# **RIGA TECHNICAL UNIVERSITY**

Faculty of Materials Science and Applied Chemistry Institute of Polymer Materials

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

**Doctoral Thesis** 

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

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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.

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Per aspera ad astra

Errj Sansonetti

### ANNOTATION

**Keywords**: Alkyd emulsion, surface energy, thermally treated wood protection, iron oxide pigments, photodegradation, weathering.

Wood has great potential for uses in outdoor conditions, but it can be easily degraded due to the action of environmental factors (solar radiation, moisture, fungi, insects, etc.). The protection of wood is then a very actual research topic, and it is also the object of this work. The main goal of this Doctoral Thesis is to obtain a water-based alkyd paint formulation in the form of emulsion, and to optimize its composition with necessary additives, in particular, with nanosized red iron oxide pigments, which can protect the decorative qualities of thermally treated wood (TTW) during outdoor exposure. In the literature review, the main factors responsible for the degradation of wood and their effect on the structure and properties of wood are summarized. The chemistry of coatings for the protection of wood and the challenges that are faced in reformulation of paints, due to more stringent regulations which limit the use of organic solvents and promote greener alternatives, like water-based paint formulations, are considered. In Europe, this is stated by the Directive 2004/42/EC of the European Parliament on the limitation of emissions of volatile organic compounds (VOC) from decorative paints and varnishes.

In the first part of the experimental section, the optimal composition of the alkyd emulsion and the effects of additives on the film properties have been investigated. The different chemo-physical properties of thermally treated wood compared with those of untreated wood have been also evaluated. After thermal modification, wood becomes more hydrophobic and this has been confirmed from the changes of the surface energy of thermally treated wood: the polar component of the surface energy decreases with increasing temperature of thermal modification. In the second part of the experimental section, artificial and outdoor weathering tests have been done to determine the suitable concentration of red iron oxide nanoparticles, which can give better protection against photodegradation. Results show that red iron oxide pigments at a concentration of 8 % in alkyd emulsion are efficient to protect the wood surface against discoloration. During the outdoor weathering test, the performance of alkyd emulsion has been compared with that of the solvent-based formulation. Results confirm that the waterbased alkyd emulsion gives better protection of the thermally treated wood surface than the solvent-based formulation, thus confirming that the replacement of organic solvent with water gives a product with equivalent or better properties for the protection of thermally treated wood in outdoor conditions.

The Doctoral Thesis has been written in English, it contains 49 figures, 13 Tables, 10 appendices and 197 literature references. In total there are 101 pages.

## ANOTĀCIJA

Atslēgas vārdi: Alkīda emulsija, virsmas enerģija, termiski modificētas koksnes aizsardzība, dzelzs oksīda pigmenti, fotodegradācija, novecināšana.

Koksnei piemīt liels potenciāls tās lietošanai āra apstākļos, bet vides faktoru (saules starojums, mitrums, sēnes, kukaiņi, utt.) iedarbības rezultātā tās virsma var viegli degradēties. Koksnes aizsardzība ir ļoti aktuāls pētījuma temats, un tas ir arī šī promocijas darba objekts. Galvenais darba mērķis ir iegūt emulsijas veida alkīda pārklājumu uz ūdens bāzes, uzlabot tā kompozīciju ar nepieciešamām piedevām, īpaši ar nanoizmēra sarkanā dzelzs oksīda pigmentu, kas var nodrošināt termiski modificētas koksnes dekoratīvo īpašību saglabāšanu āra ekspluatācijas laikā. Darbā zinātniskās literatūras apskatā apkopota informācija par galvenajiem koksnes noārdīšanos izraisošiem faktoriem un to ietekmi uz koksnes struktūru un īpašībām. Tiek apskatīti koksnes aizsardzībai paredzētu pārklājumu veidi un izaicinājumi jaunu pārklājumu izstrādāšanā, kas radušies stingrāku noteikumu dēļ, kas ievērojami ierobežo organisko šķīdinātāju lietošanu un atbalsta zaļākas alternatīvas, tādas kā pārklājumi uz ūdens bāzes. Eiropā, to nosaka Direktīva 2004/42/EC par gaistošo organisko savienojumu (GOS) saturu ierobežojumiem krāsās un pārklājumos.

Pirmajā darba eksperimentālajā daļā pētīta optimāla alkīda emulsijas kompozīcija un piedevu ietekme uz pārklājuma plēves īpašībām. Ņemtas vērā izmaiņas termiski modificētas koksnes ķīmiskajās un fizikālajās īpašībās, salīdzinot ar nemodificētu koksni. Pēc termiskās modifikācijas koksne kļūst hidrofobāka, un šīs izmaiņas noteiktas un analizētas, mērot virsmas enerģijas. Rezultāti parādīja, ka, paaugstinoties termiskas modifikācijas temperatūrai, samazinās koksnes virsmas enerģijas polārais komponents.

Otrajā darba eksperimentālajā daļā veikti mākslīgās un āra novecināšanas testi, lai noteiktu piemērotāko sarkanā dzelzs oksīda nanodaļiņu koncentrāciju, kas var nodrošināt labāko termiski modificētas koksnes aizsardzību pret fotodegradāciju. Rezultāti liecina, ka 8% liela sarkanā dzelzs oksīda pigmentu koncentrācija ir efektīva koksnes virsmas aizsardzībai pret krāsas izmaiņām. Āra novecināšanas testa laikā alkīda emulsijas efektivitāte tika pārbaudīta, salīdzinot to ar alkīda pārklājumu uz šķīdinātāja bāzes. Rezultāti apstiprina, ka alkīda emulsija dod labāku termiski modificētas koksnes virsmas aizsardzību, nekā pārklājums uz šķīdinātāja bāzes. Tas pierāda, ka, aizvietojot organisko šķīdinātāju ar ūdeni, var iegūt līdzvērtīgu produktu ar līdzīgu vai labāku efektivitāti termiski modificētas koksnes aizsardzība.

Promocijas darbs ir uzrakstīts angļu valodā, tajā ir 49 attēli, 13 tabulu, 10 pielikumu un 197 literatūras avoti, kopā – 101 lappuse.

# ABBREVIATIONS

- 1. A alkyd
- 2. CA contact angle
- 3. *CIELab International Commission on Illumination (Commission internationale de l'éclairage)* color space
- 4. CMC critical micelle concentration
- 5. CPP critical packing parameter
- 6. DBLO double boiled linseed oil
- 7. DEab color difference (*CIELab* color space)
- 8. DSC differential scanning calorimetry
- 9. FA fatty acids
- 10. FTIR Fourier transform infrared
- 11. HAP hazardous air pollutants
- 12. HLB hydrophilic-lipophilic balance
- 13. HS high solid
- 14. LO linseed oil
- 15. LOAR long oil alkyd resin
- 16. LSIWC Latvian State Institute of Wood Chemistry
- 17. MOAR medium oil alkyd resin
- 18. o/w oil in water
- 19. RH relative humidity
- 20. S solvent
- 21. SD standard deviation
- 22. SE surface energy
- 23. SEM scanning electron microscope
- 24. ST surface tension
- 25.  $T_{\rm b}$  boiling point
- 26.  $T_{\rm g}$  glass transition temperature
- 27. TM thermal modification
- 28. TRC total resin content
- 29. TTW thermally treated wood
- 30. VOC volatile organic compounds
- 31. W water
- 32. WTT Wood Treatment Technology
- 33. w/o water in oil

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### **INTRODUCTION**

Wood has been used for centuries as a material in many different fields and for many purposes. Still nowadays it occupies an important role as a construction or decorative material, thanks to its natural and renewable source, wide availability, and ease of processing with modern technologies. The main negative aspect of wood as a construction or decorative material, especially for exterior uses, is the low resistance to the degradation caused by environmental factors, such as sunlight, moisture, and biological agents. It is fundamental to minimize and delay the causes of degradation to enhance the service life of wood, and this can be done in several ways.

Among the available methods, in the last decades, treatments and modification of wood without using of harmful chemical compounds have gained a lot of interest, also due to the restrictive legislation regarding the use of biocides and other toxic compounds, which have been used in the last two centuries to protect the wood, with the development of the wood processing industry. One of these methods is thermal modification (TM) of wood, which can be considered an environmentally friendly approach in protection of wood [1]. TM of wood, in the last years, has become an attractive alternative way to preserve wood, thanks to its improved properties in terms of dimensional stability [2], [3] moisture content [4], [5] and biological resistance [6], [7] but with a decrease of its mechanical properties [8], [9].

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 [10], [11]. The increased hydrophobic character is correlated to a different wettability of thermally treated wood (TTW), which is caused by modifications in its chemical composition and in the structure of the wood surface [12], [13], [14], [15].

Despite its improved properties, also TTW, when exposed outdoors, is subjected to the action of the atmospheric agents, mostly UV radiation and water: absorption of light, especially by lignin, leads to the formation of radical species, responsible for the color changes of wood. [16], [17]. Repeated temperature and humidity variations cause swelling and shrinking of wood, which consequently create cracks and fissures on the surface, exposing wood's sub superficial layers to atmospheric agents [18]. 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 the UV absorbers protect wood from photodegradation.

#### Actuality of the Topic

Water-based paints are replacing solvent-based paints that use volatile organic compounds (VOC) such as hydrocarbons, which are harmful to the environment and to the health [19]. In Europe, this is stated by the Directive 2004/42/EC of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of VOC due to the use of organic solvents in decorative paints and varnishes, amending the already existing Directive

1999/13/EC ("the Paints Directive"). 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.

In fact, one of the limits of the water-based paints 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. In the case of TTW, as mentioned above, there is a change in wettability which must be considered to improve the formulations of new water-based coatings specifically prepared for TTW. It has been verified that the interactions between water and TTW are different, compared to the untreated wood; in fact, the TM of wood reduces the OH groups available for water adsorption, and consequently the wood becomes more hydrophobic [20], [21].

The wetting of a wood surface by a coating can also be measured directly by measuring the contact angle (CA) of a drop of the coating on a wood surface. To wet the surface, the surface energy (SE) of the coating should be lower than that of the wood ( $\gamma_{\text{coating}} < \gamma_{\text{wood}}$ ). Since most wood surfaces have a SE between 40 mJ  $\cdot$  m<sup>-2</sup> and 50 mJ  $\cdot$  m<sup>-2</sup> and most coatings have a SE between 30 mJ  $\cdot$  m<sup>-2</sup> and 40 mJ  $\cdot$  m<sup>-2</sup>, this is generally not a problem. Apart from the SE, the spreading of a coating droplet might also be restricted by viscosity. The shape and CA of the spreading coating droplet is influenced by the 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 [22].

The formation of the gradient of surface tension (ST) during the application of a coating occurs, in the case of emulsion paints, due to the coalescence of micelles after the application of the coating on the wood surface. This aspect is important, and it must be considered that there could be problems during the application of varnishes or paints, which are traditionally formulated for untreated wood.

The actual limiting factor for most penetration processes following the Washburn equation is the increase in viscosity during the capillary penetration process. The micro-pores in the cell wall of the wood capillaries, with a size between 0.1 nm and 1 nm, will only allow the lower molecular weight materials like water and solvent to enter the cell wall. The larger polymeric molecules will remain inside the capillary [22].

The gradient of viscosity hinders the homogeneous distribution of a 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.

If it comes to the capillary penetration of a coating into wood, the most important factor seems to be the increase of viscosity at higher solid contents. In the case of alkyd emulsions, it is preferable to keep the solid content under the value of 50 %. In conclusion, water-based dispersed polymers 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. The above mentioned 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 SE of TTW. A suitable component must be searched among renewable resources, and it can be pure linseed oil (LO) or double boiled linseed oil (DBLO), which is already in a partially polymerized state.

#### **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 of its efficiency during weathering, to obtain informations about the parameters which can improve its performance:

- 1. Investigate the changes of 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  $< 5 \ \mu m$ ).
- 4. Investigate and compare the performance of alkyd emulsion and solvent-based alkyd paint during 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 those factors which cause the 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 aesthetical 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 an 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 weathering tests of coated TTW samples. The Doctoral Thesis has been written in English on 101 pages. There are 49 figures, 13 Tables. Ten appendices are included. In the Thesis 197 literature references are cited.

#### **Approbation of the results**

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

#### **Scientific publications**

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**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. OVERVIEW OF THE THESIS**

#### **1.1. Degradation of wood**

For centuries, wood has been recognized throughout the world for its versatile and attractive engineering and structural properties. However, like other biological materials, wood is susceptible to changes and transformations in the structure and composition during its service life. Changes can be different, and a distinction is necessary between those slow changes that happen when wood is not subjected to the action of external environmental factors like sunlight, high moisture, biological agents, and air pollution, but the only processes involved are internal self-oxidative reactions, which go under the name of "aging": in this case, wood degradation proceeds slowly due to the participation of oxygen and water in contact within wood [23] and the effects on the physicochemical properties of wood are small.

Degradation happens more rapidly when wood is exposed outdoors to the abovementioned factors; in this case, all the transformations which take place are defined as "weathering" [24]. Weathering of wood has been widely studied 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 extend its service life. Actually, it can be said that the understanding of and knowledge about weathering are well established [25]. In outdoor weathering of smooth wood, original surfaces become rough as the grain raises, the wood checks, and the checks grow into large cracks; grain may loosen, and boards cup and warp and pull away from fasteners. The roughened surface changes its color, gathers dirt and mildew, and may become unsightly; the wood loses its surface coherence and becomes friable - splinters and fragments can come off. All these effects, brought about by a combination of light, water and heat, are part of weathering. The deleterious effect of wood weathering has been ascribed to a complex set of reactions induced by several factors. The weathering factors responsible for changes in wood surfaces are solar radiation (UV, visible, and IR light), moisture (dew, rain, snow, and humidity), temperature and oxygen. Moreover, an additional weathering factor has arisen with the presence of atmospheric pollutants such as sulfur dioxide, nitrogen dioxide, and ozone in the presence or absence of UV light [26], [27], [28], [29]. The effects on wood are the results of a synergic combination of all these factors.

#### **1.2.** Degradation caused by UV radiation

Among all the factors, the solar radiation is recognized as the most damaging component of the outdoor environment and initiates a wide variety of chemical changes at wood surfaces [30], [31], [32]. The electromagnetic radiation emitted from the sun, that reaches the earth surface can be divided into three components: ultraviolet (UV), visible and infrared (IR), each with its characteristic wavelength range. Among them, the UV fraction of solar radiation is recognized as the main responsible for the degradation of wood components, in particular, of lignin more than others [33], [34] and it gives origin to a wide series of photochemical reactions at the wood top layer. UV radiation has enough energy to break chemical bonds and to make reactions happen [35]. 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 [36], [37], [38], [39] with depths reaching 900  $\mu$ m. The differences in the reported depth of degradation may be reconciled by considering some of the factors that affect the penetration of UV radiation into wood. The penetration depends on the wood density and the wavelength distribution of UV radiation and visible light. Denser wood is penetrated less by UV radiation, and shorter wavelengths also penetrate less. Also, the degradation products could be carried deeper into the wood by the action of uV radiation; it has been reported that also the violet fraction of 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 [41], [42].

#### **1.3.** Degradation caused by moisture

Another fundamental factor responsible for wood weathering is moisture - relative humidity, dew, and precipitations. Water alone is not responsible for significant chemical reactions at the surface layers of wood [37], [43], [44] but it has been reported that the formation of free radicals visibly increases in the presence of high moisture in wood [25]. It has been observed that in the presence of water, photodegradation of lignin is faster [44], [45], [46]. However, the main role of water in weathering of wood is the formation of checks and cracks on the wood surface. Due to the changes in the environment relative humidity of air, a moisture gradient is formed between the surface and inner layers; surface water is released faster than inner water. This gives place to a series of stresses for the wood: the dimensional changes caused by shrinkage or swelling result in the formation of checks and cracks [47], [48]. The photodegradation of wood is accelerated for damaged surfaces because the swelling of cell walls caused by water molecules facilitates the access of solar radiation to inaccessible regions [28], [49]. Checking of wood is influenced by the wood species and from which part of the stem wood material is taken – near or far from the pith – since it strongly depends on the anatomical properties of wood [50]. Prolonged exposure of wood to water at mild temperature results in the degradation of hemicellulose and lignin, whilst cellulose is less affected [51].

Moisture in the presence of solar heating may thus result in the hydrolytic degradation of the non-cellulosic components of wood. As photo-oxidation progresses, most woods change to different shades of grayish color at the top layer, these color changes are the consequences of photochemical reactions [25]. Wood that is water saturated can resist to fungal and insect attack due to the lack of oxygen, but hydrolysis and mild degradation are still possible [48]. Weathering is affected also by the direction: it has been reported that, due to the presence of the radial rays, water moves rapidly deeper into the wood structure on tangential surfaces than radial surfaces during the weathering process. Consequently, the leaching by water increases, and the degradation on tangential surfaces is faster than the degradation on radial surfaces [52]. Leaching of water-soluble degradation products is partially responsible for the wood surface erosion, and as a result, it will become rougher [28], [53].

