protection, due to the ban of toxic substances and compounds used till that moment. TM gives to the wood improved properties in terms of dimensional stability, moisture content and biological resistance but with a decrease in its mechanical properties [6], [7]. During TM, wood becomes more or less dark, depending on the temperature and length of the process, making some species of light-colored woods more appealing for the consumers. Another property affected by TM is that wood becomes more hydrophobic. The increased hydrophobic character is correlated to a different wettability of TTW, which is caused by modifications in its chemical composition and in the structure of the wood surface [8]. Despite its improved properties, also TTW, when exposed outdoors, is subjected to degradation [9], and the use of paints is still necessary to delay such processes and enhance the service life of wood. Coatings are still widely used because they retard the water uptake, protecting the wood surface and, for wood used outdoors, the UV absorbers protect wood from photodegradation. However, recent legislation forces to reduce or eliminate the content of VOCs and hazardous air pollutants (HAP) from formulations because of the hazard they represent to the environment and the human health. As a result, formulators and users of industrial coatings now face

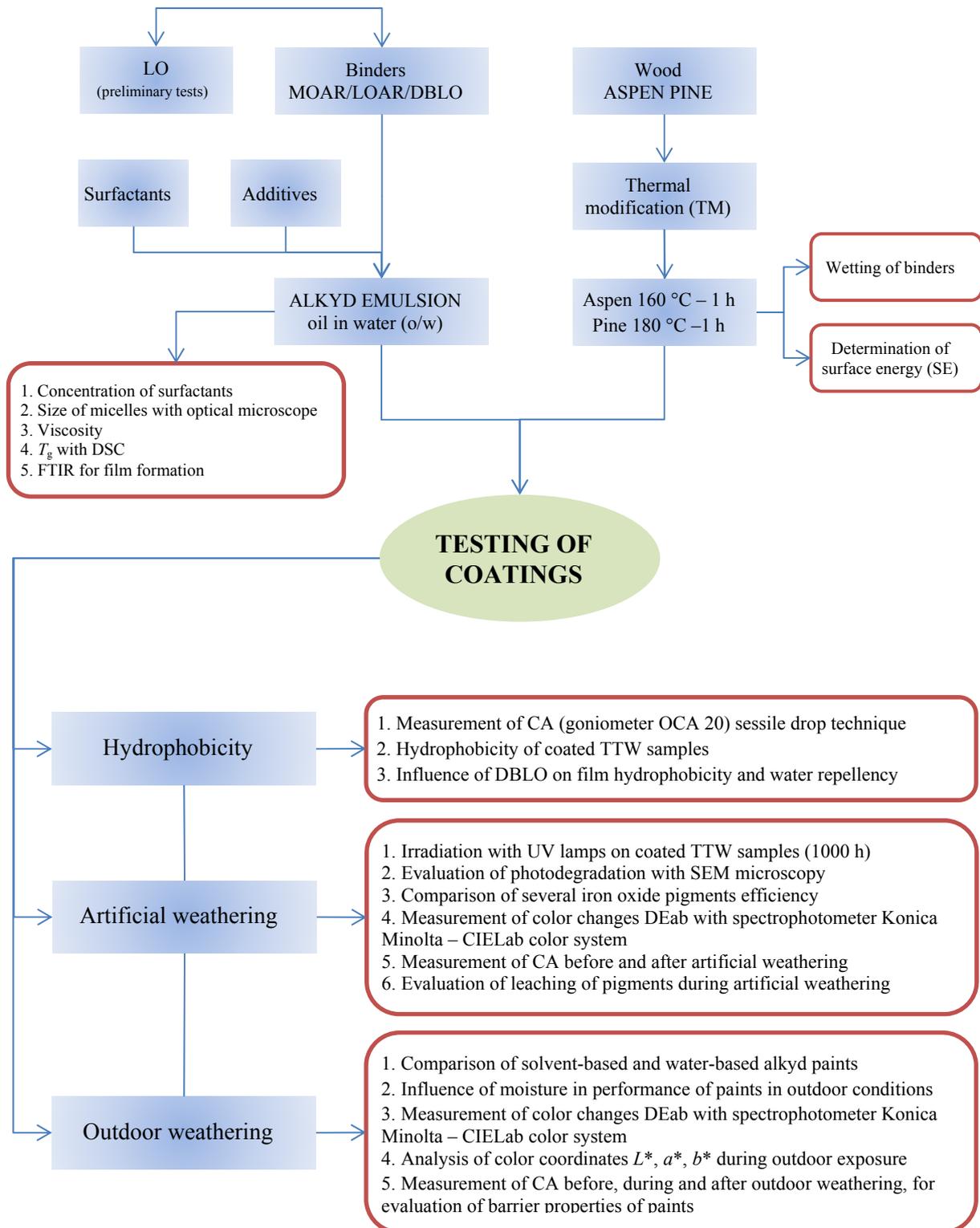
significant challenges as they try to respond to their customers' demands for cost-effective, high performance paints and coatings while meeting increasingly stringent regulations.

In the case of alkyds, among the available alternatives there are high solids and water-borne formulations. Considering water-borne formulations, there are clearly environmental and other safety advantages in replacing organic solvent with water, and this has been a major trend in the past decades, although there are some gaps in performance, compared to solvent-based formulations, that must be filled. The function of the paint is to provide physical protection against degradation and to preserve aesthetical appearance. The assessment of these protective or barrier properties is then of great importance to improve and develop further better solutions in coating technology. The type of coating and its functions are selected according to the substrate characteristics. In the case of wood as a substrate, the “film former” or “binder”, so called because this material, in the presence of other components, has the function to bind or glue them together, are organic materials which may be of natural origin (e.g., linseed oil), modified natural (e.g., nitrocellulose) or wholly synthetic (e.g., acrylics, polyurethanes). The use of alkyds is still widely spread thanks to their good attributes such as strength, flexibility, gloss retention, and good thermal stability and constitute about 70 % of the conventional binders used in surface coatings today [10].

Alkyds are very versatile resins thanks to the presence of long carbon chains attached to the alkyd backbone, which modify the mechanical properties of the polyester resin, confer solubility in specific solvents and also the ability to form crosslinks through auto-oxidation as for natural drying oils. They can also be produced using fatty acids (FA) obtained from renewable resources which make them more “green” resins.

UV protection is necessary for wood used outdoors, and this function is carried out by special additives – UV absorbers. Among them, also pigments can be included, which in paints have also the function to give color and opacity to the substrate. There are organic pigments, which are more expensive, but mainly used are inorganic pigments, added in the form of ground fine powder. Their size is in the micrometric range, but more recently, a new generation of nano-sized or transparent pigments has been produced. The size of these pigment particles is smaller than the wavelength of visible light, and this makes them transparent. Nano-sized particles have a greater specific surface than traditional pigments, which gives them different and new properties. Apart from aesthetic functions, some of these metal oxides find application also in protection against photodegradation of wood, since they are good UV absorbers, which convert into heat the energy of UV radiation which reaches the substrate surface [11]. In wood paints, zinc (ZnO) and titanium (TiO₂) oxides, which are white, and several iron oxides like iron (III) oxide, iron (III) oxide hydrate and magnetite are used. Iron oxides also absorb part of the visible light region, which explains why they come in different shades, going from yellow to red, brown and black. There are studies that confirm the efficiency of iron oxides as UV absorbers [12]. They are necessary to improve the performance of clear coating systems, which do not offer sufficient protection against the discoloration of wood. The advantages of inorganic UV absorbers are their stability against UV radiation and the cheaper costs, which make iron oxide pigments a good choice to improve paint performances.

2. MATERIALS AND METHODS



3. MAIN RESULTS OF THE WORK

3.1. The Surface Energy and Hydrophobicity of Wood

One of the chemo-physical properties of wood affected by TM is the different wettability of wood: due to the structural and chemical changes that occur during TM, wood becomes more hydrophobic. The parameter tightly connected to wettability is the SE and, as already indicated in other publications [13], it can give information about the wetting properties of wood after TM. To determine the SE of both wood species, aspen (*Populus tremula*) and pine (*Pinus sylvestris* L.), untreated and TTW samples treated at different temperatures have been used. Measurements of CA have been done using water, glycerol and formamide as probe liquids. The values of CA obtained with the three probe liquids are listed in Tables 3.1 and 3.2.

