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EFFECT OF APPLICATION PARAMETERS ON CHEMICAL AND MECHANICAL PROPERTIES IN UV COATINGS

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ABSTRACT

Vilma Turunen: Effect of Application Parameters on Chemical and Mechanical Properties in UV Coatings
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The goal of the thesis was to study the effect of different application parameters to the curing of ultraviolet coatings intended for wood substrate. Another purpose for the work was to evaluate and develop further methods for the testing of the achieved cure level from the coating. The chosen test methods for the work were gloss, pendulum hardness, chemical resistance, potassium permanganate stain and mechanical scratching test.

Two different types of UV curing coatings were selected for the work: acrylate lacquer and acylate paint. Samples from the coatings were prepared by changing the application amount and the UV energy that the coating films were exposed to. Substrate used varied depending on the test requirements. Application of coatings was done with single side bar coater film applicator and roller coaters.

The variation in curing level between the samples caused differences in the test results. In some tests the differences between the samples were minor but big differences were also noticed. Usefulness of each test also varied between the two chosen coatings. When comparing the required UV energy to achieve good results from the test performed, it was also noticed that the differences between the tests are big.

From the chemical resistance test the results were good even with the lowest energy levels tested. Based on the testing the R2 and R4 test classification from the IOS-MATT for the UV curing coatings is too easy. Biggest difference noticed from this test was between the two different application amounts from the same products. With thicker film thickness the results were slightly better than with thinner film.

Usefulness of the gloss and pendulum hardness test varied between the two different coatings chosen. Gloss varied more during the testing with the matt lacquer sample and the effect of lowering the curing energy was visible as the gloss increased when the curing energy was lowered. Same effect was not achieved as distinctive with the pendulum hardness. With the paint on the other hand the usefulness of the two tests was opposite to the lacquer. The gloss remained stable during the testing of the paint, but the pendulum hardness lowered when the curing energy was lowered.

In the potassium permanganate stain test the difference between samples were big even with minor changes to the curing energy The difficulty in the stain test was in the rating of the results. Creating a suitable rating criteria for this test was not achieved during the analysis done in this thesis.

Mechanical scratching was performed as a single scratch test. The type of the surface defect caused by the scratching varied between the two coating types. Due to this, rating criteria that could be used for the evaluation of the defect of different type of coatings was not made based on the testing done in this thesis.

From the application parameters the most limiting factor according to the test results was the film thickness of the coating. With too thin film thickness the films did not cure properly due to the oxygen inhibition phenomena. Too high film thickness in the other hand required more UV energy to cure.

Keywords: UV curing coatings, cure level, efficient cure, chemical resistance, mechanical resistance, potassium permanganate stain test, gloss, and pendulum hardness.

TIIVISTELMÄ

Vilma Turunen: Applikaatioparametrien vaikutus kemikaalien kestoon sekä mekaanisiin ominaisuuksiin UV kovettuvissa pinnoitteissa
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Työn tarkoituksena on tutkia kuinka eri applikaatioparametrit vaikuttavat puun pinnoille tarkoitettujen ultraviolettisäteilyllä kovetettavien pinnoitteiden kovettumiseen ja ominaisuuksiin. Työssä myös tutkitaan kovettumisasteen arviointiin käytettäviä testimenetelmiä, sekä pyritään kehittämään näitä. Työhön valittiin viisi eri testimenetelmää; kiilto, heilurikovuus, kemikaalinkestotesti, väriainetesti kaliumpermanganaatilla sekä mekaaninen naarmuttaminen.

Kaksi erityyppistä UV kovettuvaa pinnoitetta valittiin työhön: akrylaattilakka sekä akrylaattimaali. Näytteet valittuihin testeihin valmistettiin muuttamalla UV energian määrää, jolle kappaleet altistettiin, sekä muuttamalla pinnoitteen kalvonpaksuutta. Substraatti vaihteli testimenetelmien vaatimusten mukaisesti. Pinnoitteiden applikointi tehtiin vetoraudoilla, sekä telakoneilla.

Testien tuloksissa havaittiin eroavaisuuksia, jotka johtuivat näytteiden eri kovettumisasteesta. Joissain testeissä saman pinnoitteen eri kovettumisasteen näytteiden väliset eroavaisuudet olivat suhteellisen pieniä, mutta myös isoja eroja havaittiin näytteiden välillä. Testien hyödyllisyys vaihteli myös testattavien pinnoitteiden välillä. Eroja havaittiin myös vaadittavan UV energian määrässä, jolla saavutettiin hyväksyttäviä tuloksia eri testeissä.