#### **1.4.** Other factors causing the degradation of wood

The direct effect of temperature at room conditions on wood degradation is small. High temperature can accelerate photochemical, oxidative, and hydrolytic reactions [54], whilst low temperature can slow them [55]. Exceptionally low temperature can make the free water freeze and have a mechanical impact on the wood, promoting the formation of checks and cracks [47]. Also, air pollution can promote wood degradation. Acid rains can promote polysaccharides hydrolysis [25]. Small solid particles carried by the wind can enter the small checks and promote the surface erosion, detaching fibers which are already weakened by mass loss from photodegradation [47]. The aesthetical impact on wood, when used outdoors and in the presence of high humidity, can have biotic factors like molds, decay and staining fungi, yeasts, and algae. The main biotic factor influencing the wood appearance is represented by discoloring fungi, which strongly reduce the quality of the end products [56]. They can grow and develop in harsh conditions, which are not favorable to other microorganisms, like frequent changes in moisture, long dry periods, high solar radiations, rapid temperature changes. Discoloring fungi do not cause any or only very little cell wall attack; they live on nutrients in the parenchyma cells of sapwood, and they mainly modify the appearance of wood without affecting its mechanical properties, causing a blue, grey or black, radially striped wood discoloration of sapwood [57]. Other factors influencing the rate of weathering are the type of wood itself, its density, the composition in terms of earlywood and latewood, and the fiber orientation on the surface.

#### **1.5.** Type of wood and evaluation of weathering

The results obtained from the weathering of hardwood and softwood have led to contradictory conclusions. Some studies report that softwoods are more resistant to weathering [58] while other results confirm a better resistance of hardwoods to weathering, with photodegradation of softwoods happening faster and to a larger extent [55], [59], [60]. Depending on the type of wood species, weathering is different mainly due to the differences in the extract content, lignin amount and density [43]. It has been observed that there is an inversely proportional relationship between the speed and depth of photodegradation and wood density [39], [43], [61]. Due to its lower density, the photodegradation of earlywood is faster, compared to latewood, which has a higher density. Consequently, also the erosion of earlywood and latewood are clearly distinct [37], [62], [63]. The main parameters evaluated during the weathering process are color changes, chemical changes in the surface composition, and wood micro- and macro-structural changes [64]. The color changes are measured using a spectrophotometer and, according to the *CIELAB* color method, the variations of three parameters  $-L^*$ ,  $a^*$  and  $b^*$  – are determined. The chemical changes of the

wood composition are mostly evaluated with FTIR spectroscopy, and structural changes can be evaluated visually or using different types of microscopy.

#### **1.6.** Protection of wood

The expression "wood preservation" means all the measures that are taken to ensure a long service life of wood. According to its destination of use, a wood material requires the proper protective treatment to ensure a longer lifetime and increase its durability and resistance against the action of external factors, like environmental and biological agents. This necessity dates back to ancient times, since humankind had started to use wood as a construction material and during centuries till nowadays a wide range of available methods and alternatives have been developed. Even in the Bible, it is mentioned how God recommended a way to protect Noah's ark with pitch [65]. There are records of wood preservation dating back to ancient Greece during Alexander the Great's reign, where bridge wood was soaked in olive oil. The Romans protected their ship hulls by brushing the wood with tar. The Greeks and Romans designed paints containing drying oils extracted from linseeds, soybeans, and sunflower seeds. Independently, the ancient Asian cultures developed lacquers and varnishes, and by the 2<sup>nd</sup> century BC, these had been used as coverings on a variety of buildings, artwork and furnishings in China, Japan, and Korea. The ancient Chinese knew how to make black lacquer from the sap of the lacquer tree *Rhus Vernicifera*. It was not until the thirteenth century that the protective properties of drying oils began to be recognized in Europe. During the Industrial Revolution, wood preservation became a cornerstone of the wood processing industry. The Industrial Revolution can be considered the beginning of the modern wood preservation era [65], when commercial treatments developed with the protection of railroad crossties using creosote; since then, many other innovations and results have been achieved, with consumers, in the last decades, becoming more and more interested in less toxic materials.

#### **1.7.** Coating of wood

Wood used outdoors requires the application of coatings, which have basically a double function: to provide physical protection against degradation and to preserve the aesthetical appearance. There is a wide choice of possible ways to achieve this result. According to the Directive 2004/42/CE of the European Parliament and of the Council of 21 April 2004, "coating" means any preparation, including all the organic solvents or preparations containing organic solvents necessary for its proper application, which is used to provide a film with decorative, protective or other functional effect on a surface, where, respectively, "film" means a continuous layer resulting from the application of one or more coats to a substrate. A coating can have a decorative, protective, or special function, or a combination of all these functions. A durable coating with good decorative properties should retain its gloss and color for an extended period, either being resistant against solar radiation or being degraded in a smooth and uniform way. A durable coating with good protective properties should retain its

chemo-physical properties as long as possible in order to extend the interval between maintenances [48]. These protective properties, often called the barrier properties, play an important role in the selection of the appropriate material to apply as a coating, for higher durability. As an example, ingress of water or moisture into wood causes dimensional changes which may result in cracking and checking of the film, and hence a loss of durability [32], [66], or promotes growing of destroying or staining fungi [7], [67]. 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. A coating material will produce a film once applied on the substrate, and this film can be transparent and unpigmented (lacquers and varnishes), or opaque (paints); the final results depend on the nature of the substance that forms the continuous film. 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; it represents organic materials, which may be of natural origin (e.g. linseed oil), modified natural (e.g. nitrocellulose) or wholly synthetic (e.g. acrylics, polyurethanes). To fulfill its functions, the film must meet the following requirements [68]:

- 1. it must be elastic and flexible, due to the changes in moisture content, and environmental humidity; wood is subject to linear dimensional changes, it swells or shrinks, and the coating must withstand the tensions arising during these "movements" of wood, avoiding checking and cracking;
- 2. it must have a known water vapor permeability, to avoid an excessive amount of water into the wood, but also to allow the flowing of water vapor that forms inside the wood when the temperature increases;
- 3. it must have good adhesion to the substrate, which basically depends on the binder nature, but it also can be improved with appropriate technical solutions [69], [70];
- 4. it must resist photodegradation, caused by solar electromagnetic radiation, and at the same time protect the wood substrate from photodegradation.

#### 1.7.1. Chemistry of coatings

Various types of organic substances are used in the preparation of coating materials for wood. In ancient times, only natural products such as oils or resins were available. The performance of these products was later improved by thermal or chemical modifications. The continued evolution of industrial chemistry from the 1920s has produced many different synthetic film formers such as alkyds, polyurethanes and polyesters which find wide application in all coating sectors including wood. Coatings, among them also wood coatings, can be classified in several categories, according to their characteristics:

- 1. Function of the coating (primer, undercoat, topcoat);
- 2. Hiding power (transparent, semitransparent, opaque);
- 3. Nature of the binder (acrylic, alkyd, polyurethane, oils, etc.);
- 4. Destination of use (outdoors, indoors, smooth, or rough surfaces);

- 5. Type of carrier (solvent-borne, water-borne, powder in this case no liquid carrier is used to aid the application of binder and other components on the substrate, mainly metals);
- 6. Film formation technology (solvent evaporation, crosslinking polymerization).

Coatings are usually applied as multi-layered systems that are composed of primer and topcoat, whose number in some cases may vary up to six layers. Each coating layer is applied to perform certain specific functions, though its activities are influenced by the other layers in the system [71]. The binder or film former is, of all the components, the only one that is always present among all the various types of formulations. Many binders are too thick to be applied and must be thinned. The type of thinner, if present, varies with the binder. The binder imparts properties such as gloss, durability, flexibility, and toughness. Binders can be distinguished, according to the mechanisms of film formation, into thermoplastic or thermosetting materials. Thermoplastic mechanisms suggest the evaporation of the binder carrier (solvent) and consequent hardening of the binder, without any chemical reaction of crosslinking. The binder is simply dissolved in the solvent and a solid film forms when the solvent evaporates. This category includes classic nitrocellulose lacquers, acrylic latex, vinyl, and bitumen coatings. In thermosetting mechanisms, the formation of a film is obtained through the evaporation of the solvent and then curing of the binder with crosslinking reactions. The film formation mechanism of the simplest example involves, first, the evaporation of solvents followed by the reaction with atmospheric oxygen over a period of days, weeks and even months to create a high molecular weight polymer, which becomes insoluble in the solvent; this category includes alkyd paints. Oxidative cure coatings are catalyzed by metal complex driers; these catalysts were traditionally hydrocarbon carboxylate chelates of lead, but due to lead's toxicity, cobalt and other elements, such as zirconium, zinc, calcium, and iron, have replaced the lead in more popular products. Today, more environment-friendly alternatives to cobalt are investigated too, to replace it with less toxic compounds [72], [73].

#### **1.7.2.** Composition of coatings

A modern coating composition can vary from a simple to a complex mixture of components, which can be divided into the following categories: solvents, binders, pigments, and additives. Solvents and binders are the main components of coatings; pigments and additives are added to obtain desired properties like hiding power, color, ease of manufacturing, wetting and dispersing, improved applicability and film formation, service life performance, rheology, biocide, etc. [74], [75]. The main purposes of solvents are to dissolve the binder and adjust the viscosity of the coating. With the notable exception of water, all solvents, thinners, and diluents used in surface coatings are organic compounds of low molecular weight. Solvents are volatile and do not become part of the film, neither influence the formed film's properties. They also control the flow and application properties, and in some cases, can affect the stability of the paint while in a liquid state. Their main function is as the carrier for non-volatile components. An important parameter of the solvent is its

evaporation rate, which can influence the application and appearance of the coating materials: it is necessary to find a compromise between the fast evaporation rate and good substrate wetting, curing and levelling of the film [76]. The simplest coating formulation can be constituted just by the binder, which is the film forming component that directly adheres to the substrate, and binds to the substrate the other components of the coating, in case they are included in the formulation. The most important binders used are reported in Table 1.1. They are divided into naturally and synthetically derived film formers.

Table 1.1

Film formers, synthetically derived	Film formers, naturally derived
Alkyds Polyurethanes Amino resins Polyesters Acrylics Vinyls Epoxies	Drying oils and modified drying oils Natural resins and modified natural resins Cellulose derivates

Types of Film Formers in a Coating, Classified According to Their Origin [68]

#### 1.7.3. Drying oils

A wide class of naturally derived film formers is formed by vegetable oils and their derived fatty acids (FA), among them linseed oil, tung oil, soybean oil, sunflower oil, tall oil, coconut oil, fish oil, dehydrated castor oil, etc.; they still play an important role in surface coatings today because of their availability as a renewable resource, their variety and their versatility. Considering their degree of unsaturation, described by their iodine value, oils are classified as "drying" (iodine value>130), "semi-drying" (100 < iodine value < 130) and "non-drying" (iodine value < 100), and these values give a measure of the ability of the unmodified oil to spontaneously oxidize and crosslink to a dry film [77]. This behavior is directly related to the concentrations of the various FA contained in the structure, as they are responsible for the formation of a coherent solid film from liquid oil. FA may be saturated (no double bonds), mono-unsaturated (one double bond) or polyunsaturated (two or more double bonds); to be considered "drying", an oil must contain at least 50 % of polyunsaturated acids [76]. Only drying oils can form a cohesive, solid film when used alone for the preparation of wood coatings. One of the most common and widely used drying oil in wood coatings is linseed oil, a good drying oil containing over 60 % of polyunsaturated linoleic and linolenic acids. The FA pattern of linseed oils can have a natural variation depending on the climate where the crops were grown, the quality of the linseeds, possible genetic variations of the crop and how the raw oil is being refined [78]. It can be used separately, but it is extensively used to produce air-drying alkyd resins and urethane oils. Tung oil, the most reactive oil, is a traditional ingredient in exterior varnishes and in penetrating treatments for wood. Tung oil with eleostearic acid as its major component is an example of conjugated oil systems, and its

viscosity is relatively higher than for most other drying oils [79] but also makes the film more UV-Vis-light sensitive, leading, for example, to more rigid films [78]. The conjugated double bonds of oils, such as those of tung oil, give polymerization and oxidation more rapidly than non-conjugated oils [80]. Natural oils contain different amounts of FA. Semi-drying and non-drying oils can be used for the modification of alkyds and as plasticizers in nitrocellulose coatings [68], [81]. Heating of drying oils, in the absence of metal driers, leads to the production of "stand oils", partially polymerized oils, where the viscosity increase actually is due to the dimerization reactions through the double bonds of unsaturated FA moieties. "Stand oils" find application in oleoresinous vehicles and in alkyd resins. The rate of production depends on the type of the drying oil used: linseed oil needs a treatment of few days in the absence of air, but tung oil reacts very quickly at 260 °C [82]. Compared to simple drying oils, stand oils dry faster, form a harder film, show higher water repellency and are less prone to yellowing.

#### 1.7.4. Alkyds

Alkyds, or alkyd resins, are polymers resulting from the reaction between a dibasic acid or anhydride and a polyol, modified by the addition of FA and other components. The term is derived from alcid, which is a combination of the words alcohol and acid, later modified in alkyd [83]. From a chemical perspective, an alkyd is not different from polyester although in practice alkyds are polyesters modified with unsaturated FA [48], [84]. Historically, the most common dibasic acid derivative and alcohol used in alkyd synthesis are phthalic anhydride and glycerol, a well-known technology for producing polyester resins called Glyptals, combining it with the empirical knowledge of producing oleoresinous paints already existing for several centuries. The first alkyd resin was synthesized in the middle of the 1920s by Kienle, whilst the commercial production of these new resins dates back to the middle of the 1930s, rapidly reaching a predominating position in the paint industry [85].



Fig. 1.1. Example of an alkyd resin used as a binder compound in alkyd paint. The FA chain shown is linoleic acid [83].

A typical alkyd resin is prepared by heating, for example, linseed oil, phthalic anhydride, and glycerol to obtain a polyester containing FA, as schematically shown in Fig. 1.1, where the disposition of the components along the polymeric chain can be seen.

As an alternative to glycerol, other polyols like pentaerythritol can be possibly used in the production of alkyd resins [86], [87] or modifying the glycerol structure in the alkyd synthesis

process [88]. Pentaerythritol is used as an alternative to glycerol in long oil alkyd formulations to impart high viscosity, fast-drying, greater hardness, better gloss, gloss retention and superior water resistance [89]. 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 autoxidation as for natural drying oils [48]. By far the most common polyester resins are linear polymers whose unsaturation comes from the maleic anhydride used in the condensation reaction [81]. Modified or hybrid alkyd-based resins exhibiting improved properties are currently available. The alkyd resins are modified by the incorporation of urethane, polyamide, silicone, phenol formaldehyde or vinyl resin constituents during the manufacturing process. For example, part of the dibasic acid can be replaced by toluene diisocyanate to yield a modified urethane alkyd [90]. The improved properties exhibited by these hybrid resins range from the thixotropic characteristics displayed by polyamide modified alkyds to the fast-drying behavior of vinyl modified alkyds. Alkyd resins can be modified to make them more compatible with a water medium for use in water reducible coatings: the modification is made on the FA, prior to the reaction with polyol and dibasic acid, for example, with methyl methacrylate or ethylhexyl acrylate [91]. Alkyds have the advantage of being low cost resins and based on renewable resources like vegetable oils [92]. The used oils and their amount are responsible for the properties of the resins, such as film elasticity, water repellency, viscosity, drying rate, adhesion, and color [68], [93]. The drying time, hardness, color, and moisture resistivity of the resin depend on the degree of unsaturation of the oil used [94]. Alkyd resins are widely used and constitute about 70 % of the conventional binders used in surface coatings today [93] due to their good attributes such as strength flexibility, gloss retention, and good thermal stability, although other reports confirm a decrease in the alkyd resins market. Only in the European Union, within the 2006-2010 periods, the alkyd resins consumption decreased by 30 %. The decline is reasoned partly by economic recession and lowering of the EU construction industry. However, alkyd coatings still remain the leaders of the EU coating market [95]. Alkyd resins possess a few weaknesses: low water or solvent resistance, due to the relatively low crosslinking density, strong solvents can give swelling and leave stains, and also hot water can hydrolyze the resin, and exterior durability, they are easily degraded by ultraviolet radiation [48], [96]. Alkyd resins are classified according to the FA content used in the reaction of their formation and can be divided into three categories as shown in Table 1.2 [97].