Table 3.1

Contact Angle (°) of Untreated and Thermally Treated Aspen with Standard Deviation (SD)

ASPEN	UNTREATED	160 °C	170 °C	180 °C
Water	62.1 ± 10.7	81.2 ± 5.2	85.1 ± 4.4	99.0 ± 3.9
Glycerol	59.6 ± 6.0	76.1 ± 3.4	79.1 ± 3.9	79.5 ± 3.3
Formamide	36.7 ± 8.2	55.4 ± 5.0	64.1 ± 5.4	63.5 ± 2.8

Table 3.2

Contact Angle (°) of Untreated and Thermally Treated Pine with Standard Deviation (SD)

PINE	UNTREATED	160 °C	170 °C	180 °C
Water	88.9 ± 0.8	91.9 ± 6.6	98.3 ± 7.0	108.2 ± 4.0
Glycerol	80.2 ± 1.9	84.5 ± 1.5	90.4 ± 3.7	97.4 ± 1.2
Formamide	49.1 ± 4.0	62.7 ± 5.1	58.3 ± 3.1	55.3 ± 2.7

The CA of water increases with increasing TM temperature, confirming that the wood becomes more hydrophobic. Formamide has the smallest CA. The results show the growth of CA with increasing temperature of TM; the only exception is for formamide and pine wood samples: passing from the TM temperature of 160 °C to 180 °C, the CA decreases. One explanation is the increased porosity of wood after TM and the low ST of formamide which is quickly absorbed. Another explanation is the decrease of the pH of wood caused by the degradation of hemicelluloses during TM, already observed for pine wood after TM [14]. The obtained values of CA are used to calculate the SE before and after TM at the selected temperatures for pine and aspen wood, namely, 160 °C, 170 °C and 180 °C. There are several methods to calculate SE, depending on the mathematical approach and the information that can be obtained. The method used in this work is the Wu method which can measure the polar and dispersive components of SE [15]. At least two test liquids with known polar (P) and

dispersive (D) components are required; one of the liquids must have a polar component greater than zero. Equation (3.1) is used to calculate SE.

$$\gamma_{sl} = \gamma_s + \gamma_l - \frac{4\gamma_s^D\gamma_l^D}{\gamma_s^D + \gamma_l^D} - \frac{4\gamma_s^P\gamma_l^P}{\gamma_s^P + \gamma_l^P} \quad (3.1)$$

where γ_{sl} – interfacial energy between the substrate and the liquid; γ_s – SE of the substrate; γ_l – SE of the liquid; γ^D – dispersive component of SE; γ^P – polar component of SE.

Results are given in Tables 3.3 and 3.4 for the SE of aspen and pine, respectively.

Table 3.3

Surface Energy of Aspen before and after Thermal Modification

Sample	$\gamma = \gamma^D + \gamma^P$, mN/m	γ^D , mN/m	γ^P , mN/m
Untreated	44.37	24.29	20.08
160 °C	34.11	23.23	10.88
170 °C	30.43	19.70	10.73
180 °C	40.11	38.82	1.29

Table 3.4

Surface Energy of Pine before and after Thermal Modification

Sample	$\gamma = \gamma^D + \gamma^P$, mN/m	γ^D , mN/m	γ^P , mN/m
Untreated	33.01	24.80	8.22
160 °C	28.13	19.60	8.53
170 °C	28.62	23.68	4.93
180 °C	31.55	30.91	0.64

The results are different, but for both species, the common trend is the decreasing of the polar component γ^P of SE. The primary component of SE is always the dispersive component and its ratio increases with increasing temperature of TM. For both species, after TM at 160 °C and 170 °C, the dispersive component of SE slightly changes, whilst the polar component γ^P is almost down to half of the initial value. The SE after the TM at 180 °C is slightly decreased. At this temperature, a higher hydrophobic character of wood is obtained; in fact, the polar component γ^P decreases by 93.6 % for aspen and by 92.2 % for pine. The great decrease of γ^P at 180 °C is compensated by an increase in the dispersive component γ^D of 59.8 % for aspen and of 24.6 % for pine. In conclusion, TM changes the surface properties of wood, and its wettability and SE are affected. The decrease of the polar component of SE can be assumed as the evidence of the reduced wettability and hence higher hydrophobicity of wood after TM.

3.2. Formulation of Water-Based Coating for Thermally Treated Wood

3.2.1. Selection of Surfactants and Their Suitable Concentration

Several surfactant types have been tested for emulsification. Results are different. With surfactants from the Dynol and Surfynol series, emulsification of alkyd resins and DBLO is not obtained, they are not soluble in water and there is fast separation of phases. Attempts with the Carbowet surfactants series give white homogeneous emulsions. The concentrations of surfactants are shown in Fig. 3.1. The surfactants selected to emulsify alkyds and DBLO in the final paint formulation are Carbowet 125 and Carbowet 144, used in equal amounts, as they have longer chains and can contribute to a better stability, giving a thicker layer at the oil-water interface.

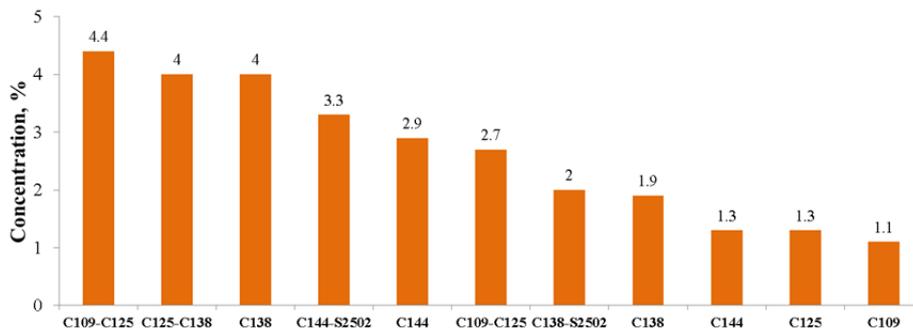


Fig. 3.1. Emulsification tests of alkyds and DBLO with several surfactants and their concentrations, C – Carbowet; S – Surfynol.

To determine the size of micelles, two emulsions containing only water, alkyds, DBLO and the two selected surfactants have been prepared. The selected concentrations of surfactants are 1.4 % and 2.0 %. Two white and homogeneous emulsions have been obtained, which testifies that the micelles have a micrometric size. Results are shown in Figs. 3.2 and 3.3. The lowest diameter measured with the microscope software is 7 μm , and the largest group of micelles is the group with a diameter of up to 20 μm for both concentrations, which is almost half of the measured micelles. For both concentrations, the distributions are remarkably similar, and the first two groups of micelles with the diameter up to 40 μm have practically the same number of micelles. For the two concentrations, 1.4 % and 2.0 %, they are 67 % and 66 % respectively, of the total number of micelles.

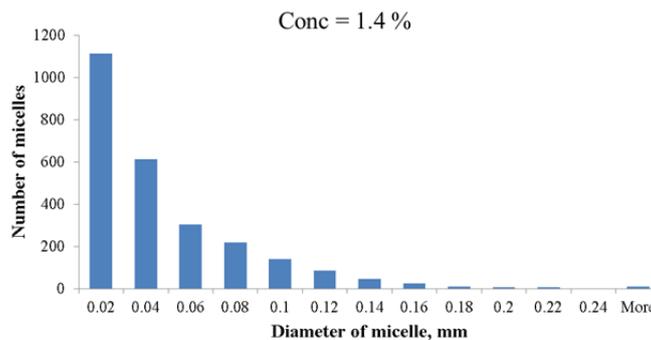


Fig. 3.2. Distribution of micelle sizes for the emulsion with 1.4 % of the selected surfactants.

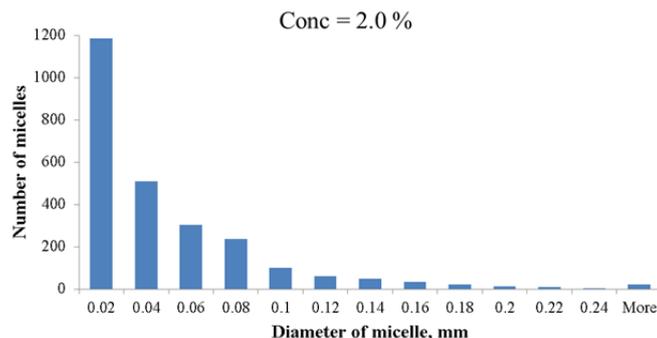


Fig. 3.3. Distribution of micelle sizes for the emulsion with 2.0 % of the selected surfactants.

In conclusion, both concentrations of surfactants give emulsions with micelles of similar sizes. It is preferable to use the surfactants at a lower concentration to avoid inconveniences, like foam formation, and to have lower impact on the final properties of the film.

3.2.2. Efficiency of Different Driers

Cobalt is the most widely used primary drier, but due to the growing concerns on the toxicity of cobalt salts, alternatives to cobalt-based driers are highly demanded [16]. Potential primary metal driers which can replace cobalt are manganese, iron or vanadium, which are less toxic. The catalytic activity of the available three driers during the film formation process has been monitored using FTIR spectroscopy. Different spectra during 24 h for the cobalt drier are shown in Fig. 3.4. Dry 0615 Aqua (manganese) and Borchhi Oxy Coat 1101 (iron complex) have similar spectra. They only differ in the area of characteristic peaks, which can be considered as an indicator of different rates of auto-oxidation during film formation. The main changes involve double bonds like, for example, specific peaks at 3007 cm^{-1} and 970 cm^{-1} . The peak on the right side of the graph at 970 cm^{-1} indicates that reactions of cross-linking of alkyd molecules take place: there is progress in network formation and an increase in viscosity; the peak, in fact, is formed when conjugated double bonds turn into isolated double bonds, which indicates the progress of cross-linking. The area of this peak increases for each tested drier. Simultaneously, the peak at 3007 cm^{-1} disappears; this is the peak of isolated *cis* double bonds, which is present in linoleic acid and it is most probably given by the DBLO mixed with the alkyd resins.

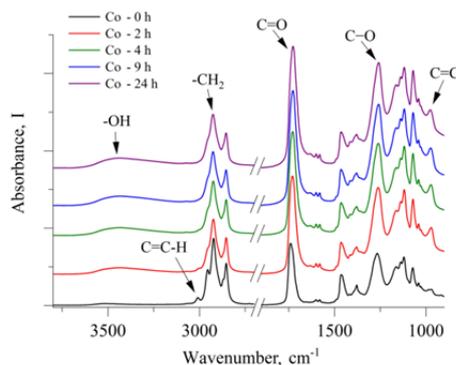


Fig. 3.4. FTIR spectra of alkyd and DBLO for cobalt drier at different times during curing.