#### Table 1.2

Alkyd classification	FA content, %
Short alkyd	< 45
Medium alkyd	45 - 60
Long alkyd	> 60

Classification of Alkyd Resins According to the Amount of FA Present in Their Structure

#### **1.8.** Solvents and paint reformulations

Alkyd resins need to be thinned in organic solvents, because of their high viscosity, to be properly applied, and traditionally solvent-based formulations have been always used with alkyd resins. Typical solvents used in alkyd coatings are aliphatic or aromatic hydrocarbons such as white spirit or mineral spirit, xylene, or toluene [98]. Conventional solvent-based alkyd coatings generally contain up to 60 wt% solvents which contribute to hazardous emissions of VOC. These compounds are potentially hazardous for both human health and for the environment; therefore, efforts are being made to reduce or remove their presence in paints without negatively affecting their performance [99], [100]. The function of organic solvents relates to certain properties it brings – it facilitates the application of paint, its drying, and the formation of a regular paint film, with high gloss [48], [101]. During the application and drying, the solvent evaporates, and ideally a dry paint film no longer contains the solvent. However, when evaporating, these solvents are released into the atmosphere, with a negative impact on the environment. A main concern in solvent-borne formulations is the photochemical reactivity of solvents: they can be divided into highly reactive or lowly reactive, according to their ability to form ozone in the atmosphere (ozone impact) [102]. The aliphatic hydrocarbons, esters, alcohols, and ketones commonly used to formulate mediumand high-solids coatings have relatively low reactivity. Aromatic solvents, mostly xylene and toluene, generally have a higher reactivity. By replacing high reactivity solvents with low reactivity ones, it is possible to formulate solvent-borne coatings with a lower ozone impact. Another alternative approach to these technologies is to use VOC-exempt solvents such as acetone and p-chlorobenzotrifluoride, but both compounds show poor performance features when used in coatings formulations [103]. However, the trend is to limit and reduce the list of VOC-exempt compounds, and in the last 30 years, due to the environmental legislation and economic constraints, manufacturers of coatings, ink and adhesives have come under increasing pressure to reduce or eliminate the content of VOC and hazardous air pollutants (HAP) from formulations, because of the hazard they represent to the environment and the human health [104]. In Europe, this is stated by the Directive 2004/42/EC of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of VOC due to the use of organic solvents in decorative paints and varnishes, amending the already existing Directive 1999/13/EC [105]. 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.

A solution is the development of new compliant coatings technologies; specifically, in the case of alkyds, among the available alternatives, there are high solids and water-borne formulations. High solid (HS) alkyd resins do not differ from traditional solvent-borne formulations, except for that HS have a higher content of resins with a lower viscosity, and thus a lower amount of solvent is required to achieve the optimal properties necessary for application on substrates [85]. There are different ways to achieve low viscosity with high solid content in alkyd formulations, such as lowering molecular weight, narrowing the molecular weight distribution, increasing oil length, and using reactive diluents [106]. One of

the most efficient and widely used approaches to obtain a high-solid system is to incorporate reactive diluents in the system. A reactive diluent must have good compatibility with alkyds, low volatility ( $T_b > 300$  °C), is economical replacement of the solvent, and participates in the film formation by taking part in the curing [107], [108]. On the other hand, a whole range of studies have been conducted to obtain water-borne formulations; there are clearly environmental and other safety advantages in replacing solvent with water and this has been a major trend in the past decades. Unfortunately, water brings operational disadvantages, and, in the case of wood, this includes increased grain-raising, and problems arising from the high latent heat of water [68]. The main concerns about water-borne alkyd coatings are related to how to combine the technical advantages of alkyd resins with the environmental, health and safety benefits of solvent free systems. Two primary approaches to obtain water-borne alkyd resins are available. In one method, several hydrophilic monomers are induced into the alkyd formulation to form the main alkyd chain, alkali is added for neutralization and the chain is dispersed into water to obtain water-reducible alkyd resin [109]. The second possibility is to prepare alkyd resins coatings in the form of emulsions, which potentially can reach a zero VOC level [110]. For this latter approach, it is necessary to use surfactants, which are fundamental in the preparation of this type of coatings, although higher water permeability can be expected, compared to the other alkyd paints, due to their presence [48].

#### **1.9.** Additives and pigments in paints

Together with solvents and resins, paints need other components added in small amounts, usually <1 %, whose role is to modify the properties of the paint before or during application, or during film formation [68]. When air-drying paints and coatings come in contact with atmospheric oxygen, they tend to form a surface skin. Anti-skinning agents are therefore added as coating additives to induce uniform drying and prevent the skin formation during storage and shrinkage. Chemically, these agents are molecules containing the functional group oxime C=NOH, they are antioxidants which inhibit the catalytic activity of the drier, forming complexes with them, but after the application of paint, they evaporate along with the solvent in the drying process, allowing the formation of a film [111]. Autooxidation of binders can be a slow process and driers are additives necessary to accelerate the film formation, reducing the time of oxidation and cross-linking reactions. They can be divided into primary, secondary, and auxiliary driers. Secondary and auxiliary driers, including zirconium, barium, lead, zinc, calcium, aluminum, and potassium, are claimed to improve the stability and solubility of the primary driers in the paint formulations, enhance the hardness of the coating and improve through-drying of the film [112]; they have a low catalytic power used alone [111]. Cobalt, iron, manganese, vanadium, and cerium-based catalysts are classified as primary driers. A possible mechanism of oxidation of resin starts with the formation of alkyl radicals R through hydrogen abstraction which is followed by the formation of peroxyl radicals ROO through oxygen absorption. Such radicals give then hydroperoxides which can decompose into active radical species like RO· and ROO· via the Haber-Weiss cycle process, resulting in the cross-linking of the resin and the film formation [113]. It is most uncommon

to use a primary drier in a coating formulation without either a secondary or an auxiliary drier added. The most widely used metal in primary driers is cobalt [21] but alternative transition metals are studied and needed to replace cobalt due to health concerns; potential alternatives to cobalt driers are manganese and vanadium driers [114]. Pigments in paints have the function to give color and opacity to the substrate. There are organic pigments, which are more expensive, but mainly used are inorganic molecules, added in the form of ground fine powder. Their size is in the micrometric range, but more recently, a new generation of nanosized 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 [115]. Nanosized particles have a greater specific surface than traditional pigments, which gives them different and new properties, and they are used also in the paint industry, in particular, transparent metal oxides find application in paints to preserve their transparency and give greater gloss; for example, in the case of wood, they leave its grain visible, whilst larger particles are more opaque. Apart from aesthetic functions, some of these metal oxides find application also in protection against photodegradation since they are good UV absorbers, which convert into heat the energy of UV radiation which reaches the substrate surface [116]. In wood paints, the following metal oxides are used more often: zinc (ZnO) and titanium (TiO<sub>2</sub>), in the form of white powder, which have a good tradition as UV absorbers, and several iron oxides [117]. Examples of iron oxide forms are iron (III) oxide, iron (III) oxide hydrate and magnetite. They also absorb part of the visible light region, which explains why they come in different shades, going from yellow to red, brown, and black. They exhibit relatively high color intensity for inorganic pigments, the color shades depend on the size of the particles, and manufacturers can obtain purer shades by narrowing the distribution of particle size during synthesis or a particular shade by mixing particles with different sizes [118]. There are studies that confirm the efficiency of iron oxides as UV absorbers [117], [119]. They are necessary to improve the performance of clear coating systems, which do not offer sufficient protection against discoloration of wood, although they can cause a change in the original color of wood [115], [117]. The efficiency is determined not only from their size but also from the concentration in the paint; for this reason in the case of very thin layers of paint, the concentration of pigments must be great enough to ensure the necessary protection [119]. The use of UV absorbers is necessary if the wood is used in outdoor conditions. The advantages of inorganic UV absorbers are their stability against UV radiation and the cheaper costs. Studies confirmed that nano-sized TiO<sub>2</sub> and ZnO can also prevent the growth of microorganisms, through a reactive free radical mechanism, initiated from their photocatalytic behavior, although the same mechanism can degrade the coating film: in the case of nanosized ZnO, increased cracking and peeling of the film on TTW samples was observed, which caused the loss in adhesion [115], [120].

#### **1.10.** Characteristics and properties of surfactants

The term surfactant is an abbreviation for Surface Active Agent, which literally means active at a surface: a surfactant is a molecule with a tendency to absorb at surfaces, if one of

the phases is gas (usually air), and interfaces, the boundary between two immiscible phases. Five types of interfaces can be distinguished:

- 1. Solid-vapour;
- 2. Solid-liquid;
- 3. Solid-solid;
- 4. Liquid-vapour;
- 5. Liquid-liquid.

Surfactants show their activity by lowering the free energy of the phase boundary, after their absorption and orientation at the interface. In other words, when a boundary is covered by surfactant molecules, the ST (or the amount of work necessary to expand the interface) decreases, and the higher the concentration of surfactants at the interface, the larger will be the ST reduction. There is a limit to the ST and interfacial tension reduction due to surfactants and, generally, that point is when micelles start to form in bulk solution [121]. Together with ST reduction, formation of micelles is the other fundamental property of surfactants: single molecules of surfactants dissolved in a solvent show a tendency to form colloidal-sized aggregates, the so-called micelles. Micelle formation, or micellization, can be considered as an alternative mechanism to adsorption at the interface, to reduce the free energy of the system. For a surfactant in water, micellization is the way to avoid contact between water and the hydrophobic group of the surfactant, which form clusters (micelle) where the hydrophobic parts of the surfactant are packed together toward the interior of the micelle [122]. It is an important phenomenon since surfactants' behavior in solution changes when they are present as micelles or as a single molecule. Only not aggregated surfactant molecules in solution show ST reduction, or they manifest properties like detergency, dispersing, emulsifying, wetting, or foaming. Micelles may be seen also as a reservoir of surfactants, where the exchange rate of a surfactant molecule between micelles and bulk solution depends on the size and structure of the surfactant [123].

#### **1.11.** Structure of surfactants

Surfactants are amphiphilic molecules, and sometimes the term amphiphile can be used as a synonym of surfactant. This word is derived from ancient Greek amphi, meaning "both", and it relates to the fact that a surfactant molecule consists at least of two parts, one hydrophilic and one hydrophobic [121]. They can be schematically represented as in Fig. 1.2.



Fig. 1.2. Schematic illustration of a surfactant composition.

Inside the molecule of a surfactant, the following components can be distinguished:

- 1. Hydrophobic portion (tail): consisting of one or two hydrocarbon chains, which can be branched, linear, aliphatic, or aromatic, of different length;
- 2. Hydrophilic portion (head group): consisting of alkyl moieties of different dimension and hydrophobicity, can be also cyclic;
- 3. Central core of the head group: consisting of charged or polar atoms;
- 4. Counter-ion: it interacts with the head group through electrostatic forces if the head group is ionic.

#### **1.12.** Types of surfactants

Surfactants can be classified as natural and synthetic, and synthetic surfactants can be either traditional or polymeric. The primary classification of surfactants is made based on the charge of the polar head group. It is common practice to divide them into four main classes: anionics, cationics, nonionics and zwitterionics. The latter class includes surfactants that contain both a cationic and anionic charge in normal condition; they are usually referred to as amphoteric, but this term cannot be considered as a synonym of zwitterionic [121]. An amphoteric surfactant is a molecule that, according to the pH value, can be anionic, cationic or zwitterionic. Most ionic surfactants are monovalent, but there are also important examples on divalent anionic amphiphiles. For ionic surfactants, the choice of counter-ion influences their physicochemical properties. The typical counter-ion for anionic surfactants is sodium; other cations like potassium, lithium or calcium are used for specialty purposes. The counterion for cationic surfactants usually is a halide or methyl sulfate. The hydrophobic group usually is a hydrocarbon (alkyl or alkylaryl) one, but, in alternative, also polydimethylsiloxane or fluorocarbon groups are possible. The two latter types of surfactants are particularly effective in non-aqueous systems [123].

#### 1.12.1. Cationics

In most of cationic surfactants, the positive charge is on a nitrogen atom; both amine and quaternary ammonium-based products are common. Amines can be considered as surfactants only in the protonated state; therefore, only at low pH values, on the contrary, quaternary ammonium compounds are not pH sensitive. Cationics have the advantage to be compatible with nonionics and zwitterionics, but not with anionics [121]. Thanks to their positive charge, they readily adsorb onto solid surfaces, which are usually negatively charged, and can impart special characteristics to the substrate. It is possible to take advantage of this property, developing emulsions that disrupt in contact with a solid surface, allowing deposition of active substances on the substrate's surface [122]. Compared to other types of surfactants, they show poor detergency and poor foaming. Other characteristics of cationics are as follows:

1. They are the third largest class of surfactants and generally are more expensive than anionics and nonionics;

- 2. Hydrolytically stable cationics show higher aquatic toxicity than other types of surfactants;
- 3. They are used as emulsifiers in asphaltic emulsions and coatings in general, in inks, wood pulp dispersions, magnetic slurry, etc.;
- 4. Many cationic surfactants are bactericides.

#### 1.12.2. Anionics

Anionic surfactants are the largest group of surfactants. They are used in greater volume than any other type of surfactants. The worldwide production of surfactants is roughly estimated to be 13 million tons in 2008, and about 60 % of them are anionic surfactants. One main reason for their popularity is the ease and low cost of manufacture. Their main use is in detergent formulations, with the highest efficiency obtained by alkyl and alkylaryl chains in the range C12–C18 [121]. Other important characteristics of anionics are as follows:

- 1. They are generally not compatible with cationics (with some important exceptions);
- 2. They are generally sensitive to hard water and salt;
- 3. A short polyoxyethylene chain between the anionic head group and the hydrocarbon tail considerably improves salt tolerance; it also increases the solubility in organic solvents.

#### **1.12.3.** Nonionics

Nonionic surfactants have either a polyether or a polyhydroxyl unit as the polar group. In the vast majority of nonionics, the polar group is a polyether consisting of oxyethylene units, made by the polymerization of ethylene oxide. The head group usually contains from 5 to 10 units of oxyethylene, but in the case of dispersants, the head group can be longer. These surfactants are obtained by reaction of ethoxylation, and they can be obtained from a wide range of starting materials, like fatty alcohols, alkylphenols, fatty acids and fatty amines [120]. Other important characteristics of nonionics are as follows:

- 1. They are the second largest surfactant group;
- 2. They are normally compatible with all other types of surfactants;
- 3. They are not sensitive to hard water;
- 4. Contrary to ionic surfactants, their physicochemical properties are not affected by electrolytes;
- 5. Temperature can affect their solubility in water; at a higher temperature, they become less hydrophilic.

#### 1.12.4. Zwitterionics

Zwitterionics contain both positive and negative charges in one molecule. Whereas the positive charge is almost invariably ammonium, the source of the negative charge can be of different nature, the most common of which is carboxylate. Often, they are referred to as amphoteric molecules, but the terms are not identical. An amphoteric substance changes from

cationic, via zwitterionic, to anionic depending on the pH value, going from low to high. It means that the surfactant is zwitterionic only in a certain pH range. At the isoelectric point, their properties resemble those of nonionic surfactants. Zwitterionics are compatible with all other types of surfactants. They are less irritating to the skin and eyes and are often used in shampoos and other cosmetic products; they may be adsorbed onto negatively or positively charged surfaces without forming a hydrophobic film. Common types of zwitterionics are N-alkyl derivatives of simple amino acids, such as glycine, betaines, and amino propionic acid [120]. Other important characteristics of zwitterionics are as follows:

- 1. They are the smallest group of surfactants, also due to the high price;
- 2. They are not sensitive to hard water, and generally are stable in acids and bases, in particular, betaines retain their properties in strong alkali;
- 3. They are insoluble in most organic solvents, including ethanol.

#### **1.13.** Micellization

A fundamental property of surfactants is the formation of micelle – the ability of surfactants to form colloidal-sized clusters, which remain in solution as thermodynamically stable, dispersed species with properties distinct from those of the single surfactants. Almost from the very beginning of the study on the properties of surfactant solutions, it has been recognized that their bulk properties are unusual and indicate the presence of colloidal particles in the solution. The formation of these colloidal particles starts at a concentration called critical micelle concentration (CMC), whose value can be determined by changes of physical properties of surfactant solutions, like breaks in the electrical conductivity, ST, light scattering, self-diffusion, etc. [121].



Fig. 1.3. Correlation between CMC and ST, when the ST becomes constant, micelles start to form in solution [124].

Among the factors that affect CMC, there are the surfactant structure (class of the surfactant, tail group length, counter-ion), temperature, and the presence of cosolute. When the solvent is water, the driving force of micelle formation is the elimination of the contact between water and alkyl chain (hydrophobic part of surfactants); a very useful consequence of

this is that hydrophobic compounds can be solubilized in micelles, a property which leads directly to the formation of emulsions [120]. Some of the possible surfactants' micelle structures are shown in Fig. 1.4. The size, shape and aggregation number of micelles is affected by the type of the solvent, changes in temperature, concentration of the surfactant, additives in the liquid phase and structural groups in the surfactant, leading to the formation of spherical, rod-like or lamellar structures [125].



Fig. 1.4. Examples of possible surfactant aggregates and structures [126].

The micellar structure can be determined by the surfactant geometry, using the critical packing parameter (CPP), a dimensionless number that puts in relation the volume  $V_H$  of the hydrophobic group, the length  $l_c$  of the hydrophobic group and the cross-sectional area  $a_0$  occupied by the head group, which is expressed in the following equation (2.1) [127]:

$$CPP = V_H / l_c \cdot a_0 \tag{2.1}$$



Fig. 1.5. The critical packing parameter, a dimensionless number obtained from surfactant geometrical factors: volume, length and area of hydrophobic and hydrophilic groups of the surfactant [121].