The different rate of auto-oxidation can be ascribed also to different induction times, which change with the type of the used drier. During the induction time, evaporation of the solvent and oxygen absorption take place: it is the initial stage of film formation. At this stage, the peak at 3007 cm^{-1} still remains unchanged. In our experiment, for samples with the cobalt drier, induction time is about 1 h and for Borchio Oxy Coat 1101 and Dry 0615 Aqua – 4 h and 6 h, respectively. The difference in induction times based on this peak observation is not the only evidence available; in fact, empirically, it can be observed that the formation of a film on the glass support occurs exactly at the induction time for each drier. Such different induction times confirm the higher catalytic activity of the cobalt drier.

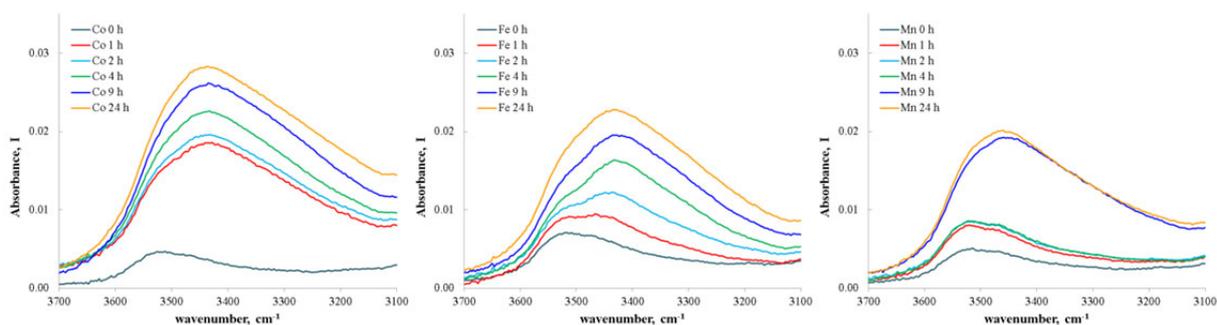


Fig. 3.5. Detailed and shifted FTIR spectra for three driers at 3450 cm^{-1} changing during 24 h.

The wide band around 3450 cm^{-1} is from stretching frequencies of hydrogen bonded -OH, and it may suggest the presence of a small number of unreacted -OH groups left in the polymeric matrix [17], but most probably the hydroxyl group is from the reaction with oxygen and the formation of hydroperoxides, which decompose into alkoxy and hydroxyl radicals [18]. Figure 3.5 shows the formation of -OH groups for the three driers. It is evident how for the cobalt drier, the area of the peak is larger and already after 1 h (red line) the peak has increased its area much faster than the other two driers. After 24 h, the value of absorbance of the peak for the cobalt drier is around 0.03, whilst for the other two driers it reaches a value slightly above 0.02. This also confirms the higher efficiency of the cobalt drier (Fig. 3.6).

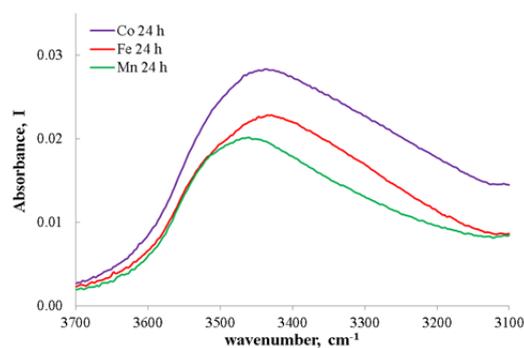


Fig. 3.6. Comparison of the area of -OH group peaks for three driers after 24 h.

Figure 3.7 shows the monitoring of -OH for the three driers during the formation of hydroperoxides relatively to the initial value of the -OH group according to the following expression:

$$\frac{A_t - A_{t=0}}{A_0}, \quad (3.2)$$

where A_t – area of -OH groups versus time (band at 3450 cm^{-1}); $A_{t=0}$ – initial value of the area of -OH groups (band at 3450 cm^{-1}); A_0 – normalized peak (band at 1275 cm^{-1}).

The peak at 1275 cm^{-1} is the ester peak (stretching of -COOC). The initial value A_0 must be considered because already -OH groups are present at the beginning of the curing process, for example, the Oxy Coat 1101 drier is diluted in water. Also in this case, it is confirmed that the most intensive formation of hydroperoxides can be observed in the presence of the cobalt drier; it is very fast in the initial stage of the auto-oxidation, whilst the two other driers require a longer time to activate. Once the highest catalytic activity is reached, the amount of hydroperoxides becomes constant and the concentration of -OH does not change.

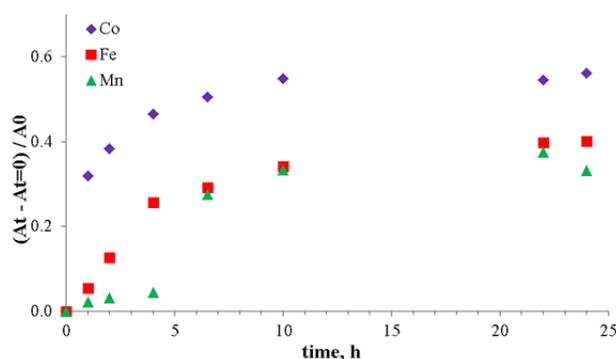


Fig. 3.7. Monitoring of -OH groups for three driers during auto-oxidation of resins.

3.2.3. Glass Transition Temperature of Coating Film

In this experiment, the glass transition temperature (T_g) has been measured for alkyd films with and without DBLO. The addition of a plasticizer to a resin has positive effects; it can give a film with increased thermal stability, plasticizing effect, compatibility and flexibility, and can decrease its T_g which has also positive effects on the properties of the film. T_g for amorphous polymers is not a specific temperature but it is an interval of temperatures, and there are several evaluation possibilities for the glass transition.

From the glass transition curves, more points can be extrapolated in the interested interval of temperature using different methods, and each of these points corresponds to T_g . The results are shown in Table 3.5 and compare three samples for both types of film.

The addition of DBLO makes T_g decrease, which is the expected effect. This is true for midpoint and midpoint DIN values, whilst for inflection points, the results are different and going on the opposite direction.

Midpoint and midpoint DIN are practically the same values because the heating rate was lower than the cooling rate during DSC. Since it is generally stated that the midpoint

temperature is most commonly identified as T_g , the results are in line with the literature sources and confirm the plasticizing effect of DBLO for alkyd resins [19].

Table 3.5

Values of T_g from Different Methods for Alkyd Films with and without DBLO

Method	Midpoint DIN*		Inflection point**		Midpoint***	
Binders	Alkyd	Alkyd + DBLO	Alkyd	Alkyd + DBLO	Alkyd	Alkyd + DBLO
T_{g1} , °C	-12.48	-13.75	-14.94	-9.02	-12.47	-13.95
T_{g2} , °C	-10.56	-12.38	-6.19	-10.61	-10.39	-11.80
T_{g3} , °C	-5.91	-8.64	-11.36	2.73	-7.57	-8.70

* Midpoint DIN – the point on the thermal curve corresponding to 1/2 of the heat flow difference between the extrapolated onset and extrapolated end.

** Inflection point – the point on the thermal curve corresponding to the peak of the first derivative (with respect to time) of the parent thermal curve. This point corresponds to the inflection point of the parent thermal curve.

*** Midpoint – the point on the tangent to the thermal curve corresponding to 1/2 of the heat flow difference between the extrapolated onset and extrapolated end.

3.3. Weathering Performance of the Developed Coating Formulation

3.3.1. Hydrophobicity Characteristics of Coated Thermally Treated Wood Samples

Measurements of CA have been done to evaluate the hydrophobicity of TTW, coated with emulsion of alkyd resins and alkyd/LO or alkyd/DBLO. The wood used is aspen modified at 160 °C.

The alkyd resins / LO and alkyd resins / DBLO ratio in emulsions is 4:1. Results are given in Fig. 3.8. Except for the first result, which however is very close to 90°, all the tested emulsions give hydrophobic wood surfaces.

On an average basis, the CA of the wood surface is higher in the presence of LO and DBLO, which confirms the positive effect of the partial substitution of alkyd resins. The variations in SD are caused by the small applied amount of the coating and the morphology of the wood.

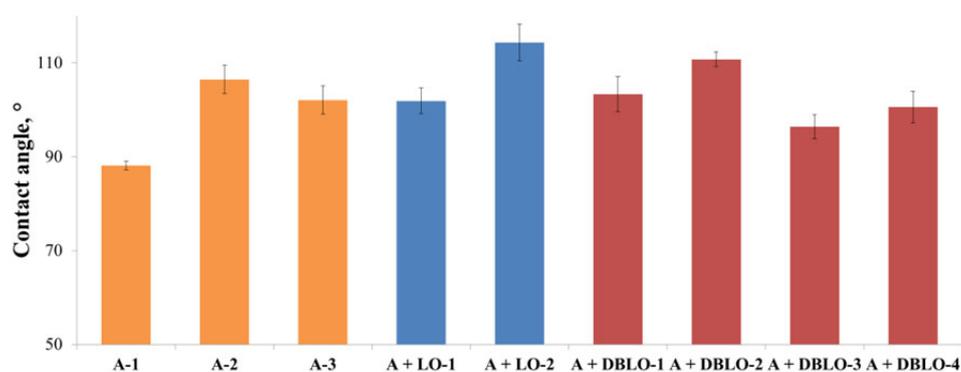


Fig. 3.8. Contact angle of thermally treated wood aspen samples coated with emulsions, containing alkyd (A) or alkyd and linseed oil (LO) / double boiled linseed oil (DBLO).