Table 1.3 lists the possible aggregate structures, according to the CPP values intervals

Table 1.3

Value of CPP	Structure of the micelle
0 – 1/3	Spheroidal in aqueous media
1/3 - 1/2	Cylindrical in aqueous media
1/2 - 1	Lamellar in aqueous media
> 1	Inverse (reversed) in non-polar media

Variation in Micelles Structures, Depending on the CPP Values

#### **1.14.** Type of emulsions

Emulsification, the formation of emulsions from two immiscible liquid phases, is probably the most versatile property of surfactants for practical applications and, as a result, it has been extensively studied. Paints, polishes, glues, pesticides, metal cutting oils, margarine, ice cream, cosmetics, metal cleaners, and textile processing oils are all examples of products that are emulsions. An emulsion is a significantly stable suspension of particles of liquid of a certain size within a second, immiscible liquid. The term *significantly stable* means relative to the intended use and may range from a few minutes to a few years. There are two main types of emulsion: the oil-in-water (o/w) emulsion, where the water is the continuous phase and the oil is the dispersed phase, and the water-in-oil (w/o) emulsion where the water is the dispersed phase, and the continuous one. The first type, o/w, is by far the most important and common type of emulsion and can be found in many examples and in different fields [122].

Three different categories of emulsions can be distinguished, based upon the size of the dispersed particles:

- 1. macroemulsions, the most well-known type, white-opaque emulsions with particles sizes > 400 nm, easily visible under a microscope;
- 2. microemulsions, transparent dispersions with particles < 100 nm in size;
- 3. nanoemulsions (miniemulsions), a type that has blue-white color, with particle sizes between those of the first two types from 100 nm to 400 nm.

Two immiscible pure liquids cannot form an emulsion. For a suspension of one liquid in another, to be stable enough to be classified as an emulsion, a third component is necessary. The emulsifying agent is usually a surface-active agent, although not necessarily of the type that is usually considered a surface-active agent (finely divided solids, for example, may act as emulsifying agents). Traditional surfactants in combination with water and a more hydrophobic amphiphile, such as an alcohol or a carboxylic acid, present a rich variety of colloidal association structures. The presence of such association structures has a pronounced influence on the stability of dispersed systems such as emulsions and foams. To achieve a more stable emulsion, a mixture of two or more substances is recommended: a very common combination consists of a water soluble surfactant and an oil soluble one; in this way, the interfacial film is more resistant, thus conferring higher stability to the emulsion [128]. The

choice of surfactants depends on the type of emulsion that is intended to be obtained, either o/w or w/o. The role of the surfactants in the emulsification process is to reduce the interfacial tension between water and oil to low values, and rapidly cover the surface of dispersed phase droplets with a monolayer of surfactants, to ensure stability [129]. Low molecular weight surfactants are more appropriate in doing this than high molecular weight surfactants or polymer [130].

#### **1.15.** The Hydrophilic-Lipophilic balance concept

The simplest rule to select a surfactant in emulsion formation is the Bancroft's rule, which says that water soluble emulsifiers give o/w emulsions, and oil soluble emulsifiers give w/o emulsions – this is a purely qualitative rule. A more accurate way to select the appropriate surfactant was introduced by Griffin and it is the hydrophilic-lipophilic balance (HLB) of a surfactant [131], initially restricted only to nonionic surfactants, and later extended by Davies [132], who assigned to each group which composes the surfactant molecule a HLB value, that could be used to calculate the total HLB of the whole molecule. The equation used by Davies is HLB =  $7 + \Sigma$ (hydrophilic group numbers) +  $\Sigma$ (hydrophobic group numbers). Table 1.4 lists the typical applications of surfactants, according to their HLB value

Table 1.4

HLB values	Applications
3-6	w/o emulsifier
7-9	Wetting agent
8-14	o/w emulsifier
9 – 13	Detergent
10 - 13	Solubilizer
12 – 17	Dispersant

Typical Surfactant Applications, Depending on the HLB Values Ranges

The Griffin or Davies methods give a useful prediction for emulsifier selection, but this is true if we work at room temperature. Changes in temperature can affect the surfactant, which, for example, is suited for an o/w emulsion at room temperature, but becomes a w/o emulsifier at higher temperature, or, for a ready emulsion, a very low temperature can affect the emulsion stability [133]. However, considering that many factors influence the emulsification, HLB cannot be used as a universal tool to select the appropriate emulsifier to predict which type of emulsion will be formed with a specific surfactant. It has been found empirically that a combination of surfactants, one of which is more hydrophilic while the other is more lipophilic, is often superior to a single surfactant of intermediate HLB in making a stable emulsion. Most probably, the combination of two surfactants with quite different CPP values gives better packing at the interface than one surfactant. The combination of a low-HLB and a high-HLB surfactant is a useful concept in emulsification, and it is frequently used in practice.

Apart from those of surfactants, there are also HLB values assigned to various substances that are frequently emulsified, such as vegetables oils, paraffin wax, extractives, etc. in an emulsification process; where these substances are used, it is recommended to select an emulsifier or a combination of emulsifiers, whose HLB values are equal to the substance HLB value. The HLB method is useful although with some limitations; it can be affected by the presence of impurities in the oil, the presence of electrolytes in the water, and the presence of cosurfactants or other additives in the emulsion [121].

#### 1.16. Stability of emulsion

Emulsion break-down can occur by various mechanisms, as illustrated in Fig. 1.6. Creaming or sedimentation occurs because of the density difference between the phases. Creaming is more common than sedimentation because most emulsions are of the o/w type and the oils tend to be of lower density than the aqueous phase. Some oils, such as chlorinated hydrocarbons, have higher densities than water. However, an addition of a chlorinated solvent to the oil component was once used as a way to improve the storage stability of emulsions.

Droplets can also flocculate, which means that they enter the so-called secondary minimum, an energetically stable situation where the droplets are close to each other but still retain their integrity. Creaming, sedimentation, and flocculation are all reversible phenomena and the original state can often be regained by the application of high shear [121]. A much more severe phenomenon is coalescence, a process in which droplets merge into each other. Coalescence can be seen as an irreversible phenomenon, and its final stage is the separation of phases with emulsion disruption. Another destabilization mechanism is Ostwald ripening, in which a smaller droplet of the dispersed phase merges with larger ones, thus reducing the surface areas of the dispersed phase and, at the same time, increasing the micelle radius; this phenomenon is caused by the diffusion of molecules of the dispersed phase trough the continuous medium. The stability of the emulsion can be achieved in different ways; through the control of the droplet dimension, for example, it is possible to ensure a longer half-life, even years. In this way the potential energy barrier at the surface is high enough to avoid the coalescence between droplets. The smaller the droplets, the higher the potential energy barrier will be. There are other ways to achieve these energetic barriers and prolong the emulsion stability; studies have shown that the rigidity of the surfactant layer at the interface also plays an important role [134].

Other factors are as follows:

- 1. electrostatic stabilization, based on the repulsive interaction between the charged interfaces of micelles;
- 2. steric stabilization, which can be achieved by nonionic surfactants with a long head group, thus creating a steric obstacle to the droplets' fusion;
- 3. particle stabilization by means of solid particles; an important requirement is that their dimension is smaller than the emulsion droplets and they should be relatively hydrophobic.

For a higher stabilization of emulsion, these mechanisms can be used simultaneously.


Fig. 1.6. Possible mechanisms of emulsion destabilization and disruption [121].

#### **1.17.** Alkyd emulsions

When used in solvent-borne formulations, alkyd resins form a normal solution, where polymer molecules are completely dissolved and form a homogeneous one-phase system. In water-borne formulations, due to the insolubility of alkyd resins in water, surfactants are needed to emulsify the resin, which will be dispersed in relatively large micellar aggregates; thus, the main difference with solvent-borne paints is that alkyd emulsions are two-phase systems, where water is the continuous phase and alkyd the dispersed one [135]. The role of surfactants is to simplify the formation of droplets during emulsification and afterwards stabilize them against the disruption of the emulsion. The appropriate surfactant must be selected in order to reduce the free energy of the various interfaces of the system, thus providing kinetic stability to the formulation: the majority of surfactants used in coatings formulations are standard anionic and nonionic amphiphiles, such as fatty alcohol sulfates, alkylaryl sulfonates and alcohol ethoxylates. Cationic and amphoteric surfactants are rarely used [136]. A stable emulsion can be made from most alkyds, provided that the resin viscosity is not too high and sufficient shear forces are applied in the emulsification process [121].

Most resins used are long oil alkyds since these resins are suitable for emulsification due to their relatively low viscosity. Also, medium, and short oil alkyd resins are gaining interest in emulsification, but in their case, the emulsification process must be carried out at higher temperature, to reduce resin viscosity at a suitable level [137], [138]. In alkyd emulsions, the resin is dispersed as fine droplets in water. A crucial factor for acquiring good colloidal stability is that small droplets and narrow droplets' size distribution are obtained in the emulsification process [139]. Depending on the used surfactant, two main types of stabilization mechanisms operate: steric stabilization, provided by nonionic surfactants, and electrostatic stabilization using ionic surfactants. The repulsive interactions, steric or electrostatic, due to the surfactants at the water-droplet interface, create a static protection of the droplets. The emulsification process is successful if droplets are protected very rapidly after their formation. For this reason, the diffusion of the surfactant is a key factor [140]. For a more efficient stabilization of the droplets, both types of surfactants can be combined in the emulsification process, as can be seen in Figure 1.7 [136].



Fig. 1.7. Mixed monolayer of nonionic and anionic surfactants at the droplet interface [136].

Nonionic and anionic surfactants give stable alkyd emulsions, their emulsifying properties show a different dependence on the concentration, and normally anionic surfactants are effective at lower concentration than nonionic surfactants. Also, temperature influences the emulsification process: it has been observed that for both types of surfactants, emulsifying properties increase with increasing temperature [140]. There are two possible methods of emulsification of alkyd resins in water: direct or phase inversion emulsification. In direct emulsification, the alkyd resin is simply added to the aqueous phase containing the surfactant. Energy then is imparted to the system by mixing, to create the new surfaces of the droplets and thus forming o/w dispersion. With the phase inversion method, water is gradually added to the alkyd resin containing the surfactant, initially forming a w/o emulsion, but continuing the addition of water, a critical dispersed phase fraction is reached and the dispersion inverts to produce the required o/w emulsion [141]. The phase inversion method has been applied also with short oil alkyd resin which was solid at room temperature; in this case, a temperature of 90 °C was necessary to liquefy alkyd resin containing the emulsifier; gradually adding hot water, a fine dispersion of alkyd resin with small size droplets was obtained [142]. The main drawbacks for an alkyd emulsion, compared to solvent-borne formulations, are slower drying and water sensitivity. The decrease of the drying rate can be explained by the adsorption of the drier (mainly cobalt salts) on the pigments' surfaces, in the event that these are included in the formulation, also by the formation of stable and less active complexes with water or amines (frequently used as neutralizing agents in water-borne alkyd formulations), and unequal distribution between phases [143], [138]. Surfactants are responsible for film softness and water sensitivity, since they act as a plasticizer and tend to migrate from the bulk to the resin-air interface during drying [137]. In the last decades, polymerizable surfactants have become of interest as emulsifiers in emulsion and suspension polymerization. By using surfactants that become covalently attached to the resin, many of the problems encountered with conventional emulsifiers can be avoided or at least minimized. Both the stability of the resin and the properties of the dried film can be considerably improved [144], [145].

# 2. MATERIALS AND METHODS

#### 2.1. Paint composition, preparation and characterization

The preparation of an alkyd emulsion requires a different sequence compared to a traditional solvent-based paint, in which the components of the formulation can be added to the solvent, and then by means of stirring, a homogeneous solution is obtained. In the case of an alkyd emulsion, two immiscible liquids are mixed together and dissolved one into another with the help of surfactants, thus forming a homogenous system, which can be more or less stable [146].

# 2.2. Binders

The binders used in this research to investigate the formation of the emulsion are two types of alkyds, linseed oil (LO) and double boiled linseed oil (DBLO); these binders were provided by Riga Varnish and Paint Factory (Rīgas Laku un Krāsu Rūpnīca). The used alkyds were one long oil alkyd resin (LOAR), and one medium oil alkyd resin (MOAR). LOAR was obtained by the reaction of tall oil FA, benzoic acid, pentaerythritol and phthalic anhydride; MOAR was obtained by the reaction of soybean oil FA, pentaerythritol and phthalic anhydride; anhydride. Their composition is shown in Figs. 2.1 and 2.2, respectively.



**Components of LOAR** 

Fig. 2.1. Composition of long oil alkyd resin.



**Components of MOAR** 

Fig. 2.2. Composition of medium oil alkyd resin.

One of the advantages of alkyd resins is the possibility to modify the polyester backbone with a wide range of FA, thus obtaining different alkyds with different properties. The use, in the production process, of FA obtained from renewable resources reduces the environmental impact of these types of resin.



Fig. 2.3. Schematic representation of alkyd synthesis, the polycondensation reaction gives the polymeric chain [147].

LO was used in the initial stages of the research and then replaced with DBLO, which is, more precisely, a commercial product named "Pernica": this product consists of DBLO, with siccative added, and diluted with white spirit to reduce its viscosity. DBLO is obtained heating LO in the presence of air. Heating the oil causes it to polymerize and oxidize, effectively making it thicker and reducing its drying time compared to LO. DBLO is a dark amber colored oil having a distinctively sharp smell. It has a higher viscosity than LO. For both oils, the reaction of cross-linking is possible thanks to the presence of unsaturated FA: linolenic acid, whose molecule has a 18 carbon atoms linear backbone with three double bonds, and linoleic acid, whose molecule has a 18 carbon atoms linear chain with two double bonds; their structural formulas are presented in Fig. 2.4.



Fig. 2.4. Chemical structures of linolenic and linoleic FA, both are C18 in length but have different number of double bonds.

The choice of using initially LO and then DBLO to partially replace alkyd resins has the following advantages:

- 1. LO and DBLO are natural products obtained from renewable sources, thus making the paint more environmentally friendly;
- 2. It reduces the cost of paint, since they are less expensive than alkyd resins;
- 3. It improves the elasticity of the film, which is very important in case of paints for wood.

The presence of LO in paints has a negative effect to increase the permeability of water: this is an unwanted property for the wood-coating system, as the barrier properties of a coating are a fundamental parameter to ensure the durability and protection of wood [48].

# 2.3. Surfactants

Samples of 9 surfactants were provided by the Air Products Company: they were selected according to their chemico-physical properties and as recommended by the producer for use in water-based paint formulations. Their generic characteristics are listed in Table 2.1.

Table 2.1

Name of surfactant	Туре	Concentration (%)	HLB	Aspect
Carbowet 109	Nonionic	60–100	13.1	Liquid
Carbowet 125	Nonionic	100	12.5	Liquid
Carbowet 138	Nonionic	100	13.9	Liquid
Carbowet 144	Nonionic	100	14.4	Solid wax
Dynol 800	Nonionic, gemini	70 –	n.a.	Liquid
Dynol 810	Nonionic, gemini	80	n.a.	Liquid
Surfynol 104A	Nonionic, gemini	50	4	Liquid
Surfynol 440	Nonionic, gemini	100	8	Liquid
Surfynol 2502	Nonionic, gemini	100	8	Liquid

Surfactants Tested and Some of Their Properties

The Dynol and Surfynol series are acetylenic based surfactants, all containing a triple bond: Dynol 800 and 810 are the same ethoxylated 2,5,8,11-tetramethyl-6-dodecyn-5,8 diol, but at 2 different concentrations, Surfynol 104A is a solution of 50 % 2,4,7,9-tetramethyl-5-decyne-4,7-diol in 2-ethylexanol, Surfynol 440 is ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and Surfynol 2502 is ethylene oxide-propylene oxide copolymer diether with 2,4,7,9-tetramethyl-5-decyne-4,7-diol (all surfactants of the Surfynol series are derived from 2,4,7,9-tetramethyl-5-decyne-4,7-diol). The Carbowet series surfactants are linear ethoxylated alcohols, with a chain length varying from 9–11 (Carbowet 109, 125, 138) to 12–15 atoms of carbon (Carbowet 144). Different concentrations and combinations of surfactants were tested. Their structural formulas are shown in Figs. 2.5 and 2.6, respectively.



Fig. 2.5. Chemical structure of Dynol and Surfynol surfactants.



Fig. 2.6. Chemical structure of Carbowet surfactants; polar head groups are obtained from polymerization of ethylene oxide.

# 2.4. Additives

# 2.4.1. Pigments

To enhance the efficiency of the paint in surface protection against deterioration caused by UV radiation, inorganic pigments must be included in the composition. In this work, inorganic pigments consisting of transparent (or nano-sized) iron oxide particles were used. The pigments used were Xfast Red 2817, Sicotrans Red L 2818, which are provided in the form of powder, and Luconyl NG Red 2817, which is in the form of aqueous solution, produced by BTC Europe GmbH, designed for water-based paints. Xfast Red 2817, Sicotrans Red L 2818 and Luconyl NG Red 2817 are red pigments consisting of transparent iron [III] oxide, with a Color Index (CI) 77491. The fourth pigment used was Sicoflush L Red 2817, which is, as the other three mentioned pigments, also transparent iron [III] oxide pigment preparation, in the form of liquid dispersion but recommended for solvent-based coatings. For the artificial weathering tests, six alkyd emulsions were prepared with a concentration of pigments of 4 % and 8 % of the total composition, using Xfast Red 2817, Sicotrans Red L 2818 and Luconyl NG Red 2817. For the outdoor exposure test, one alkyd emulsion was prepared with a concentration of pigments of 8 % of the total composition, using only Sicoflush L Red 2817.

#### 2.4.2. Wetting agents

To facilitate the dispersion of pigments in the paint, a wetting agent is added. It has the function to disrupt the pigments' agglomerates into smaller particles and to envelope their surface to avoid in this way the adsorption and deactivation of driers, which is a negative aspect of water-based paints. The used wetting agent is a solution at 50 % of the modified copolymer in  $H_2O$ , available with the commercial name Tego Dispers 752W: it is an anionic wetting and dispersing additive especially recommended for transparent iron oxides, thanks to the presence of groups with high affinity for pigments.

### **2.4.3.** Driers

Several driers were tested in this work, to check their efficiency in water-based paints. The first two driers are designed for water-based formulations and can be used also in pigmented paints: Dry 0615 Aqua is based on manganese, and Borchi Oxy Coat 1101 contains an iron complex. The third drier is cobalt octoate and it is a well-known efficient drier for alkyd paints, but traditionally used in solvent-based formulations.

### 2.4.4. Biocide

TTW has different chemical properties compared to untreated wood, but it is not resistant against stain fungi, molds, or mildews; therefore, it is necessary to add a biocide agent to the paint. In this work, the commercial biocide complex Wocosen 45 TK was used, based on the active ingredients – propiconazole (34 %) and IPBC, 3-iodo-2-propynyl butyl carbamate (16 %); it is formulated for use in water-based and solvent-based wood preservatives, paints and coatings.

# 2.4.5. Antifoam agent

During the emulsification process with an ultrasonic mixer, the formation of foam was observed with surfactants, which is an undesired property in the preparation process, and to avoid it, water soluble linear silicone oil (55 % solid content) was used as an antifoam agent. It turned out to be very efficient at very low concentrations. This antifoam agent can be added at any stage of the process; in this work, it was added at the end, before the emulsification process with the ultrasonic mixer. The final concentration used was 0.2 %.

# 2.5. Sequence and technique of emulsification

To mix alkyd, DBLO and other additives with water and surfactants to obtain a stable emulsion, the right emulsification approach must be selected. Two directions were tried.

In the first approach, the surfactants were solubilized in water to obtain a clear solution and then binders and additives were singularly added; then the solution was stirred after each addition with a magnetic stirrer to emulsify them, but in this way the emulsion did not form. The procedure was done at room temperature. In the second approach, initially, a mixture was obtained mixing alkyds, DBLO, pigments and other additives, till it became a homogeneous mass, and then, respectively, water and surfactants were added. To mix the system, ultrasonication was used, because it is a more powerful way to create an emulsion compared to the magnetic stirrer. To facilitate the emulsification, a high shear is necessary, since water, binders and additives are immiscible. The emulsion components were mixed using an ultrasonic homogenizer MRC Sonic-650, with a power of 650 W, set at 85 % of total power. Total mixing time was 10 min to 20 min; it consisted of repeated sessions of mixing and pauses -9 s of mixing, followed by 1 s of a pause, respectively. The homogenizer was equipped with a temperature detector for the sample and to avoid the heating of the emulsion; a bath of ice and water was used to keep the temperature of the emulsion low.

#### 2.6. Characterization of coating

The viscosity of paint was measured with a Ford viscosity cup B3-246 (Russia), with a volume of 100 ml, measuring the time of flowing of the paint in seconds, with a precision of  $\pm 1$  s. The rate of flow is proportional to the kinematic viscosity. During the measurement of the paint flow, the temperature was kept constant at  $(20 \pm 0.5)$  °C. The dry content of the paint (%) was determined, weighting in a metal plate a fixed amount of paint on a balance with the precision of 0.01 g, and then putting it in a drying oven at a temperature of  $(140 \pm 1)$  °C, until the mass became constant. The first check was made after 1 h of drying in an oven. The glass transition temperature  $T_g$  was determined with differential scanning calorimetry (DSC), using a calorimeter Mettler Toledo 82E (Malaysia). The temperature interval was from -50 °C to +100 °C, with a rate of temperature increase of 5 °C/min. The films for the determination of  $T_{\rm g}$  were obtained from two different emulsions, one containing DBLO and alkyds, and one containing only alkyds, to verify the influence of DBLO on the film properties. In this specially prepared paints, pigments were not included in the formulation, each of the two paint was put in a metal plate, weighted and then allowed to dry at room temperature, around  $(20 \pm 2)$  °C, until they reached a constant weight and the film was dry. To determine  $T_{\rm g}$ , small pieces of the film were cut and three samples for each paint were prepared, each one with a mass of 0.008 g.

# 2.7. Determination of size of micelles

The size of micelles and their intervals of distribution were determined with an upright microscope Leica DM5500B using the transmitted light technique. The images were collected putting a drop of the emulsion between two laboratory microscope slides, pressed together to obtain a thin layer of emulsion; in this way the micelles were visible at the selected magnification of 400x. The images of micelles were obtained and visualized on the computer monitor; the software includes a tool for the elaboration of the images and for the measurement of the micelle dimensions (diameter, circumference, volume, etc.). The results were obtained analyzing several pictures containing more than 5000 spherical shaped micelles of different sizes; their diameters were measured, and the data were collected to determine their size distribution.

#### 2.8. Testing of driers with alkyd and DBLO

To check the efficiency of alternative and less toxic driers in the formation of a resins film, FTIR spectroscopy was used, measuring spectra of the alkyds and DBLO mixture with three different driers: Dry 0615 Aqua, based on manganese, Borchi Oxy Coat 1101, based on an iron complex, and well-known cobalt salt. The spectrometer was a Thermo Fisher Nicolet iS50 set at a resolution of  $4 \text{ cm}^{-1}$  and 32 scans. The FTIR data were collected using an

attenuated total reflectance technique with ZnSe and diamond crystals. The test was conducted during 24 h, three solutions of the used alkyds and DBLO with the same composition were prepared, then the driers were added at a concentration of 1.5 % of the total resins content, without the addition of secondary driers. Immediately after the preparation, a layer of approximately 30  $\mu$ m thickness of wet resins was applied on a glass support and let drying to air at room temperature. At regular intervals of time, small amounts of the layer of resins were used to measure FTIR spectra and observe the progress in autooxidation, to evaluate the efficiency of driers and the rate of drying. The changes in the peaks indicate the progress of the oxidation of resins and of the film formation.

# 2.9. Selection of wood samples

Wood of two common species in Latvia, aspen (*Populus tremula*) and pine (*Pinus sylvestris* L.) was used in this work. Samples were selected without visible defects or cracks on their surface. Before being used for the tests, they had been stored for at least one month in a conditioning room at  $(20 \pm 2)$  °C and relative humidity (RH)  $(65 \pm 5)$  %. For the weathering tests, artificial and outdoor, samples were cut to the necessary size. In other experiments made to measure the SE of wood, to measure the wetting of the wood surface with alkyds and DBLO, to check the homogeneity of the application of paints and to measure CA for different alkyd and DBLO emulsions, random samples with different dimensions were used, since the size of the samples was not a fundamental characteristic for conducting the mentioned experiments.

# 2.10. Thermal modification of wood

The TM of the wood boards was done using a specially designed autoclave from the Danish Company WTT (Wood Treatment Technology). It works according to the close system principle approach, using high pressure in a water vapor saturated system to obtain, at relatively low temperature, a wood product with substantially changed properties.



Fig. 2.7. WTT multifunctional pilot plant for modification of wood.

The autoclave has the following dimensions:

- Internal length 1100 mm;
- Internal diameter 410 mm.

During the TM process, heat is provided by hot oil flowing through the shell of the autoclave (heat exchange mechanism). Aspen wood samples are treated at 170 °C for one hour and pine wood samples are treated at 180 °C for one hour. The TM of wood consists of three stages:

- 1. temperature increase up to the modification temperature.
- 2. holding at the modification temperature for the selected time (in this case, 1 h).
- 3. slow cooling to room temperature.

The pressure inside the autoclave during TM is around 6.0 bar. To saturate the atmosphere with water vapor in the autoclave, in addition to the moisture coming from wood boards, a specifically designed cup with water, which will evaporate during the heating stage, is put in the autoclave. The process is fully automated, based on the input of values and parameters previously set up. Before and after TM, wood boards are weighted, and their moisture content is measured. With these data, it is possible to calculate the mass loss during the TM process, as shown in the equation (3.1):

mass loss = 
$$\left(1 - \frac{m_{f}(100 - w_{rel}^{f})}{m_{i}(100 - w_{rel}^{i})}\right) \cdot 100$$
 (3.1)

where:

m<sub>i</sub> – mass of board before modification, g;

m<sub>f</sub> – mass of board after modification, g;

w<sup>i</sup><sub>rel</sub> – relative moisture content before modification, %;

 $w_{rel}^{f}$  – relative moisture content after modification, %.

#### 2.11. Artificial weathering samples

The TTW samples for the artificial weathering test were cut in small boards measuring 150 mm  $\times$  70 mm  $\times$  15 mm, and the boards were planed to have a smooth surface. One set of samples was coated with two layers of paint and one set of samples with three layers of paint, allowing to dry for 24 h before the application of the next layer of coating. Coating was applied manually with a brush, avoiding the formation of a thick visible film on the surface of the sample. The layers of coating were let dry at room temperature. The test has been conducted according to a method for determining the resistance of wood coating to artificial weathering performed in an apparatus equipped with fluorescent UV lamps, condensation, and water sprays devices. In this case, only UV irradiation was used to test the efficiency of pigments in protecting the color of the wood surface and to find the proper concentration of pigments necessary for this purpose. Samples were weathered in a QUV Accelerated Weathering tester equipped with UVA-340 lamps, emitting in the wavelength region from 365 nm to 295 nm, with a peak emission at 340 nm, at a temperature of (60 ± 1) °C. The length of the experiment was 1000 h and at fixed intervals of time, the chamber was turned off, the samples were left to cool to room temperature and then the color of wood samples

was determined. For each sample, the measurements were done at the same 5 points and the average value was calculated. The changes of wettability of the coated samples surface have been monitored, measuring the CA before and after the artificial weathering test.

#### 2.12. Outdoor weathering samples

The TTW samples used for outdoor weathering test were cut into boards measuring  $370 \text{ mm} \times 90 \text{ mm} \times 20 \text{ mm}$  and prepared for the test according to the standard LVS EN 927– 3. The test was made in Riga (geographic coordinates 56°56'45"N, 24°06'21"E). All the samples were planed to have a smooth surface. Initially, they had been painted with one layer of transparent base paint without pigments. Once the base layer was dried the pigmented paints were applied. One half of each sample was coated with two layers of solvent-based alkyd paint and the other half with three layers. For the alkyd emulsion, after the application of the first layer of paint, it was observed that the same result was visually obtained as for the samples coated with two layers of the solvent-based paint. Probably, due to the presence of the base layer, the penetration was lower compared to the solvent-based paint, so it was decided to apply only two layers on one half of the samples and use these conditions to test the efficiency of paints during outdoor exposure. The only results which were monitored were for the half of the TTW samples with two layers of alkyd emulsion. Paints were applied manually with a brush, avoiding the formation of a thick visible film on the surface of the sample. Each layer was let to dry for 24 h at room temperature before the application of the next layer of coating. Before starting the test, the color of samples was measured with the spectrophotometer. The samples were put on a stand facing south with and angle of 45 ° from the ground; at determined times, samples were collected and taken to the laboratory to measure the color changes, wettability and visual damages on their surface.

### 2.13. Measurement of the color of wood

To evaluate the changes of wood color during weathering, a spectrophotometric characterization method was used, based on the *CIELAB* color space model, which was defined by the International Commission on Illumination (CIE) in 1976 (see Fig. 2.8). It expresses color as three numerical values,  $L^*$  for the lightness and  $a^*$  and  $b^*$  for the green–red and blue–yellow color components. *CIELAB* color space was designed to be perceptually uniform with respect to human color vision, meaning that the same amount of numerical change in these values corresponds to about the same amount of the visually perceived change. This model can give a numerical evaluation for the color change. The space itself is a three-dimensional real number space, allowing the representation of infinitely many possible colors, through the combination of the values of  $L^*$ ,  $a^*$  and  $b^*$  components. The value of the Lightness  $L^*$  can vary from 0, corresponding to the darkest black, to 100, corresponding to the brightest white, whilst the two color components  $a^*$  and  $b^*$  range between –120 and +120. The  $a^*$  axis represents the green–red component, with green in the negative direction and red

in the positive direction. The  $b^*$  axis represents the blue–yellow component, with blue in the negative direction and yellow in the positive direction.



Fig. 2.8. CIELAB color space representation, with coordinates  $L^*$ ,  $a^*$  and  $b^*$  [148].

The color of the wood samples was measured before, during and after the weathering, with a Konica Minolta spectrophotometer CM-2600d (Japan), equipped with a Xenon lamp, a D65 light source simulating the daylight, with geometry  $d/8^{\circ}$ , a diameter of 8 mm, and measurements of reflection in the wavelengths range from 360 nm to 740 nm. Color coordinates for each sample were measured at 5 points and the average values were calculated.

# 2.14. Measurement of contact angle

Measurement of CA is a common and practical technique to obtain information about the surface property such as wettability, and consequently, to know if the material is either hydrophobic or hydrophilic. A wetting liquid is a liquid that forms a CA with the solid surface which is smaller than 90°. A non-wetting liquid creates a CA between 90° and 180° with the solid surface. For the measurement of CA, a goniometer Dataphysics (Germany) OCA20 was used, equipped with a video camera to capture pictures of the droplets, and SCA20 software for the determination of the probe liquid droplet contour and for the computation of CA and SE. CA was used to evaluate the changes of wettability of coated wood samples during the artificial and outdoor weathering. The method used is the static sessile drop technique, which consists of the deposition of a single droplet on the solid surface without any further addition of liquid as shown in Fig 3.9. The probe liquid was distilled water, each droplet had a volume of 10 µl, and data were recorded for each droplet, during 30 s, at a fixed interval of 1 s. The software traced the contour of the droplet on the surface of the sample; from the drop contour, two values of CA were obtained on the left and on the right intersection point solid-liquid-air; the final value of CA is the mean of these two values. For each sample of the artificial weathering test, the final values of CA were calculated as the average of 6 water droplets. For each sample of the outdoor weathering test, the final values of CA were calculated as the average of 5 water droplets.



Fig. 2.9. Schematic representation of static sessile drop measurement.

CA was also used to calculate the SE of pine and aspen wood after TM. Attention was focused, in particular, on changes in wettability, which has a practical relevance and economic significance. Wettability is important in coating, painting, and gluing: all these procedures can be enhanced by understanding the wetting behavior of wood after TM. To predict and understand the wetting of wood, it is necessary to study the surface free energy of wood [149], [150]. Without water, the other probe liquids are glycerol and formamide, which are generally considered suitable for this task, as already done in other works [151]. The device is equipped with an automated dispenser to always have the same volume of liquid (10  $\mu$ l for water, 7  $\mu$ l for glycerol and formamide). From the obtained values of CA and the ST of each probe liquid, the SE of wood can be calculated. Depending on the probe liquid, the number of droplets varies from 3 to 7 for each wood sample, and the obtained CA is the average value of these measurements. According to the used theory for the analysis of the SE, detailed information can be obtained on the polar and dispersive components of the SE of TTW.

CA was also measured for wood samples coated with different emulsions prepared during preliminary tests, in which the binders mixtures included or excluded LO or DBLO. These results can give information to characterize the film and to see how LO and DBLO contribute to the hydrophobicity of the coating film. During these measurements, water was used as a probe liquid, and the obtained CA was the average value of 5 measurements.

# **3. RESULTS AND DISCUSSION**

### **3.1.** Determination of the surface energy of wood

After TM, wood changes its chemo-physical properties: the most evident change is how wood becomes generally darker. It has been observed that the higher the temperature of TM the darker the wood becomes [2], [152], [153]. TM affects all the chemo-physical properties of wood, composition, structure and density, compared with unmodified wood [11], [154]. One of the changes in wood after TM, which is of interest in the field of paints and coatings, is its modified wettability: this means that the structural and chemical changes resulting from TM modify the relation between wood and water and eventually the wettability and other properties related to wettability are affected; in general, it can be assumed that wood becomes more hydrophobic [10], [155].

The parameter tightly connected to wettability is SE, as already indicated in other publications [149], [150], [156], and it is necessary to study it, to obtain information about the wetting properties of wood after TM. In this work, the determination of SE was done for both wood species, aspen (*Populus tremula*) and pine (*Pinus sylvestris* L.), and SE was compared among untreated and TTW samples, treated at different temperatures. For each temperature, six samples were selected, in order to measure CA in the radial direction, and cut approximately 100 mm long and 10 mm wide. Measuring CA in this way, the sorption of liquid into capillaries is reduced [157].