During the drying, LO and DBLO can migrate to the upper layer of the film and act as surface active polymers, as has been already observed in another work [20].

This can be seen in Figs. 3.9 and 3.10. In the presence of LO and DBLO, for the same samples shown in Fig. 3.8, CA decreases during 30 s due to the hydrocarbon tails that make the ST of water decrease and increase the wetting of the surface. For the film containing only alkyds as binders, CA is constant during 30 s.

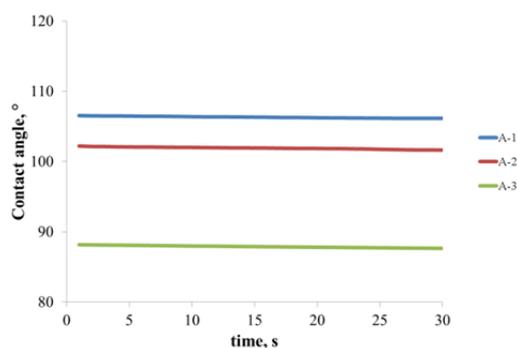


Fig. 3.9. Curve of the contact angle of coated thermally treated wood samples with different emulsions containing only alkyd resins (A).

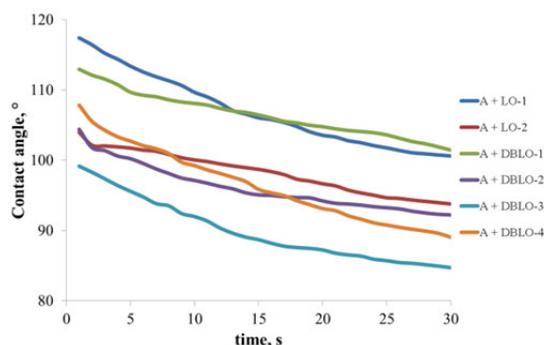


Fig. 3.10. Curve of the contact angle of coated thermally treated wood samples with different emulsions of alkyd resins (A) and linseed oil (LO) / double boiled linseed oil (DBLO).

In conclusion, the drying of LO and DBLO is confirmed to be slower and their partial migration towards the upper layer of the film can be considered possible, looking at the different wetting curves obtained with CA measurements. The presence of LO or DBLO does not negatively affect the hydrophobicity of coating, which remains high also in their presence, and they can be added in the final formulation.

3.3.2. Contact Angle before and after Artificial Weathering

The CAs of coated aspen and pine TTW samples are shown in Figs. 3.11 and 3.12, respectively. Alkyd emulsions have been prepared using three types of red iron oxides (Xfast, Sicotrans, Luconyl). During artificial weathering the samples have been irradiated only with UV lamps during 1000 h, without any water spraying to avoid leaching of pigments during this process because the main task at this stage is to check the efficiency of pigments against UV photodegradation and their optimal concentration for this purpose.

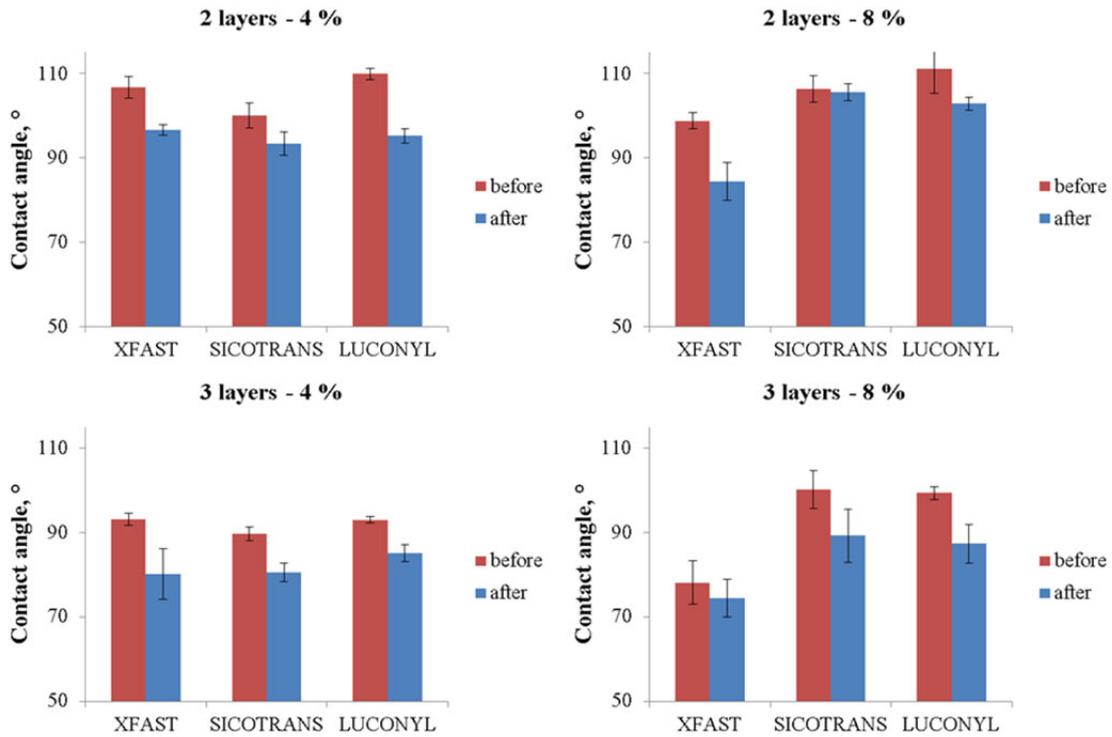


Fig. 3.11. Contact angle of coated thermally treated aspen wood samples before and after artificial weathering.

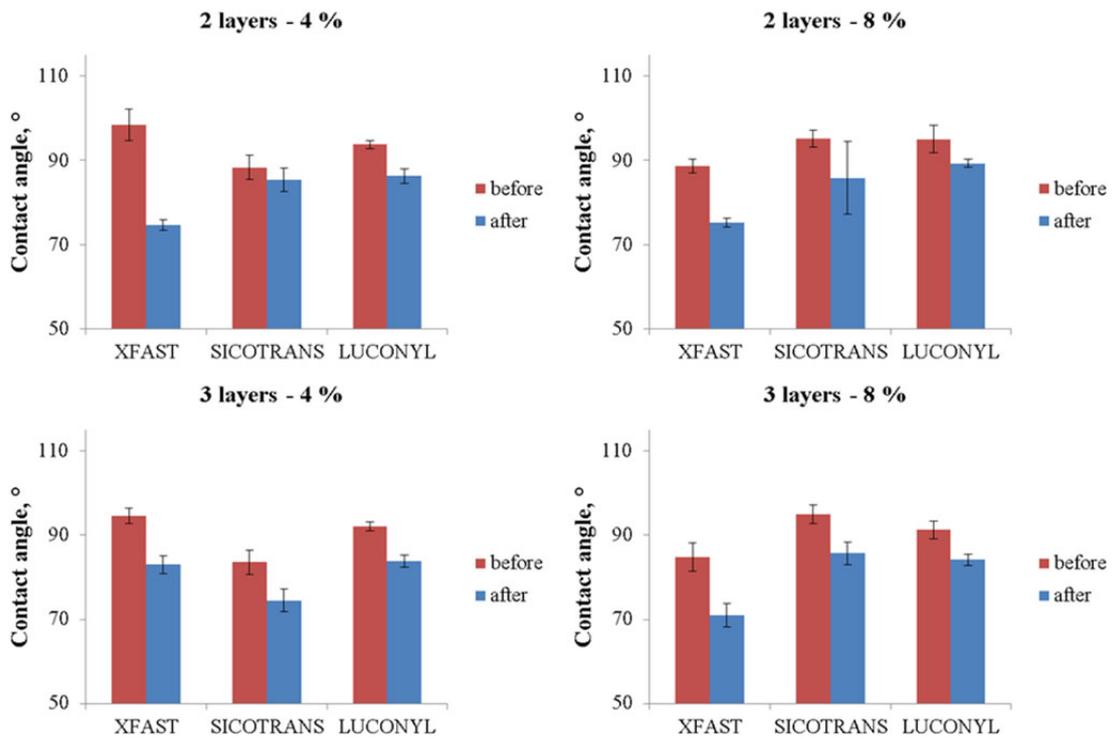


Fig. 3.12. Contact angle of coated thermally treated pine wood samples before and after artificial weathering.

The samples coated with two or three layers of paint have a good hydrophobicity, as can be seen from the values of CA above 90°. After the artificial weathering, CA is slightly

decreased, but the barrier properties are still good. The high hydrophobicity could be surprising, considering that the used iron oxide pigments are hydrophilic compounds. An explanation could be that the hydrophilic iron oxide is also coated and sealed by the binders. In another work, an increase in CA was observed with increasing iron oxide pigment concentration, which can be related to the roughness of the wood surface [21], but in this case, passing from the pigment concentration of 4 % to 8 %, such a correlation was not observed.

3.3.3. Contact Angle before and after Outdoor Weathering

The average wettability values are shown as CA in Table 3.6 for coated aspen and pine TTW samples. Surprisingly, the initial values of CA are lower than 90°, which is considered the point of switch from hydrophobic to hydrophilic character, since it has been demonstrated from measurements of CA for TTW samples coated with alkyd emulsions (Fig. 3.8) and from the artificial weathering test that this type of coating has good hydrophobic properties, and values of CA greater than 90° can be definitely expected.