CA was measured using the static sessile drop technique, which consists in the deposition of a single droplet on the solid surface without any further addition of liquid. The probe liquids used were water, glycerol and formamide. The device is equipped with an automated dispenser that always dispenses the same volume of liquid (10  $\mu$ l of water, 7  $\mu$ l of glycerol and formamide).

Table 3.1

Component	Water, mN/m	Glycerol, mN/m	Formamide, mN/m
γ	72.80	64.00	58.00
$\gamma^{D} \left( \gamma^{LW} \right)$	21.80	34.00	39.00
$\gamma^{P}\left(\gamma^{AB}* ight)$	51.00	30.00	19.00
$\gamma^{\rm A}$	25.50	3.92	2.28
$\gamma^{\rm B}$	25.50	57.40	39.60
	* }	$\gamma^{AB} = 2\sqrt{\gamma^A \gamma^B}$	

Surface Tension (ST) of Probe Liquids and Their Components

Table 3.1 lists the ST of the three probe liquids and their components, the dispersive component  $\gamma^{D}$ , also referred to as Lifshitz–van der Waals (LW) component  $\gamma^{LW}$  and the polar component  $\gamma^{P}$ , also referred to as  $\gamma^{AB}$  (acid-base component), which is further divided into acid and base components  $\gamma^{A}$  and  $\gamma^{B}$ , respectively. The ST is then obtained from three values,

the dispersive component  $\gamma^{LW}$ , and the polar component  $\gamma^{AB}$ , intended as a combination of acid and base components  $\gamma^{A}$  and  $\gamma^{B}$ , respectively, according to the Lewis definition. The acid-base interactions do not include hydrogen bonding. Only a few probe liquids are used because they have sufficiently high ST not to wet out entirely the surface (zero CA), have high boiling points, and are reasonably safe. For both species of wood, aspen (*Populus tremula*) and pine (*Pinus sylvestris* L.), the TM temperatures are 160 °C, 170 °C and 180 °C and SE is calculated to evaluate how the polar and dispersive components change at each TM temperature.

# **3.2.** Effect of TM on the wettability of wood

The values of CA obtained with the three probe liquids are listed in Tables 3.2 and 3.3

Table 3.2

ASPEN	UNTREATED	160 °C	170 °C	180 °C
Water, °	$62.1 \pm 10.7$	$81.2\pm5.2$	$85.1\pm4.4$	$99.0\pm3.9$
Glycerol, °	$59.6 \pm 6.0$	$76.1 \pm 3.4$	$79.1\pm3.9$	$79.5\pm3.3$
Formamide, °	$36.7 \pm 8.2$	$55.4 \pm 5.0$	$64.1 \pm 5.4$	$63.5 \pm 2.8$

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

Table 3.3

Contact Angle of	Untreated and	Thermally	Treated Pine	with	Standard	Deviation (	(SD)
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PINE	UNTREATED	160 °C	170 °C	180 °C
Water, °	$88.9\pm0.8$	$91.9\pm6.6$	$98.3\pm7.0$	$108.2\pm4.0$
Glycerol, °	$80.2 \pm 1.9$	$84.5\pm1.5$	$90.4\pm3.7$	$97.4 \pm 1.2$
Formamide, °	$49.1\pm4.0$	$62.7 \pm 5.1$	$58.3\pm3.1$	$55.3 \pm 2.7$

Water gives the highest values of CA, and for both wood species, with the increase of the TM temperature, also CA increases, thus confirming the fact that wood becomes more hydrophobic after TM. Of the three probe liquids, formamide has always the smallest CA. During measurements, it was observed that the CA is higher on latewood than earlywood, as already confirmed from other works, due to the difference in surface roughness and different tracheid dimensions [158], [159]. In some cases, droplets spread too quickly on the surface, when using formamide, and eventually it was not possible to measure a meaningful CA because of the lack of symmetry of the droplet (right and left CA were totally different). The results shown in Tables 3.2 and 3.3 for both wood species, have a common growing trend line for each probe liquid, that indicates the increase of CA with the TM temperature; the only exception is for pine wood samples: going from the TM temperature of 160 °C to 180 °C, the CA does not increase linearly as it could be expected, but it goes in the opposite direction. A

possible reason is the structural changes in wood after TM, which becomes more porous and in the case of formamide which has the lowest ST, a faster absorption can be expected.

Another possible reason is the decrease of pH, which has been observed with increasing temperature and time of TM [160], [161], [162]. The decrease in pH can be explained by the production of organic acids during TM, already observed for pine, mainly by the degradation of hemicelluloses [163]. Also, the Lewis acid component as determined using CA data is a good relative measure for the variability of classical acidity and pH between different wood species [164].

The obtained values of CA are used to calculate the SE before and after TM at the selected temperatures of 160 °C, 170 °C and 180 °C for aspen and pine wood. There are several methods to calculate SE, depending on the mathematical approach and the information that can be obtained. The first approach is the Zisman theory, which simply defines the solid SE as being equal to the highest ST among those liquids that wet the solid completely [165]. After Zisman, two major directions have been developed, namely the components theories, which consider the different nature of intermolecular forces involved in surface wetting, and the equation of state theory, which can be considered as a further evolution of the Zisman method [166]. The component methods are generally more complicated but have the advantage of giving more information than the equation of the state and Zisman methods.

The method used in this work is the Wu method, which considers the polar and dispersive components of SE. In his equation, however, instead of the geometric mean, Wu used the harmonic mean for more accurate results, in particular, for high-energy systems [167]. 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. The following Equation is used for the calculation of SE.

$$\gamma_{sl} = \gamma_s + \gamma_l - \frac{4\gamma_s^D \gamma_l^D}{\gamma_s^D + \gamma_l^D} - \frac{4\gamma_s^P \gamma_l^P}{\gamma_s^P + \gamma_l^P}$$
(4.1)

where:

 $\gamma_{sl}$  – interfacial energy between the substrate and the liquid;

 $\gamma_s$  – SE of the substrate;

 $\gamma_1$  – SE of the liquid;

 $\gamma^{D}$  – dispersive component of SE;

 $\gamma^{\rm P}$  – polar component of SE.

In Tables 3.4 and 3.5, the SE of aspen and pine are reported, respectively, for the corresponding temperatures of TM.

The results are different, but for both species, the common trend is the decreasing of the polar component  $\gamma^{P}$  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 changed, whilst the polar component  $\gamma^{P}$  is almost down to half of the initial value. The SE after TM at 180 °C slightly decreased. At this temperature, a higher hydrophobic character of wood is obtained; in fact,

the polar component  $\gamma^{P}$  decreases by 93.6 % for aspen and by 92.2 % for pine. The great decrease of  $\gamma^{P}$  at 180 °C is compensated by the increase of the dispersive component  $\gamma^{D}$  by 59.8 % for aspen and by 24.6 % for pine.

Table 3.4

Sample	$\gamma = \gamma^{\rm D} + \gamma^{\rm P},  {\rm mN/m}$	γ <sup>D</sup> , mN/m	$\gamma^{P}$ , 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

Surface Energy of Aspen Before and After Thermal Modification

Table 3.5

Surface Energy of Pine Before and After Thermal Modification

Sample	$\gamma = \gamma^{\rm D} + \gamma^{\rm P},  {\rm mN/m}$	γ <sup>D</sup> , mN/m	γ <sup>P</sup> , 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

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.

### **3.3.** Wetting of TTW samples with binders

The properties of alkyd resins for protection of wood are well known and investigated, but mostly in solvent-based paints. In this study, the choice of alkyd resins, as the main binders, and the addition of DBLO to replace partially the alkyd resins in this coating were based on the consideration of the hydrophobic nature of wood after TM and the possibility for DBLO to be a suitable diluent, which can reduce the ST of alkyd as already investigated in another work [168]. To verify if the addition of DBLO can contribute to a better wetting of the wood surface, and hence improve the adhesion and penetration, preliminary tests with measurements of CA have been done using as probe liquids pure alkyd resins and mixtures of alkyd resins and DBLO, which was added at two different percentages, 12 % and 21 %, respectively. The obtained results for CA shown in Figs. 3.1 and 3.2 confirm that the addition of DBLO to alkyd resins increases the wetting of the TTW surface, thus increasing the surface of the contact between binders and wood. DBLO can be considered as an effective diluent, which is able to reduce the ST of alkyd resins.



Fig. 3.1. Contact angle of thermally treated aspen at 160 °C with alkyd and double boiled linseed oil (DBLO) at three different concentrations.



Fig. 3.2. Contact angle of thermally treated pine at 180 °C with alkyd and double boiled linseed oil (DBLO) at three different concentrations.

Alkyd resins alone also give a good wetting of wood surface, as can be seen from the low values of CA, but the presence of DBLO improves the wetting of wood, and the effect is higher with increasing amount of DBLO: with the concentration passing from 12 % to 21 %, the CA decreases by 16 % and 22 % for aspen, and by 12 % and 24 % for pine, respectively.

The bulking effect of the coating polymers in the cell voids and cell wall structure can improve the dimensional stability, check the resistance of the wood surface, and the penetration of the paint into the wood rays and cell lumens provides some mechanical strength to the wood [169]. This type of paint is formulated to form a very thin layer of coating on the surface of wood, but it is applied in a sufficient amount to leave visible the structure and grain of wood.

In conclusion, the adhesion is an important parameter in the wood-paint system, and the addition of DBLO gives a positive contribution to adhesion. By replacing part of alkyd resins with DBLO, other advantages are obtained; in fact, DBLO is a renewable resource, and it is cheaper than alkyd resins. DBLO contributes to the hardness of the film, although partially reduces its elasticity.

### **3.4.** Emulsification of binders

When passing from solvent-based to water-based formulations of alkyds, due to the insolubility of resins in water, it is necessary to use surfactants to dissolve them in water and obtain a homogeneous and uniform system. The role of a surfactant is to reduce the interfacial free energy of the two immiscible phases, to create new interfaces and facilitate the dissolution of the dispersed phase in the continuous one. Depending on the structure and

composition of a surfactant, it is possible to form o/w or w/o emulsions. The selection of a suitable surfactant depends also on the emulsifying substance, in this case, alkyds and vegetable oil, so they must have general characteristics that appeared to be necessary for emulsification of vegetable oils and alkyds.

In general, the most suitable surfactants are anionic and nonionic surfactants; cationic surfactants do not appear, from experimentation, to be useful for emulsification of vegetable oils and alkyds [136], [170]. Nonionic surfactants have traditionally been alkylphenol ethoxylates, but the environmental concern has caused a changeover to other ethoxylated surfactants, such as fatty alcohol ethoxylates or fatty acid monoethanolamide ethoxylates. Ethoxylates are the surfactants mainly responsible for dispersion stabilization [136].

The parameter which can help to quantify the emulsifying tendency of a surfactant and in which cases it can be suitably used, as determined by Griffin's studies, is the HLB, a balance of the size and strength of the hydrophilic and lipophilic moieties of a surfactant molecule [171]. The cases in which surfactants can be used, and what is their most suitable function, are already shown in Table 1.4.

### **3.5.** Testing of surfactants

The surfactants tested in this work and some of their properties are listed in Table 2.1. They are all nonionic surfactants, and they have been selected according to the producer's indications, as they are recommended for water-based paints.

The Carbowet series surfactants are linear ethoxylated alcohols, with a chain length varying from 9–11 (Carbowet 109, 125, 138) to 12–15 atoms of carbon (Carbowet 144).

The Dynol and Surfynol series are acetylenic based surfactants, all containing a triple bond: Dynol 800 and Dynol 810 are the same ethoxylated 2,5,8,11-tetramethyl-6-dodecyn-5,8 diol, but at 2 different concentrations, Surfynol 104A is a solution of 50 % 2,4,7,9-tetramethyl-5-decyne-4,7-diol in 2-ethylexanol, Surfynol 440 is ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and Surfynol 2502 is ethylene oxide-propylene oxide copolymer diether with 2,4,7,9-tetramethyl-5-decyne-4,7-diol (all surfactants of the Surfynol series are derived from 2,4,7,9-tetramethyl-5-decyne-4,7-diol).

To test these surfactants, attempts were made to emulsify alkyds and DBLO, using surfactants separately and mixed, at different concentrations up to 6 %. For example, two cases are listed:

- 1. Surfynol 104a (3.5 %) and Surfynol 2502 (2 %), tot. 5.5 %.
- 2. Dynol 810 (2.5 %) and Surfynol 440 (2.5 %), tot. 5 %.

The results show that Dynol and Surfynol series surfactants are not effective in the emulsification of alkyd resins and DBLO, they are not soluble in water and there is fast separation of phases. Although they are gemini surfactants, characterized by a particular structure consisting of two hydrophilic head groups and two hydrophobic tail groups, and for this reason they have a higher surface activity because of the larger total number of carbon in the hydrophobic chains [122], they are not good and suitable in this case.



The second series is the Carbowet surfactants series. Attempts were made to emulsify alkyds and DBLO also with these surfactants, using them separately and mixed, at different concentrations. Figure 3.3 shows the concentrations of surfactants. The results confirm that they are good emulsifiers and a white homogeneous emulsion can be obtained from them.

Carbowet surfactants can be used alone or combined together. In some cases, Carbowet surfactants were used also with Surfynol series surfactants: it is a common combination – the use of two surfactants with opposite character, one water-soluble and one oil-soluble – to contribute to the stability of the micelles. In general, one pure surfactant produces interfacial films that are not mechanically resistant as a film from two different surfactants can be [122].

The surfactants selected to emulsify alkyds and DBLO in the final paint formulation are Carbowet 125 and Carbowet 144, as they have longer chains and can contribute to a better stability, giving a thicker layer at the oil-water interface.

#### **3.6.** Size of micelles

The stability of an emulsion depends on several factors, and one of them is the size of micelles. A standard droplet in a colloidal dispersion, with a radius of 1  $\mu$ m, has a half-life of less than 1 s. The role of a surfactant is to create a potential energy barrier to extend the half-life of the droplets to days or years to obtain stabilization [121].

Stabilization can be achieved in different ways, which can also be combined. In general, it can be assumed that the smaller the droplet the better the stability, and the concentration and type of the surfactant has an important role in this case [172].

To check the influence of the concentration of surfactants on the size of droplets, two emulsions containing only water, alkyds, DBLO and surfactants have been prepared; they only differ in the concentration of surfactants, and their diameters have been measured with a microscope.

The concentrations of surfactants are 1.4 % and 2.0 %, respectively; in both cases, emulsions were white and homogeneous in their aspect. The results are shown in Figs. 3.4 and 3.5 for both concentrations, namely, 1.4 % and 2.0 %, respectively.



Fig. 3.4. Distribution of micelle diameter sizes for the emulsion with 1.4 % of the selected surfactants.



Fig. 3.5. Distribution of micelle diameter sizes for the emulsion with 2.0 % of the selected surfactants.

The white color of the emulsion is evidence that the size of the micelles is in the micrometric range. It is not possible in this case to obtain transparent emulsions with the available surfactants, which have a smaller size of micelles in the nanometric range. The goal is to obtain a stable system or at least stable enough within the time of use of the paint. Further studies to improve stability are necessary, which is not the main task of this research. The micelles are grouped into intervals of diameters; the values shown in Figs. 3.4 and 3.5 are the highest limit of the diameters for each interval. The lowest diameter, which can be measured with the microscope software, starts from 0.007 mm (7  $\mu$ m), and the largest group of micelles is the group with a diameter of up to 0.02 mm (20  $\mu$ m) for both concentrations, which is almost half of the measured micelles. For both cases, the distributions are similar and the first two groups of micelles with a diameter of up to 0.04 mm have practically the same amount of micelles. For the two concentrations, 1.4 % and 2.0 %, they are 67 % and 66 %, respectively, of the total number of micelles.

The concentration of surfactants of 1.4 % gives a similar emulsion as for the concentration of 2.0%. It is preferable to use the surfactants at a lower concentration for the final formulation; this will reduce other inconveniences, such as, for example, foam formation and will have lower impact on the final properties of the film.



Fig. 3.6. Spherical micelles of alkyd emulsion.

# **3.7.** Formation and properties of film

One of the main problems in the case of alkyd emulsions, compared to traditional solventbased paints, is drying. It is known that traditional metal driers like cobalt lose or reduce their ability to promote autooxidation and formation of an alkyd film, which is an undesired property because in this way the drying time is prolonged: this is due to partial deactivation of driers through absorption on pigment particles or complexation in water [83], [173]. Driers are divided into primary and secondary driers. Primary driers have always a catalytic activity in the oxidation process, whilst secondary driers show a catalytic activity only when used together with primary driers and, combined with them, become active, modifying the activity of primary driers [174], especially the through-drying, and contribute to improved film properties as, for instance, gloss and film hardness. Cobalt is the most widely used primary drier, but due to the growing concerns on the toxicity of cobalt salts, alternatives to cobaltbased driers are highly demanded [83], [114], [175]. Potential primary metal driers which can replace cobalt are manganese, iron or vanadium, which are less toxic. In a study to test the efficiency of the iron drier for alkyd resins, it was observed that the coating showed comparable drying rates, but dissimilar crosslinking kinetic activity compared with the cobalt drier [73]. In another research, to improve the catalytic activity of the iron drier, special additives were used to reduce the drying time and obtain better film hardness [175]. Also manganese has good potential to replace cobalt as a primary drier when used as a complex, and in the presence of bipyridine, significantly increases the rate of oxidation of ethyl linoleate, surpassing even the activity of the cobalt drier [72]. In this study, to test the efficiency of driers, Dry 0615 Aqua, based on manganese, Borchi Oxy Coat 1101, based on an iron complex, and cobalt have been used in three different emulsions, at the same concentration of 0.43 %. For each drier, 1 g of emulsion was put in a metal plate and allowed to dry for 24 h at room temperature; it was observed that a film was formed only from the emulsion containing cobalt, whilst for the other two driers, after evaporation of water, film formation was not observed. In this situation, they are not effective, but further investigation into the sequence of addition and other additives, which can improve the catalytic activity of the driers, is necessary. Despite the formation of a film with the cobalt drier, it was not yet completely dry and solid at touch; this confirms that the Co drier has a very high catalytic activity on the surfaces of alkyd films and less crosslinking happens under the superficial films as already observed in other researches [176].