Table 3.6

Contact Angle of Coated Thermally Treated Pine and Aspen Samples during Outdoor Weathering Test with Standard Deviation (SD)

Coating type	Time, days	Pine CA, °	Aspen CA, °
Solvent 2 layers	0	83.9 ± 1.4	82.7 ± 1.4
	30	84.6 ± 6.9	74.3 ± 8.6
	60	90.0 ± 5.1	82.0 ± 2.1
	90	81.4 ± 5.5	74.3 ± 0.3
	250	68.3 ± 1.9	54.0 ± 3.7
	350	51.4 ± 24.2	37.5 ± 7.7
	440	42.6 ± 1.0	–
	640	–	–
Solvent 3 layers	0	86.7 ± 0.4	80.6 ± 0.0
	30	82.1 ± 3.8	78.1 ± 2.0
	60	80.4 ± 8.7	80.9 ± 2.6
	90	78.6 ± 5.0	74.3 ± 2.4
	250	66.0 ± 2.5	61.3 ± 3.7
	350	66.1 ± 8.4	54.4 ± 0.8
	440	46.1 ± 16.0	41.1 ± 3.5
	640	38.6 ± 1.0	45.2 ± 13.4
Water 2 layers	0	83.6 ± 0.1	78.2 ± 5.2
	30	68.1 ± 1.0	72.4 ± 4.7
	60	70.7 ± 5.0	76.0 ± 5.8
	90	61.4 ± 1.3	63.9 ± 4.3
	250	54.7 ± 3.4	59.5 ± 4.0
	350	50.2 ± 9.6	49.2 ± 9.1
	440	44.3 ± 6.5	42.7 ± 6.2
	640	46.6 ± 5.8	36.7 ± 2.7

A possible explanation could be in the characteristics of the surface of the specific wood samples used, where earlywood is prevalent compared to latewood. Earlywood is more

porous and rougher than latewood, and these characteristics give better wetting of the wood surface. Also for this experiment, there is the same condition already applied for the artificial weathering test of a non-film forming coating to keep the wood texture visible. In the initial stage of outdoor weathering for both wood species, there are no strong differences of wettability for solvent-based or water-based alkyd paints. The barrier properties of paint are good, as the water droplets after deposition are not absorbed in the wood but remain on the surface, thus confirming the efficiency of alkyd resins in delaying water absorption. During the first three months, the barrier properties can be still considered efficient, since there are no significant decreases of CA during this period. After 250 days of exposure, the CA begins to decrease, and for aspen coated with 2 layers of solvent-based paint, it is not possible to measure CA after 440 days due to the rapid absorption of water droplets into the wood.

Three layers of solvent-based paint and two layers of alkyd emulsion also show a decrease in their CA values, but it still can be measured. This is a consequence of the formation of checks and cracks due to swelling and shrinking of wood, which is an unavoidable process in outdoor conditions. During outdoor exposure, wood loses its initial smoothness, whilst the roughness of the surface increases, and this explains the great values of SD for some of the CA values because the wettability of wood can change from point to point depending on the conditions of the surface [3]. From the obtained results, it can be concluded that two layers of alkyd emulsion have the same barrier properties as three layers of solvent-based alkyd paint.

3.4. Color Stability of Coated Thermally Treated Wood Samples

During weathering, wood clearly changes its color mainly as a result of the action of photodegradation, which is an undesired characteristic.

Figure 3.13 shows the differences in structure of aspen wood before and after UV irradiation. The pits of the wood after TM have lost their membrane and the apertures are clearly visible, but the structure of wood is still compact and no checks are observed. After UV irradiation, the pit apertures slightly elongate in an oval shape and small cracks are formed. The fibers start to separate and wood becomes less compact. This is the evidence of the degradation carried out by UV radiation.

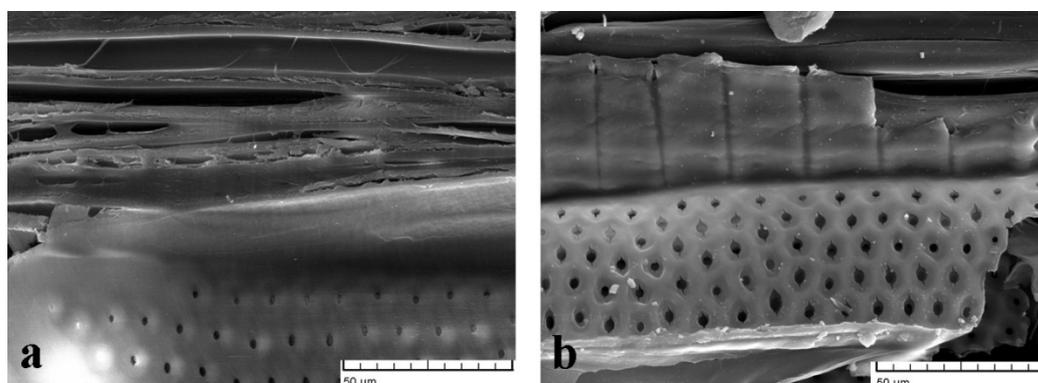


Fig. 3.13. Comparison of the uncoated thermally treated aspen wood structure before (a) and after (b) UV irradiation at 2000 \times magnification.

Pigments can enhance the paint formulation, providing the protection against the photodegradation of wood. The used pigments have been characterized by the measurement of reflectance in the interval of wavelengths from 360 nm to 740 nm, which corresponds to the portion of wavelengths of the visible spectrum. The results given in Fig. 3.14 for samples coated with two layers of alkyd emulsion containing 4 % of iron oxide pigments show that there are no significant differences in reflectance for the three pigments, which is not surprising, since they are the same type of iron oxide; all the three pigments have the same color, according to the information provided by the producer, which is confirmed by the similarity of the measured reflectance. The small differences can be due to the size and aggregation state of the particles of iron oxides.

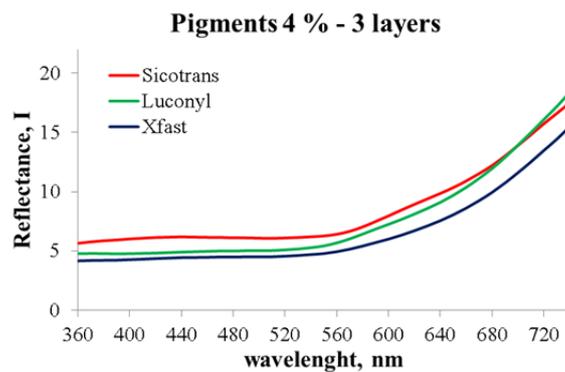


Fig. 3.14. Reflectance of three types of iron oxide pigments for samples coated with two layers of alkyd emulsion with a pigments' concentration of 4 %.

3.4.1. Color Changes during Artificial Weathering

The artificial weathering test has been done preparing alkyd emulsions containing red iron oxide pigments at two concentrations, namely, 4 % and 8 %. The concentrations have been selected according to a previous project on wood coatings, where the optimal concentration of pigments for solvent-based paint was determined, and considering the claims of our Latvian patent for a coating for thermally treated wood. The prepared alkyd emulsions have been applied on both aspen and pine TTW samples which have been coated with two or three layers of alkyd emulsion. The color changes are shown in Fig. 3.15, and from these results, it is possible to evaluate the role of the concentration of pigments and the number of layers of coating against photodegradation.

Color changes of a surface are visible when DEab has a value between 2 and 3 and more [22]. The obtained results show that both the concentration and the number of layers play an important role against photodegradation.

The best results are obtained with a concentration of pigments of 8 %. In fact, DEab, except for samples coated with two layers of paint containing Luconyl pigments, is always lower than 3 units independently of the number of layers.

The highest color changes are for samples coated with 2 layers of alkyd emulsion with a pigment's concentration of 4 %. DEab has a value between 2 units and 3 units after 175 h of UV irradiation.

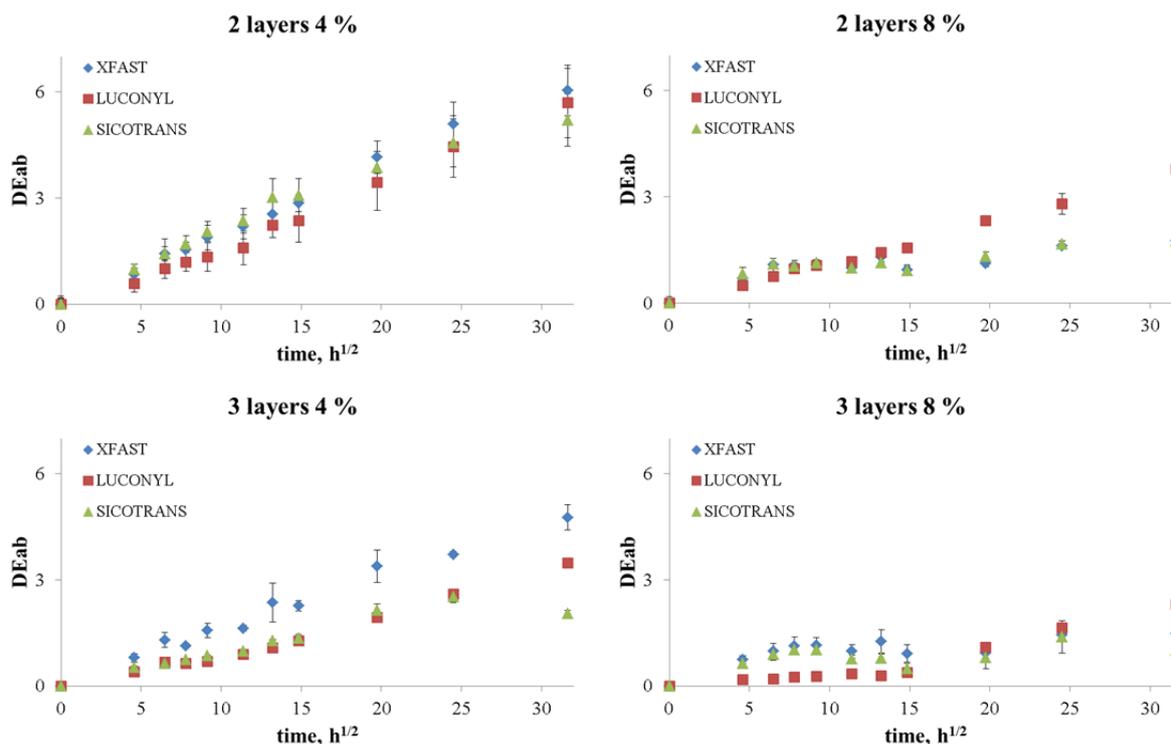


Fig. 3.15. Color changes of coated thermally treated wood – comparison of three types of iron oxide pigments at two concentrations.

Also with a concentration of pigments of 4 % acceptable results can be obtained; for example, with Sicotrans pigments and three layers of paint, the final value of DEab, after 1000 h, is only 2.1 units, which is the best result among the three pigments. In terms of efficiency, there is no pigment that is better than another, since they are practically the same molecule.

The results confirm that pigments made of transparent iron oxides give particularly good protection against photodegradation.

Also the amount of pigments on the surface of wood samples has been calculated to check if there is a correlation with the color changes. In Fig. 3.16, the values of DEab for samples coated with two and three layers of paints after 1000 h of artificial weathering are compared.

It can be observed that three layers can give better results, although there is no close correlation between the amount of pigments and DEab, as can be seen from the values of the coefficient of determination R^2 .

Different values of DEab for the same amount of pigments could be due to the non-homogenous distribution of pigments during the application of paint and their deposition in the cavities of the wood surface.

Moreover, three layers of coating lead to the overlaying of pigment particles, which can scatter more of UV radiation and avoid its direct contact with wood.

For example, for the same amount of pigments 8.57 g/m^2 , DEab passes from 1.6 units up to 6.8 units, which is a more than 4 times higher value. The only difference is the concentration of pigments in the alkyd emulsion, which is 4 % for DEab = 6.8 and 8 % for DEab = 1.6. Not only the amount of pigments is important but also their distribution and aggregation form could play an important role against photodegradation.

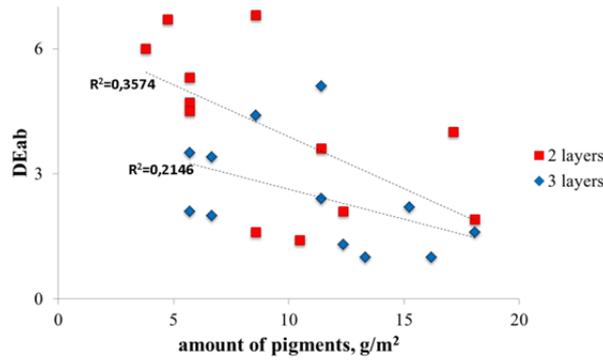


Fig. 3.16. Correlation between the amount of pigments and color changes DEab after 1000 h.

Visually it can be observed that at the end of the artificial weathering process, the surface of TTW samples becomes lighter for both aspen and pine wood. This is confirmed from the values of the parameter L^* as can be seen in Figs. 3.17 and 3.18.

The samples coated with alkyd emulsion containing 8 % of pigment concentration have better results. For both aspen and pine wood, lightness L^* is practically unchanged for the first 225 hours ($15 h^{1/2}$) of artificial weathering, only in the last part of the experiment L^* increases. For the wood samples coated with alkyd emulsion containing 4 % of pigment small constant changes can be observed during the whole experiment.

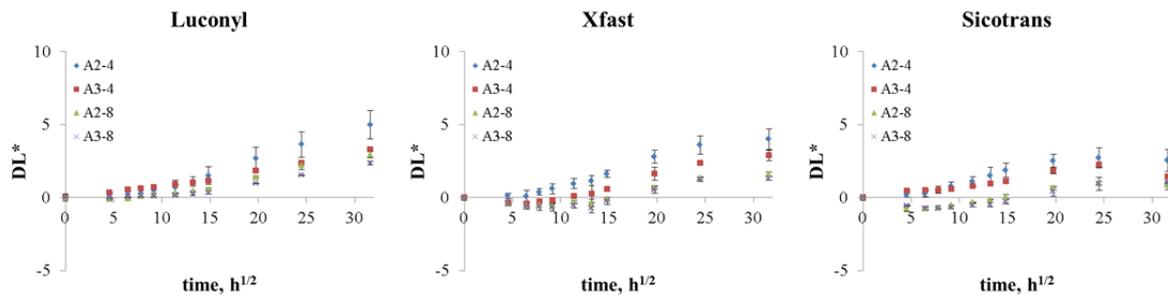


Fig. 3.17. Lightness L^* of coated thermally treated aspen (A) during artificial weathering. AN-M: N – number of layers, M – % of pigments.

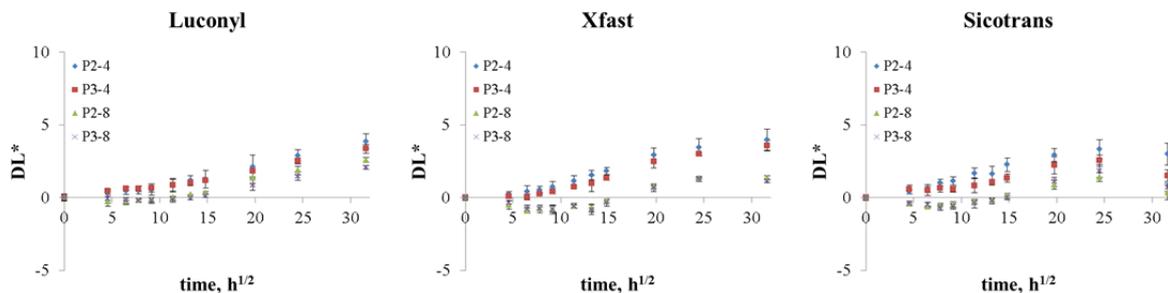


Fig. 3.18. Lightness L^* of coated thermally treated pine (P) during artificial weathering. PN-M: N – number of layers, M – % of pigments.

In conclusion, it is recommended to use the higher concentration of pigments to provide a better protection of the wood surface – in this way the photodegradation of lignin is blocked and the discoloration of wood is delayed – especially as in the case when a non-film forming

coating is used similarly to the procedure of other researches [12]. The type of iron oxides, their size and aggregation state also can have a key role against discoloration.

3.4.2. Color Changes during Outdoor Weathering

During weathering in outdoor conditions, not only the amount of UV radiation changes but wood samples are also subjected to the action of water in the form of moisture or precipitations. In this test, the alkyd emulsion is compared to a solvent-based paint with the same concentration of binders and pigments. The uncoated TTW sample is used as the control sample.

The results demonstrated in Figs. 3.19 and 3.20 show that two layers of the alkyd emulsion give a better protection against discoloration than three or two layers of the solvent-based alkyd paint.

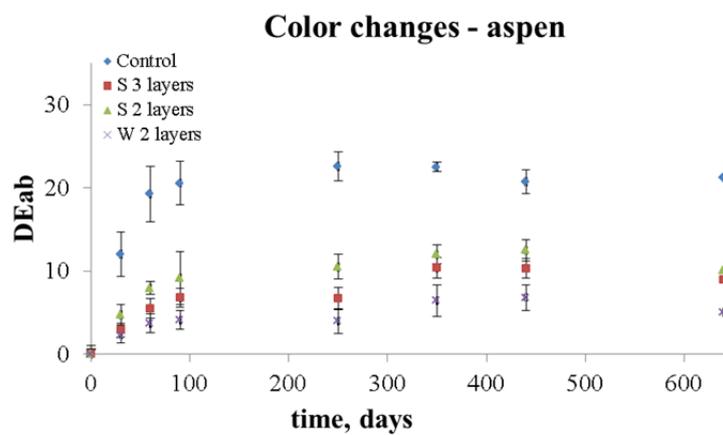


Fig. 3.19. Color changes of aspen during outdoor weathering, S – solvent; W – water.

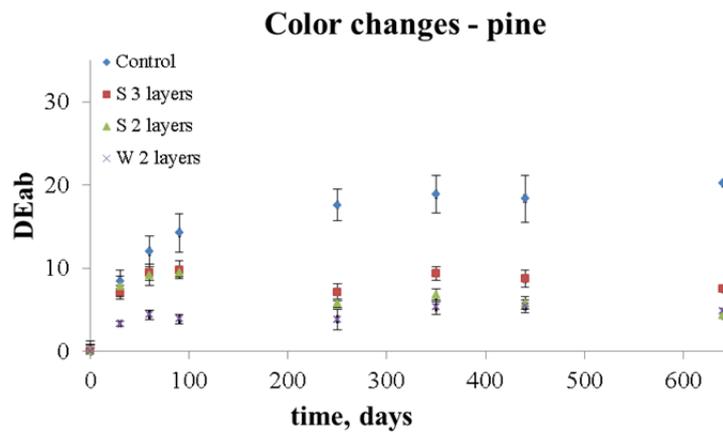


Fig. 3.20 Color changes of pine during outdoor weathering, S – solvent; W – water.