Fig. 3.7. After 24 h the film with the drier Dry 0615 aqua (left) is not formed yet, whilst cobalt (right) has formed a solid film.

# **3.8.** Efficiency of different driers and drying time

To compare the catalytic activity of the three driers, curing of resins as a part of the film formation process has been monitored using FTIR spectroscopy. In Fig. 3.8, different peaks corresponding to specific chemical groups or bonds are visible, for the solution containing the cobalt drier. The results for Dry 0615 Aqua (manganese) and Borchi Oxy Coat 1101 (iron complex) are quite similar, but the areas of characteristic peaks are different, which can be considered as an indicator of different rates of auto-oxidation during the curing of resins. The important changes during film formation are related to double bonds, which change during auto-oxidation and this can be seen, for example, from specific peaks at 3007 cm<sup>-1</sup> and 970 cm<sup>-1</sup>. The peak on the right side of the graph at 970 cm<sup>-1</sup> indicates that reactions of cross-linking of alkyd molecules take place: there is a 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<sup>-1</sup> 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. 3.8. 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  $3007 \text{ cm}^{-1}$  still remains unchanged [73]. In our experiment, for samples with the cobalt drier, the induction time is about 1 h, and for Borchi Oxy Coat 1101 and Dry 0615 Aqua, at least 4 h and 6 h, respectively; such a big difference in induction times based only on this peak observation is not the only evidence available. In fact, from an empirical point of view, at the induction time corresponds approximately also the formation of a solid film on the glass support prepared for the FTIR tests. This is a confirmation of a higher efficiency of the cobalt drier.



Fig. 3.9. Detailed and shifted FTIR spectra for three driers at 3450 cm<sup>-1</sup> changing during 24 h.

The wide band around 3450 cm<sup>-1</sup> 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 [177] but most probably the hydroxyl group is from the reaction with oxygen and the formation of hydroperoxides [73]. Hydroperoxides then decompose into alkoxy and hydroxyl radicals [178]. In Fig. 3.9, the formation of -OH groups is shown for the three driers. It is evident that for the cobalt drier, the area 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 cobalt 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 (see Fig. 3.10).



Fig. 3.10. Comparison of the area of -OH group peaks for three driers after 24 h.

Figure 3.11 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:

$$\frac{A_t - A_{t=0}}{A_0}$$
, (4.2)

where:

 $A_t$  – area of -OH groups versus time (band at 3450 cm<sup>-1</sup>);  $A_{t=0}$  – initial value of the area of -OH groups (band at 3450 cm<sup>-1</sup>);

 $A_0$  – normalized peak (band at 1275 cm<sup>-1</sup>).

The peak at 1275 cm<sup>-1</sup> is the ester peak (stretching of -COOR). The initial value A<sub>0</sub> 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. 3.11. Monitoring of -OH groups for three driers during auto-oxidation of resins.

# **3.9.** Effect of drier on the stability of the emulsion

Another experiment was conducted to check the effect of the concentration of the drier in film formation, and three emulsions containing the cobalt drier at three different concentrations -0.43 %, 0.86 % and 1.29 % – were prepared. It was observed that the concentration of the cobalt drier influences the stability of the emulsion. After 24 h from the preparation of the three emulsions, a layer of creaming was observed in all three samples, but with different thickness: the higher the concentration, the thicker the creaming layer, as shown in Fig. 3.12.

The process is reversible; by manual mixing the emulsion returns uniform and homogeneous, but for precaution, it is recommended to use sonication before applying a new layer of paint on the wood surface. Samples of wood were coated with two thin layers of paint for each concentration of the cobalt drier and allowed to dry for 24 h before the application of the next layer. Both layers after 24 h are dry at touch, independently of the concentration, thus confirming the efficiency of the cobalt drier for alkyd resins. It is recommendable to use the lowest concentration of the drier to have less problems of stability with emulsion and also to possibly use the lowest amount of cobalt. Also, an anti-skinning additive is necessary, since the increased concentration of the binder in the creaming layer during storage can lead to the formation of a film which can give economical loss [173].



Fig. 3.12. Thickness of the creaming layer of three emulsions after 24 h at different concentrations of cobalt drier.

#### 3.10. Glass transition temperature of coating

An important property of coating films is flexibility, which determines how much resistant the coating is during the service life. In the case of wood, moisture gradients induce swelling and shrinking thus making its dimensions to vary, provoking mechanical stress to the wood, and it is very important to apply coatings with a sufficient flexibility in order to follow without rupture the continual dimensional changes of wood in exterior service [179].

An important indicator in this situation is the glass transition temperature  $(T_g)$ , which indicates the gradual and reversible transition in amorphous materials from a hard and relatively glassy state into a viscous or rubbery state with increasing temperature. If a coating film has a  $T_g$  that is higher than the usual temperature of service, then the film is in the more rigid, glassy state, which is characterized by brittleness, and in this case, due to shrinking and swelling, cracking of the film is facilitated and its barrier properties are reduced.

The optimal condition then is to have a  $T_g$  lower than the usual temperature of the service of the film; in this situation, the film will be in the rubbery state, and can adapt to the changing of wood dimensions, with less formation of checks and cracks. It has been observed that, in general, during weathering,  $T_g$  increases and several conditions can affect its value [117], [179].

In this experiment, the DBLO added to the alkyd is supposed to act as a plasticizer, and to check this hypothesis,  $T_g$  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 [180] and can decrease its  $T_g$  which has also positive effects on the properties of the film [181]. The  $T_g$  for amorphous polymers is not a specific temperature but it is an interval of temperatures and there are

several evaluation possibilities for 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 a  $T_g$ . The results are shown in Table 3.6 and compare three samples for both types of the film.

Table 3.6

method	Midpoint DIN*		Inflection point**		Midpoint***	
binders	alkyd	alkyd + DBLO	alkyd	alkyd + DBLO	alkyd	alkyd + DBLO
<i>T</i> <sub>g1</sub> , ℃	-12.48	-13.75	-14.94	-9.02	-12.47	-13.95
<i>T</i> <sub>g2</sub> , ℃	-10.56	-12.38	-6.19	-10.61	-10.39	-11.80
<i>Т</i> <sub>g</sub> 3, °С	-5.91	-8.64	-11.36	2.73	-7.57	-8.70

Values of  $T_{\rm g}$  from Different Methods for Alkyd Films with and without DBLO

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

In general, the addition of DBLO makes the  $T_g$  to decrease, which was 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 the glass transition temperature, the results are in line with the literature sources and confirm the plasticizing effect of DBLO for alkyd resins.

#### **3.11.** Evaluation of the hydrophobicity of coated wood samples

The use of paint for the protection of TM wood has the main function to delay photodegradation and penetration of water under the wood surface, which can start and propagate a series of degradation reactions [6], [182]. To verify if the replacement of part of alkyd resins with LO or DBLO can affect positively or negatively the hydrophobicity of paint, thus reducing or increasing the water permeability, different emulsions containing alkyd resins and alkyd/LO or alkyd/DBLO have been prepared and applied on samples of aspen modified at 160 °C to measure CA. To leave the appearance and texture of wood visible after TM, the alkyd emulsion is applied on the wood surface in a small amount; in this way it does not form a thick film. The ratio between alkyd resins / LO and between alkyd resins / DBLO considered optimal in the emulsions is 4:1. Fig. 3.13 shows the CA of water on the surface of wood samples coated with different alkyd emulsions.

The values of CA are measured during 30 s and the equilibrium is reached after 4 s, when the diameter of the water droplet becomes constant. For these samples, two or three layers of paint are applied and allowed to dry for 24 h before the application of the next layer of paint.



Fig. 3.13. 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).

It is generally assumed that a surface is considered hydrophobic when the CA is above 90 ° and hydrophilic when the CA is below 90 °. Except for the first result, which however is very close to 90°, all the tested emulsions give good results in terms of the hydrophobicity of the wood surface. The presence of LO or DBLO positively affects the hydrophobicity, which, in fact, is increased on an average basis; CA is higher in the presence of LO and DBLO, which confirms the positive effect of the partial substitution of alkyd resins. The final results, which are the average value of more CA for each sample, can be affected by the morphology of the wood surface, it is well known that different parts of wood have different wetting properties: earlywood is more porous and has greater roughness; thus it wets more easily than latewood, which has the opposite characteristics [156], [183]. Moreover, the coating is applied in a very thin layer for a decorative purpose, to leave visible the wood grain. In this way, the obtained CA values are a measure of the hydrophobicity at the interface of the woodcoating system; this explains the different standard deviations obtained for the CA, which can be larger or smaller depending on the samples. The emulsions prepared for these CA tests have total resin content (TRC) varying from 20 % to 30 %. The presence of LO or DBLO can affect the final composition of the cured film: it is possible to have a non-homogeneous distribution of binders in the film itself, giving place to stratification during the curing of the film. In the stage of the film formation when the solvent has evaporated, part of LO and DBLO can migrate to the upper layer of the film; this migration from the substrate towards the surface is driven by different densities of alkyds and LO or DBLO, and tends to minimize the interfacial energy, so it can be assumed that LO or DBLO could act as surface active polymers as already observed in a study with other compounds obtained from chemical modification of LO [184]. If we compare the CA of samples coated only with alkyds and that of those containing also LO or DBLO, a different slope of the curve can be observed during the 30 s of measurements. In Fig. 3.14, there is only alkyd as a binder, and the values of CA are practically constant during 30 s, with a horizontal curve. The situation is different in the presence of LO and DBLO: as shown in Fig. 3.15, the slope is higher, and the final CA is by 10 % (A + LO-2) to 17 % (A + DBLO-4) smaller than the initial values. The possible reason

is the presence of LO and DBLO and their migration on the upper layer of the film as supposed above: as these two oils have a slower drying than alkyds, if they migrate on the upper layer of the film, they can act as surfactants and, in contact with water, their hydrocarbon tails make to decrease the ST of water, thus an increase of wetting of the surface can be expected.



Fig. 3.14. Curve of the contact angle of coated thermally treated wood samples with different emulsions containing only alkyd resins (A).



Fig. 3.15. Curve of the contact angle of coated thermally treated wood samples with different emulsions containing alkyd resins (A) and linseed oil (LO) or 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, considered 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.

#### **3.12.** Artificial weathering of wood samples

One of the most noticeable and fast changes happening on the wood surface during weathering is the change of color mainly as a result of the action of photodegradation and photo-oxidation, and it applies also for TTW [185], [186], [187].

Figure 3.16 shows the differences in structure 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

apertures elongate in an oval shape and small cracks have formed. The fibers start to separate, and wood becomes less compact. This is the evidence of the degradation carried out by UV radiation.



Fig. 3.16. Comparison of the uncoated thermally treated wood structure before (a) and after (b) UV irradiation with SEM at 2000× magnification.

Pigments can enhance the paint efficiency, providing protection against the photodegradation of wood. The main goal of this part of the work is to determine the optimal concentration of pigments, and artificial weathering can give useful information in this case. Initially, the three types of pigments can be characterized by their reflectance spectra to see how much they differ from each other. The spectrophotometer used to measure the color changes is also equipped to measure reflectance once the light irradiates the surface, but only for the interval of wavelengths going from 360 nm to 740 nm, which corresponds to the region of the visible spectrum. As an example in Fig. 3.17, for samples coated with two layers of alkyd emulsion containing 4 % of iron oxide pigments, there are no significant differences in reflectance for the three pigments, which is not surprising, since they are the same type of iron oxide; so, the use of one or another pigment does not give fundamental differences in terms of decorative properties. All the three pigments have the same color, according to the information provided by the producer, which can be deducted also considering the similarity of the measured reflectance. The small differences can be due to the size and aggregation state of the particles of iron oxides [188], [189].



Fig. 3.17. Reflectance of three types of iron oxide pigments for samples coated with two layers of alkyd emulsion with the pigments' concentration of 4 %.

The three pigments are offered in different formulations and composition, two in a powder form and one aqueous solution, and to select one of them as the most effective additive for the alkyd emulsion, it is necessary to check their efficiency against weathering and the capability to protect the appearance of wood. 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. The results are shown in Fig. 3.18, and it can be evaluated how the number of applied layers and the concentration of pigments are efficient against photodegradation.



Fig. 3.18. Color changes of coated thermally treated wood – comparison of three types of iron oxide pigments at two concentrations.

The artificial weathering test was done preparing alkyd emulsions containing red iron oxide pigments at two concentrations of 4 % and 8 %. The concentrations were selected according to a previous project on wood coatings, where it was determined the optimal concentration of pigments for solvent-based paint, and also considering the claims of our Latvian patent for a coating for thermally treated wood. The prepared alkyd emulsions were applied on both aspen and pine TTW samples, which were coated with two or three layers of alkyd emulsion. The comparison of the obtained results gives information about the role of both parameters against photodegradation: concentration and number of layers. The threshold of clearly visible color changes for the human eye is generally established and accepted to be a value of DEab between 2 and 3 and more [190], [191]. The obtained results show that both the concentration and the number of layers play an important role against photodegradation. As it could be expected, the higher concentration of 8 % gives the best results; in fact, except

for the samples coated with two layers of the paint containing Luconyl pigment, at the end of the artificial weathering test, DEab is lower than 3 units independently of the number of layers. The highest values of DEab can be observed for samples coated with 2 layers of the alkyd emulsion having a concentration of pigment of 4 %. For these samples, after 175 h of UV irradiation, the value of DEab is between 2 units and 3 units; then, at the threshold of visible color, it changes. However, the analysis of the obtained results shows that, also with the pigments' concentration of 4 %, acceptable results can be obtained, for example, with Sicotrans pigments and three layers of paint, the final value of DEab is only 2.1 units, which is the best result among the three pigments. Speaking about the pigments singularly, there is not a better one than the others, since they are practically the same molecule. The results confirm that pigments based on transparent iron oxide give particularly good protection against photodegradation.

Other important factors we must consider in this case is the amount of pigments on the surface of wood samples and whether there is a correlation with color changes, DEab. In Figure 3.19, the values of DEab for samples coated with two and three layers of paints, after 1000 h of artificial weathering, are compared. Considering the highest threshold of DEab = 3as the limit for visible color changes, it can be observed that the number of layers applied on the surface influences the color changes: 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  $R^2$ . There are cases where for the same amount of pigments, DEab has very different values; in this case, it should be investigated whether there is a non-homogenous distribution of pigments during the application of paint, which could be a possibility; although visually the painted wood surface looks uniform, it has been verified that the applied pigments are preferentially deposited in the cavities of the wood surface [192]. Moreover, in the case of three layers of paint, a thicker film can be expected which also is more efficient in reducing photodegradation. In this case, the application of more layers of coating leads to the overlaying of pigment particles, which can scatter more UV radiation and avoid its direct contact with wood.



Fig. 3.19. Correlation between the amount of pigments and the color changes DEab.

An evident example is for two samples with two layers of coating with the same amount of pigments 8.57 g/m<sup>2</sup>, where 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. 3.20. Lightness  $L^*$  of coated thermally treated aspen (A) during artificial weathering. AN-M: N – number of layers, M - % of pigments.



Fig. 3.21. Lightness  $L^*$  of coated thermally treated pine (P) during artificial weathering. PN-M: N – number of layers, M - % of pigments.

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. 3.20 and 3.21, respectively. In particular, for pine, the earlywood portion of the surface is more affected, and it becomes clearer than the latewood. For aspen wood samples, the increase of lightness is more uniform, and it regards the whole surface of the sample. The samples coated with alkyd emulsion containing 8 % of pigment concentration have better results. For both aspen and pine wood, the lightness  $L^*$  is practically unchanged for the first 225 hours (15 h<sup>1/2</sup>) 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. 3.22. Increase of the surface lightness of coated aspen (left) and pine (right) wood samples after artificial weathering.

In conclusion, it is recommended to use the higher concentration of pigments to provide a better protection of wood surface, especially as in the case when a non-film forming coating is used similarly to other researches [12]. The type of iron oxides, their size and aggregation state also can have a key role against discoloration.