Faster color changes occur in the first three months for both wood species; after that, the color changes occur constantly but slowly. The color changes are much higher than in the case of artificial weathering, for example, in the case of pine already after 3 months DEab is close to 10 units for solvent-based alkyd paint, but for the alkyd emulsion DEab is about 4 units.

The higher color changes can be explained with the action of moisture and swelling and shrinking caused by its variations, which facilitates photodegradation [3]. The

photodegradation involves mostly lignin which among the main components of wood absorbs relatively strongly in the UV and in the shorter wavelengths of visible light.

The higher color changes in control samples confirm that the coating is necessary to delay discoloration, and the presence of iron oxide pigments reduces the reactions of lignin degradation, since the pigments can absorb UV radiation, thus slowing down the formation of radicals from the chromophoric groups of lignin, the main ones responsible for the color changes of wood.

Similarly to the case of artificial weathering, lightness L^* increases also during outdoor weathering, but in greater amount, and this is already observed in other works [23], although there are also cases where a decrease in lightness after outdoor weathering, depending on the wood species and extractive content, has been observed [24].

The uncoated samples have a greater increase in L^* during the first three months of outdoor weathering and then start to decrease in the final part, especially for aspen. For coated samples, the changes are slower and happen gradually. In Tables 3.7 and 3.8, all the variations of color coordinates are listed for DL^* , Da^* and Db^* .

Table 3.7

Average Color Coordinate Changes of Aspen Samples with Standard Deviation (SD)

Aspen	Time, days	DL^*	Da^*	Db^*
Control	0	0	0	0
	30	10.9 ± 1.6	-3.6 ± 0.5	-2.9 ± 1.2
	60	16.0 ± 3.4	-5.5 ± 0.1	-9.0 ± 1.1
	90	15.8 ± 4.7	-6.4 ± 0.5	-10.9 ± 1.0
	250	13.5 ± 5.2	-8.3 ± 0.4	-15.4 ± 1.1
	350	11.4 ± 5.2	-8.7 ± 0.5	-16.6 ± 1.6
	440	6.3 ± 4.1	-8.9 ± 0.5	-17.1 ± 1.5
	640	6.9 ± 0.8	-9.1 ± 0.6	-17.9 ± 1.5
Solvent 3 layers	0	0	0	0
	30	1.6 ± 0.3	1.9 ± 0.4	1.5 ± 0.3
	60	2.7 ± 0.4	3.7 ± 0.6	3.1 ± 0.6
	90	3.5 ± 0.7	4.3 ± 0.6	4.0 ± 0.9
	250	3.5 ± 0.6	3.8 ± 0.5	4.3 ± 0.9
	350	5.8 ± 0.8	5.6 ± 0.6	6.5 ± 1.0
	440	6.9 ± 0.6	4.9 ± 0.7	5.9 ± 1.0
	640	5.8 ± 0.4	3.9 ± 0.8	5.6 ± 1.0
Solvent 2 layers	0	0	0	0
	30	2.3 ± 0.3	3.2 ± 0.5	2.7 ± 0.4
	60	3.5 ± 0.4	5.3 ± 0.8	4.8 ± 0.9
	90	3.8 ± 0.4	6.1 ± 0.5	5.8 ± 0.5
	250	6.7 ± 4.4	4.5 ± 0.8	5.9 ± 0.8
	350	5.5 ± 0.8	6.6 ± 0.6	8.3 ± 1.2
	440	6.0 ± 0.7	6.5 ± 0.4	8.8 ± 1.0
	640	4.3 ± 0.8	5.0 ± 0.6	7.7 ± 1.1
Water 2 layers	0	0	0	0
	30	1.7 ± 0.4	1.4 ± 0.6	0.6 ± 0.3
	60	2.6 ± 0.5	2.4 ± 0.8	1.0 ± 0.6
	90	2.9 ± 0.6	2.5 ± 1.0	1.3 ± 0.6
	250	2.9 ± 0.7	2.4 ± 0.8	1.2 ± 0.6
	350	4.6 ± 0.9	3.8 ± 1.1	2.2 ± 0.9
	440	5.5 ± 1.3	3.3 ± 1.3	2.1 ± 1.3
	640	4.3 ± 0.9	1.6 ± 1.3	1.5 ± 1.3

The color coordinates a^* and b^* for uncoated control TTW samples of both pine and aspen decrease during the whole weathering test, which is coherent with other similar works mentioned before, although it has been observed that a^* and b^* can also increase for TTW after weathering, but this can depend on the wood species and the extractive content [25].

Table 3.8

Average Color Coordinate Changes of Pine Samples with Standard Deviation (SD)

Pine	Time, days	DL^*	Da^*	Db^*
Control	0	0	0	0
	30	6.9 ± 0.2	-0.1 ± 0.1	4.9 ± 1.2
	60	11.8 ± 1.3	-1.5 ± 0.3	0.9 ± 1.7
	90	14.0 ± 1.7	-2.3 ± 0.4	-1.4 ± 1.3
	250	13.8 ± 2.2	-5.8 ± 0.3	-9.2 ± 1.3
	350	14.0 ± 1.9	-6.4 ± 0.2	-10.9 ± 1.0
	440	10.7 ± 2.8	-7.4 ± 0.2	-12.9 ± 0.7
	640	11.8 ± 3.5	-7.8 ± 0.3	-14.3 ± 1.0
Solvent 3 layers	0	0	0	0
	30	3.8 ± 0.2	4.3 ± 0.7	4.1 ± 0.4
	60	5.3 ± 0.4	5.6 ± 0.6	5.6 ± 0.5
	90	5.6 ± 0.5	5.6 ± 0.7	5.8 ± 0.5
	250	4.4 ± 0.6	3.5 ± 0.9	4.4 ± 0.5
	350	5.8 ± 0.9	4.6 ± 0.8	5.8 ± 0.2
	440	5.4 ± 0.8	4.0 ± 0.7	5.6 ± 0.2
	640	4.4 ± 0.8	2.8 ± 0.8	5.3 ± 0.5
Solvent 2 layers	0	0	0	0
	30	5.1 ± 0.4	4.2 ± 1.0	4.2 ± 0.8
	60	5.3 ± 0.6	5.2 ± 1.0	5.4 ± 0.7
	90	4.9 ± 0.5	5.5 ± 1.2	5.9 ± 0.7
	250	3.0 ± 0.3	2.7 ± 0.8	4.0 ± 0.3
	350	3.7 ± 0.8	3.0 ± 0.5	4.7 ± 0.1
	440	3.5 ± 1.2	2.3 ± 0.4	3.9 ± 0.2
	640	2.8 ± 1.6	0.7 ± 0.7	2.8 ± 0.3
Water 2 layers	0	0	0	0
	30	1.7 ± 0.2	2.3 ± 0.4	1.7 ± 0.4
	60	2.3 ± 0.3	3.1 ± 0.3	2.1 ± 0.4
	90	2.4 ± 0.2	2.5 ± 0.8	1.7 ± 0.3
	250	2.3 ± 0.3	2.4 ± 0.7	1.8 ± 0.4
	350	3.8 ± 0.6	2.9 ± 1.0	2.0 ± 1.3
	440	4.6 ± 0.2	1.9 ± 0.9	1.3 ± 1.6
	640	4.2 ± 0.2	0.7 ± 1.3	0.7 ± 2.0

Observing Fig. 3.21, it can be seen that the initial redness of pine wood samples is very similar for coated and uncoated wood samples; this means that it is possible to select the appropriate type of pigments to mimic the natural value of this color coordinate, thus preserving its natural aspect, which is also a desirable property for the final customer. At the end of the natural weathering, the value of a^* is quite similar for all the samples, and it can be observed that after the initial increase, they converge to the same point. For aspen, the initial value of a^* is greater for uncoated control samples than for coated samples.

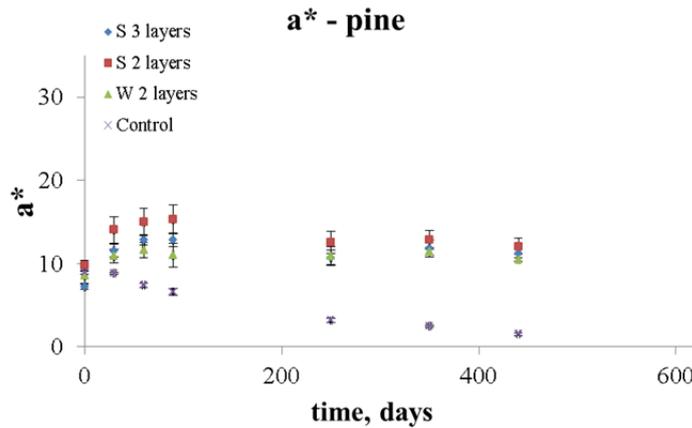


Fig. 3.21. Change of the color coordinate a^* during outdoor weathering of pine.

The other color coordinate b^* of the control samples of pine also decreases during weathering, but for coated samples it shows the same trend of a^* with a small initial increase and in general not significant changes, although the convergence to the same value is not observed (Fig. 3.22). A possibility could be to select iron oxide pigments of different colors, for example, yellow iron oxide hydrate, and mixing the appropriate proportions of both pigments, to investigate which concentration is suitable to obtain the same situation for the b^* color coordinate.