# 3.13. Contact angle before and after artificial weathering

The measurement of CA was done for both wood species, aspen and pine, and the results are shown in Figs. 3.23 and 3.24, respectively. In general, it can be observed that aspen wood samples have higher values of CA than pine, but this could be due to the fact that for pine samples, the measurements of CA were done on latewood portions of the wood surface. 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 good hydrophobicity of the coated surface could be surprising, considered that the used iron oxide pigments are hydrophilic compounds (they are water soluble). An explanation could be that the hydrophilic iron oxide is also coated and sealed by the binders. In another work, an increase of CA with increasing iron oxide pigment concentration has been observed, which can be related to the roughness of the wood surface [192], but in this case, passing from the pigment concentration of 4 % to 8 %, such a correlation was not observed.



Fig. 3.23. Contact angle of coated thermally treated aspen wood samples before and after artificial weathering.



Fig. 3.24. Contact angle of coated thermally treated pine wood samples before and after artificial weathering.

Among the used pigments, the only problem was with Xfast pigments. In this case, there is a bad adhesion to the wood surface and to the binders: during the measurement of CA, in fact, it was observed that pigments are easily washed away with the water droplet as can be seen in Fig. 3.25, leaving clear visible circular spots on the surface. For this reason, the use of Xfast pigments in the presence of water is not recommendable, as the leaching of pigments will reduce the resistance against UV radiation and the wood will be subjected to a faster color change.





# 3.14. Outdoor weathering of wood samples

The artificial weathering allowed verifying that iron oxide pigments give good protection against photodegradation, although in a controlled situation with set parameters and only under UV irradiation. More information can be obtained during weathering in outdoor conditions, where not only the amount of UV radiation changes but wood is also subjected to the action of water in the form of moisture or precipitations. This information can give a better knowledge about the performance of alkyd emulsion. To compare their performance, the wood samples were coated with two alkyd paints, one water-based and one solvent-based, with the same concentration of binders and pigments. The uncoated TTW sample is used as a control sample.



Fig. 3.26. Color changes of aspen during outdoor weathering, S – solvent; W – water.



Fig. 3.27. Color changes of pine during outdoor weathering, S – solvent; W – water.

The obtained results in Figs. 3.26 and 3.27 show that two layers of alkyd emulsion give a better protection against discoloration than two and three layers of the solvent-based alkyd paint. The color changes happen quickly during the initial stage of the test. The color changes are faster in the first three months, and this can be observed for both wood species; during the remaining period of outdoor exposure, the color changes happen constantly but slowly. It is visible that, compared to the case of artificial weathering, the color changes are much higher, for example, in the case of pine, already after 3 months, DEab is near to 10 for solvent-based alkyd paint, but for alkyd emulsion, DEab has a value of about 4. The higher color changes can be explained with the action of moisture and swelling and shrinking caused by its variations, which facilitates photodegradation [16]. 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 [29]. 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 chromophoric groups of lignin, the main ones responsible for the color changes of wood [64].
# 3.15. Analysis of color coordinates $L^*$ , $a^*$ , $b^*$

In Tables 3.7 and 3.8, all the color coordinates changes are listed for  $DL^*$ ,  $Da^*$  and  $Db^*$ . 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, [193], [194], [195] 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 [64].

Table 3.7

Aspen	time, days	DL*	Da*	Db*
	0	0	0	0
	30	$10.9 \pm 1.6$	$-3.6 \pm 0.5$	$-2.9 \pm 1.2$
	60	$16.0 \pm 3.4$	$-5.5 \pm 0.1$	$-9.0 \pm 1.1$
Control	90	$15.8 \pm 4.7$	$-6.4 \pm 0.5$	$-10.9 \pm 1.0$
Control	250	$13.5 \pm 5.2$	$-8.3 \pm 0.4$	$-15.4 \pm 1.1$
	350	$11.4 \pm 5.2$	$-8.7 \pm 0.5$	$-16.6 \pm 1.6$
	440	$6.3 \pm 4.1$	$-8.9\pm0.5$	$-17.1 \pm 1.5$
	640	$6.9 \pm 0.8$	$-9.1 \pm 0.6$	$-17.9 \pm 1.5$
	0	0	0	0
	30	$1.6 \pm 0.3$	$1.9 \pm 0.4$	$1.5 \pm 0.3$
	60	$2.7 \pm 0.4$	$3.7 \pm 0.6$	$3.1 \pm 0.6$
Solvent	90	$3.5 \pm 0.7$	$4.3 \pm 0.6$	$4.0 \pm 0.9$
3 layers	250	$3.5 \pm 0.6$	$3.8 \pm 0.5$	$4.3 \pm 0.9$
	350	$5.8 \pm 0.8$	$5.6 \pm 0.6$	$6.5 \pm 1.0$
	440	$6.9 \pm 0.6$	$4.9\pm0.7$	$5.9 \pm 1.0$
	640	$5.8 \pm 0.4$	$3.9\pm0.8$	$5.6 \pm 1.0$
	0	0	0	0
	30	$2.3 \pm 0.3$	$3.2 \pm 0.5$	$2.7 \pm 0.4$
	60	$3.5 \pm 0.4$	$5.3 \pm 0.8$	$4.8 \pm 0.9$
Solvent	90	$3.8 \pm 0.4$	$6.1 \pm 0.5$	$5.8 \pm 0.5$
2 layers	250	$6.7 \pm 4.4$	$4.5 \pm 0.8$	$5.9 \pm 0.8$
	350	$5.5 \pm 0.8$	$6.6 \pm 0.6$	$8.3 \pm 1.2$
	440	$6.0 \pm 0.7$	$6.5 \pm 0.4$	$8.8 \pm 1.0$
	640	$4.3 \pm 0.8$	$5.0 \pm 0.6$	$7.7 \pm 1.1$
	0	0	0	0
Water	30	$1.7 \pm 0.4$	$1.4 \pm 0.6$	$0.6 \pm 0.3$
	60	$2.6 \pm 0.5$	$2.4 \pm 0.8$	$1.0 \pm 0.6$
	90	$2.9 \pm 0.6$	$2.5 \pm 1.0$	$1.3 \pm 0.6$
2 layers	250	$2.9 \pm 0.7$	$2.4 \pm 0.8$	$1.2 \pm 0.6$
	350	$4.6 \pm 0.9$	$3.8 \pm 1.1$	$2.2 \pm 0.9$
	440	$5.5 \pm 1.3$	$3.3 \pm 1.3$	$2.1 \pm 1.3$
	640	$4.3 \pm 0.9$	$1.6 \pm 1.3$	$1.5 \pm 1.3$

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

Table 3.8	Ta	ıbl	e	3	.8	)
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Pine	time, days	DL*	Da*	Db*
	0	0	0	0
	30	$6.9 \pm 0.2$	$-0.1 \pm 0.1$	$4.9 \pm 1.2$
	60	$11.8 \pm 1.3$	$-1.5 \pm 0.3$	$0.9 \pm 1.7$
Control	90	$14.0 \pm 1.7$	$-2.3 \pm 0.4$	$-1.4 \pm 1.3$
Control	250	$13.8 \pm 2.2$	$-5.8\pm0.3$	$-9.2 \pm 1.3$
	350	$14.0 \pm 1.9$	$-6.4 \pm 0.2$	$-10.9\pm1.0$
	440	$10.7 \pm 2.8$	$-7.4 \pm 0.2$	$-12.9\pm0.7$
	640	$11.8 \pm 3.5$	$-7.8 \pm 0.3$	$-14.3\pm1.0$
	0	0	0	0
	30	$3.8 \pm 0.2$	$4.3 \pm 0.7$	$4.1 \pm 0.4$
	60	$5.3 \pm 0.4$	$5.6 \pm 0.6$	$5.6 \pm 0.5$
Solvent	90	$5.6 \pm 0.5$	$5.6 \pm 0.7$	$5.8 \pm 0.5$
3 layers	250	$4.4 \pm 0.6$	$3.5 \pm 0.9$	$4.4 \pm 0.5$
-	350	$5.8 \pm 0.9$	$4.6 \pm 0.8$	$5.8 \pm 0.2$
	440	$5.4 \pm 0.8$	$4.0 \pm 0.7$	$5.6 \pm 0.2$
	640	$4.4 \pm 0.8$	$2.8 \pm 0.8$	$5.3 \pm 0.5$
	0	0	0	0
	30	$5.1 \pm 0.4$	$4.2 \pm 1.0$	$4.2 \pm 0.8$
	60	$5.3 \pm 0.6$	$5.2 \pm 1.0$	$5.4 \pm 0.7$
Solvent 2 layers	90	$4.9 \pm 0.5$	$5.5 \pm 1.2$	$5.9 \pm 0.7$
	250	$3.0 \pm 0.3$	$2.7 \pm 0.8$	$4.0 \pm 0.3$
	350	$3.7 \pm 0.8$	$3.0 \pm 0.5$	$4.7 \pm 0.1$
	440	$3.5 \pm 1.2$	$2.3 \pm 0.4$	$3.9 \pm 0.2$
	640	$2.8 \pm 1.6$	$0.7 \pm 0.7$	$2.8 \pm 0.3$
	0	0	0	0
Water	30	$1.7 \pm 0.2$	$2.3 \pm 0.4$	$1.7 \pm 0.4$
	60	$2.3 \pm 0.3$	$3.1 \pm 0.3$	$2.1 \pm 0.4$
	90	$2.4 \pm 0.2$	$2.5 \pm 0.8$	$1.7 \pm 0.3$
2 layers	250	$2.3 \pm 0.3$	$2.4 \pm 0.7$	$1.8 \pm 0.4$
-	350	$3.8 \pm 0.6$	$2.9 \pm 1.0$	$2.0 \pm 1.3$
	440	$4.6 \pm 0.2$	$1.9 \pm 0.9$	$1.3 \pm 1.6$
	640	$4.2 \pm 0.2$	$0.7 \pm 1.3$	$0.7 \pm 2.0$

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

Observing Fig. 3.28, 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 values of  $a^*$  are quite similar for all the coated samples, and it can be observed that after the initial increase, they converge to the same point. For aspen wood samples, the initial value of  $a^*$  is greater for uncoated control samples than coated samples. The other color coordinate  $b^*$  of control samples of pine also decreases during weathering, but for coated samples, 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. 3.29). A possibility could be to select other colored iron oxide pigments, for example yellow iron oxide hydrate, and mixing appropriate proportions of both pigments, to investigate which concentration is suitable to obtain the same situation for the  $b^*$  color coordinate.



Fig. 3.28. Change of color coordinate  $a^*$  during outdoor weathering of pine, S – solvent; W – water.



Fig. 3.29. Change of color coordinate  $b^*$  during outdoor weathering of pine, S – solvent; W – water.

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  $L^*$  (Fig. 3.30). Similarly to the case of artificial weathering, lightness  $L^*$  increases also during outdoor weathering, but in greater amount. 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.



Fig. 3.30. Change of Lightness  $L^*$  of pine (left) and aspen (right) wood samples during outdoor weathering, S – solvent; W – water.

#### 3.16. Contact angle before and after outdoor weathering

The increase of wettability during weathering is a well-known phenomenon, which happens also for TTW; despite its improved dimensional stability, the formation of checks has been observed also in this case [197], and this is one of the reasons of the increased wettability of wood.

The average wettability values are shown as CA in Figs. 3.31 and 3.32 for coated aspen and pine TTW samples, respectively.



Fig. 3.31. Contact angle of coated thermally treated aspen wood samples during outdoor weathering, S – solvent; W – water.



Fig. 3.32. Contact angle of coated thermally treated pine wood samples during outdoor weathering, S – solvent; W – water.

Surprisingly, the initial values of CA are lower than 90°, which is considered the point of the switch from the hydrophobic character to the hydrophilic one, since it has been demonstrated from measurements of CA for random TTW samples coated with alkyd emulsions (Fig. 3.13) 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. A possible explanation could be in the characteristics of the surface of the specific used wood samples, 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.

Another possible explanation is the incomplete drying of binders at the moment of the initial measurement of CA, the hydrocarbon tails of the binders migrating at the surface of the coating film can reduce the ST of water, which can spread on the surface.

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 under the wood surface. 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 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 [29]. From the obtained results, it can be concluded that two layers of the alkyd emulsion have the same barrier properties as three layers of solvent-based alkyd paint.

# 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 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 autooxidation 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.

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# ATTACHMENTS

Attachment 1.

Creaming of alkyd emulsions of different composition after 24 h





#### Attachment 2.

Effect of the cobalt drier concentration on the stability of alkyd emulsion after 24 h



# Concentration of cobalt 0.43 %



# Concentration of cobalt 0.86 %



Concentration of cobalt 1.29 %

Attachment 3.

Influence of different types of driers on film smoothness



Film formation with the Borchi Oxy Coat 1101drier



Film formation with the Dry 0615 Aqua Drier





FTIR spectra of resins for the manganese based Dry 0615 Aqua drier versus time



FTIR spectra of resins for the iron based Borchi Oxy Coat 1101drier versus time

Reflectance of coated thermally treated wood samples with different pigment concentration and number of layers during artificial weathering



time	DEab 2 layers 4 %			DEab 3 layers 4 %		
(h)	Xfast	Luconyl	Sicotrans	Xfast	Luconyl	Sicotrans
0	0.0	0.0	0.0	0.0	0.0	0.0
21	0.8	0.6	1.0	0.8	0.4	0.5
42	1.4	1.0	1.4	1.3	0.7	0.6
61	1.5	1.2	1.7	1.1	0.6	0.7
84	1.9	1.3	2.1	1.6	0.7	0.9
130	2.2	1.6	2.4	1.6	0.9	1.0
175	2.5	2.2	3.0	2.4	1.1	1.3
220	2.9	2.4	3.1	2.3	1.3	1.4
390	4.2	3.4	3.9	3.4	1.9	2.1
600	5.1	4.5	4.6	3.7	2.6	2.5
1000	6.1	5.7	5.2	4.8	3.5	2.1

Artificial weathering – values of DEab for samples coated with the alkyd emulsion containing 4 % of pigments

Artificial weathering – values of DEab for samples coated with the alkyd emulsion containing 8 % of pigments

time		DEab 2 layers	s 8 %	DEab 3 layers 8 %		
(h)	Xfast	Luconyl	Sicotrans	Xfast	Luconyl	Sicotrans
0	0.0	0.0	0.0	0.0	0.0	0.0
21	0.7	0.5	0.8	0.8	0.2	0.6
42	1.1	0.7	1.1	1.0	0.2	0.9
61	1.1	1.0	1.0	1.1	0.3	1.0
84	1.1	1.1	1.1	1.1	0.3	1.0
130	1.0	1.2	1.0	1.0	0.4	0.8
175	1.3	1.4	1.1	1.3	0.3	0.8
220	0.9	1.6	0.9	0.9	0.4	0.5
390	1.1	2.3	1.3	0.9	1.1	0.8
600	1.6	2.8	1.7	1.4	1.7	1.4
1000	1.8	3.8	1.8	1.5	2.3	1.0

# Artificial weathering – DEab of coated thermally treated wood samples for different types of pigments



DEab of wood samples coated with the alkyd emulsion containing xfast pigments



DEab of wood samples coated with the alkyd emulsion containing luconyl pigments



DEab of wood samples coated with the alkyd emulsion containing sicotrans pigments

# Attachment 8.



Outdoor weathering of pine and aspen coated wood samples with solvent-base and waterbased alkyd paints



Change of the color coordinate  $a^*$  of aspen during outdoor weathering



Change of the color coordinate  $b^*$  of aspen during outdoor weathering

Coating type	time (days)	Pine CA, °	Aspen CA, °
	0	$83.9 \pm 1.4$	$82.7 \pm 1.4$
	30	$84.6 \pm 6.9$	$74.3\pm8.6$
	60	$90.0 \pm 5.1$	$82.0 \pm 2.1$
Solvent	90	$81.4 \pm 5.5$	$74.3 \pm 0.3$
2 layers	250	$68.3 \pm 1.9$	$54.0 \pm 3.7$
	350	$51.4 \pm 24.2$	$37.5 \pm 7.7$
	440	$42.6 \pm 1.0$	—
	640	-	—
	0	$86.7 \pm 0.4$	$80.6\pm0.0$
	30	$82.1 \pm 3.8$	$78.1\pm2.0$
	60	$80.4 \pm 8.7$	$80.9 \pm 2.6$
Solvent	90	$78.6 \pm 5.0$	$74.3 \pm 2.4$
3 layers	250	$66.0 \pm 2.5$	$61.3 \pm 3.7$
	350	$66.1 \pm 8.4$	$54.4 \pm 0.8$
	440	$46.1 \pm 16.0$	$41.1 \pm 3.5$
	640	$38.6 \pm 1.0$	$45.2 \pm 13.4$
	0	$83.6 \pm 0.1$	$78.2 \pm 5.2$
	30	$68.1 \pm 1.0$	$72.4 \pm 4.7$
	60	$70.7 \pm 5.0$	$76.0\pm5.8$
Water	90	$61.4 \pm 1.3$	$63.9 \pm 4.3$
2 layers	250	$54.7 \pm 3.4$	$59.5 \pm 4.0$
	350	$50.2 \pm 9.6$	$49.2 \pm 9.1$
	440	$44.3 \pm 6.5$	$42.7 \pm 6.2$
	640	$46.6\pm5.8$	$36.7 \pm 2.7$

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