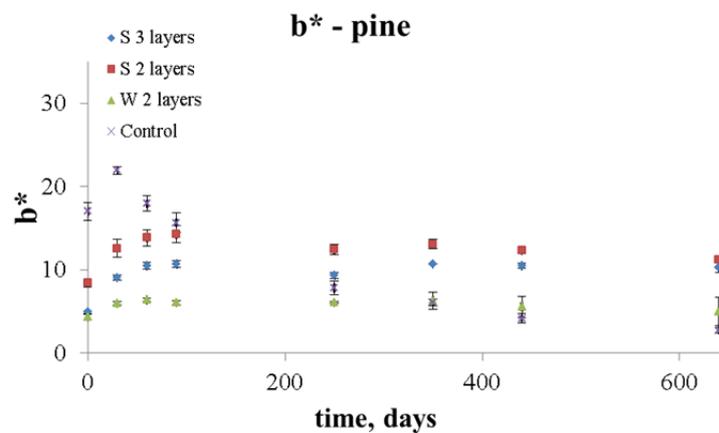


Fig. 3.22. Change of the color coordinate b^* during outdoor weathering of pine.

During outdoor weathering, the best results are obtained with samples coated with alkyd emulsion for both color coordinates. Of the three color coordinates for both wood species, the most affected parameter is lightness L^* . The situation is similar for aspen. During outdoor weathering, the surfaces of coated TTW samples maintain a uniform appearance, and eventually, leaching of pigments does not seem to be happening or it is very low; it can be assumed that there is a good adhesion of pigments to the binders and hence to the wood.

CONCLUSIONS

The obtained results certify the validity of the initial thesis and the achievement of the main goal of this work.

1. After thermal modification (TM), wood becomes more hydrophobic, and the contact angle (CA) of water on the thermally treated wood (TTW) surface increases with the temperature of TM. TM affects the properties of wood not only in its appearance, changing its color into darker tonalities, but it also affects the surface energy (SE) of wood, and with increasing temperature of TM there is a decrease in the polar component of SE. The reduced polar character of wood after TM must be considered for the formulation of specific paints for TTW.
2. The wetting of the TTW surface with alkyd resins and double boiled linseed oil (DBLO) is better than the wetting of alkyd resins alone. DBLO has the function of an effective diluent for alkyds and of the plasticizer for the alkyd film, since it can reduce the T_g of the coating film. However, the measurements of CA of the coated TTW samples have shown that DBLO and linseed oil (LO) can have some impact on the properties of the film due to the possibility of their migration on the external layer of the film, where they can facilitate the spreading of water on the coated wood surface.
3. The emulsification of alkyd and DBLO to form an o/w emulsion is possible using nonionic surfactants – linear ethoxylated alcohols. A white homogeneous emulsion is obtained with the size of micelles in the micrometric range. The other tested gemini surfactants, despite their particular structure, are not good in this case. The concentration of surfactants is selected as low as possible to avoid negative effects on the film properties. Further studies regarding the stability of the alkyd emulsion are necessary, since creaming is observed in a short period. Creaming is a reversible and enough slow process to allow the use of the emulsion for practical purposes.
4. Alternative driers to cobalt salts, based on manganese and iron, can promote the auto-oxidation of alkyd resins, but the process is slower. From the results obtained with FTIR spectroscopy, the cobalt drier is more efficient than the tested alternative driers. Using the cobalt drier, film formation occurs after 1 hour, but for iron and manganese based driers it occurs after 4 hours and 6 hours respectively.
5. The use of transparent nano-sized iron oxide pigments in the alkyd paint formulated for TTW gives good results in the protection against the photodegradation of wood. It is possible to select pigments with different tonalities and from their combination to reproduce the color of TTW. The best protection is obtained with a pigment concentration of 8 % with two or three layers of coating. In the case of the non-film forming coating, lower concentrations are not desirable.
6. The results from outdoor weathering have shown that two layers of the water-based alkyd emulsion applied on TTW samples give better protection against discoloration than two or three layers of the solvent-based alkyd paint. The barrier properties are also better in the case of the water-based alkyd emulsion, although a decrease in CA is observed at the end of the outdoor weathering.

BIBLIOGRAPHY

1. Phuong, L. X., Takayama, M., Shida, S., Matsumoto, Y. and Aoyagi, T. (2007) "Determination of the accessible hydroxyl groups in heat-treated *Styrax tonkinensis* (Pierre) Craib ex Hartwich wood by hydrogen-deuterium exchange and ²H NMR spectroscopy" *Holzforschung*, 61(5): 488–491.
2. De Meijer, M. (2004) "A review of interfacial aspects in wood coatings: wetting, surface energy, substrate penetration and adhesion" COST E18 Final Seminar CTBA, Paris, 26–27th April.
3. George, B., Suttie, E., Merlin, A. and Deglise, X. (2005) "Photodegradation and photostabilisation of wood – the state of the art" *Polymer Degradation and Stability* 88: 268–274.
4. Kataoka, Y. and Kiguchi, M. (2001) "Depth profiling of photo-induced degradation in wood by FTIR microspectroscopy" *Journal of Wood Science* 47(4): 325–327.
5. Živković V., Arnold M., Radmanović, K., Richter K. and Turkulin H. (2014) "Spectral sensitivity in the photodegradation of fir wood (*Abies alba* Mill.) surfaces: colour changes in natural weathering" *Wood Science and Technology* 48(2): 239–252.
6. Bekhta, P. and Niemz, P. (2003) "Effect of high temperature on the change in colour, dimensional stability and mechanical properties of spruce wood" *Holzforschung* 57: 539–546.
7. Biziks, V., Andersons, B., Irbe, I., Chirkova, J. and Grinins, J. (2008) "Thermal modification of soft deciduous wood" *Proceeding of the 4th meeting Nordic Baltic network of Wood Material Science and Engineering (WSE)*: 63–68.
8. Petrissans, M., Gerardin, P., El Bakali, I. and Serraj, M. (2003) "Wettability of Heat-Treated Wood" *Holzforschung* 57(3): 301–307.
9. Ayadi, N., Lejeune, F., Charrier, F., Charrier, B. and Merlin, A. (2003) "Color stability of heat-treated wood during artificial weathering" *Holz als Roh- und Werkstoff* 61(3): 221–226.
10. Ling, J. S., Mohammed, I. A., Ghazali, A. and Khairuddean, M., (2014) "Novel poly(alkyd-urethane)s from vegetable oils: Synthesis and properties" *Industrial Crops and Products* 52: 74–84.
11. Blanchard, V. and Blanchet, P. (2011) "Color stability for wood products during use: effects of inorganic nanoparticles" *Bioresources* 6(2): 1219–1229.
12. Schauwecker, C. F., McDonald, A., Preston, A. F. and Morrell J. J. (2014) "Use of iron oxides to influence the weathering characteristics of wood surfaces: a systematic survey of particle size, crystal shape and concentration" *European Journal of Wood Products* 72: 669–680.
13. Scheikl, M. and Dunky, M. (1998) "Measurement of dynamic and static contact angles on wood for the determination of its surface tension and the penetration of liquids into the wood surface" *Holzforschung* 52(1): 89–94.

14. Nuopponen, M., Vuorinen, T., Jamsä, S. and Viitaniemi, P. (2004) “Thermal modifications in softwood studied by FT-IR and UV resonance Raman spectroscopies” *Journal of Wood Chemistry and Technology* 24(1): 13–26.
15. Wu, S. (1971) “Calculation of interfacial tension in polymer systems” *Journal of Polymer Science Part C* 34(1): 19–30.
16. Micciché, F., Oostveen, E., van Haveren, J and van der Linde, R. (2005) “The combination of reducing agents/iron as environmentally friendlier alternatives for Co-based driers in the drying of alkyd paints” *Progress in Organic Coatings* 53(2): 99–105.
17. Bumbac, M., Zahrescu, T. and Nicolescu, C. M. (2017) “Thermal and radiation stability of alkyd based coatings used as insulators in the electrical rotating machines” *Journal of Science and Arts* 1(38): 119–130.
18. Pirš, B., Znoj, B., Skale, S., Zabret, J., Godnjavec, J. and Venturini, P. (2015) “Iron as an alternative drier for curing of high-solid alkyd coatings” *Journal of Coatings Technology and Research* 12(6): 965–974.
19. Chen, J., Wang, Y., Huang, J., Li, K. and Nie, X. (2018) “Synthesis of tung-oil-based triglycidyl ester plasticizer and its effects on poly(vinyl chloride) soft films” *ACS Sustainable Chemistry & Engineering* 6(1): 642–651.
20. Salata, R., Pellegrene, B. and Soucek, M. (2019) “Migration of fluorinated alkyd and fluorinated tung oil additives for partially self-stratifying coatings” *Progress in Organic Coatings* 133: 406–417.
21. Mahltig, B., Arnold, M. and Löthman, P. (2010) “Surface properties of sol–gel treated thermally modified wood” *Journal of Sol-Gel Science Technology* 55: 221–227.
22. Mokrzycki, W. and Tatol, M. (2011) “Color difference Delta E – A survey” *Machine Graphics and Vision* 20(4): 383–411.
23. Tolvaj, L., Nemeth, R., Pasztory, Z., Bejo, L. and Takats, P. (2014) “Colour stability of thermally modified wood during short-term photodegradation” *BioResources* 9(4): 6644-6651.
24. Tomak, E. D., Ustaomer, D., Yildiz, S., and Pesman, E. (2014) “Changes in surface and mechanical properties of heat treated wood during natural weathering” *Measurement: Journal of the International Measurement Confederation* 53: 30–39.
25. Srinivas, K. and Pandey, K. K. (2012) “Photodegradation of thermally modified wood” *Journal of Photochemistry and Photobiology B: Biology* 117: 140–145.