Kemikaalinkestotestauksessa tulokset olivat erittäin hyviä jopa pienimmillä energiamäärillä. Tulosten perusteella IOS-MATT testiluokitukset R2 ja R4 ovat liian helppoja kriteereitä UV kovettuville pinnoitteille. Isoimmat eroavaisuudet näytteiden välillä kemikaalinkestotestauksessa havaittiin eri kalvonpaksuuksien välillä. Korkeammilla kalvonpaksuuksilla tulokset olivat parempia kuin ohuemmilla.

Kiilto ja heilurikovuus testin hyödyllisyys vaihteli kahden testattavan pinnoitteen välillä. Lakan kanssa kiilto vaihteli enemmän ja testissä näkyi riippuvuussuhde kiillon ja kovettumiseen vaadittavan energian välillä. Samaa ei havaittu yhtä selkeästi testattavan maalin kanssa vaan kiilto oli testeissä melko stabiili. Heilurikovuuden hyödyllisyys oli taas päinvastainen kuin kiillon kanssa. Maalissa havaittiin kovuudessa enemmän riippuvuussuhdetta energian määrään, kun lakka taas oli testeissä melko stabiili.

Kaliumpermanganaatti väriainetestissä eroavaisuudet näytteiden välillä olivat suuria jopa pienillä muutoksilla kovettumisenergiaan. Haastavaa testissä oli luoda arvosteluasteikkoa tuloksille ja tätä ei tämän työn tulosten perusteella pystytty tekemään.

Mekaaninen naarmutustesti toteutettiin yhden naarmun testinä. Pinnoitteiden välillä havaittiin eroavaisuutta naarmutusterän aiheuttamasta vikatyypistä pinnoitteiden pinnassa. Tämän takia kummallekin pinnoitteelle soveltuvaa arvosteluasteikkoa ei pystytty tekemään tämän työn testien perusteella. UV energian vaikutus pinnoitteen ominaisuuksiin oli kuitenkin nähtävissä myös tässä testissä.

Applikaatioparametreista rajoittavimmaksi tässä työssä osoittautui pinnoitteen kalvon paksuus. Liian ohuilla kalvonpaksuuksilla pinta ei kovettunut kunnolla hapen inhiboivan vaikutuksen vuoksi. Korkeilla kalvonpaksuuksilla pinta taas vaati paljon enemmän UV energiaa kovettumiseen.

Avainsanat: UV kovettuvat pinnoitteet, kovettumisaste, kemikaalinkestotestaus, mekaaninen kesto, kaliumpermanganaatti väriainetesti, kiilto, heilurikovuus

PREFACE

This thesis is written for the Tampere University Master of Science degree in Material Science. Work was done in collaboration with PPG development team at Vantaa.

Without the help of my supervisors Mikko Kanerva and Jarno Jokinen this work would not have been completed. Mikko provided valuable support from the university side during the work and the conversations particularly during the testing phase were helpful and shaped the work to the final form.

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Family and friends have also supported me throughout the studies at Tampere University. My mother has always encouraged me to study further and has supported me in my different endeavours. During this work the greatest support has come from Miika with constant motivation and push towards the finish line.

Sipoo, 8.4.2024

Vilma Turunen

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

DSC	Differential scanning calorimetry
FTIR	Fourier transform infra-red
Ga	Gallium
HDF	High density fiberboard
Hg	Mercury
$KMnO_4$	Potassium permanganate
MEK	Methylethylketon
SAICAS	Surface and interfacial cutting analysis system
UV	Ultraviolet
VOC	Volatile organic substances

1. INTRODUCTION

100 % ultraviolet (UV) curing coatings are used in industrial coating business nowadays. The coatings are applied to different substrates, including plastics and wood. UV curing coatings are radiation curing coatings that require exposure to UV light that initiates the polymerization process of the coating. Formulations of UV radiation curing coatings are solvent-free and thus during the curing process there is no evaporation of solvent from the film, like in more conventional coatings. The absence of solvents allows for faster curing process and reduces the energy consumption of the industrial curing line. These are one of the biggest advantages of UV coatings in the industrial market when compared to more conventional solvent and waterborne coatings. Chemical and mechanical resistance of UV curing coatings when compared to waterborne coatings is also much better. One drawback with the UV curing coatings are the hazardous chemicals used that pose additional risk if the material is uncured. [1]

To obtain preferred properties from the coating material, it is important that the coating film is fully and optimally cured [1]. When the crosslinking density of the film is higher, the chemical and mechanical resistance of the material is better. Overcuring of the film on the other hand can cause too high hardness of the film or aging of the material in the form of colour changes or cracking of the film. Optimal application parameters are also key to achieve energy and time reduction on the industrial line. Current methods for determining the cure level and crosslinking density of UV curing coatings include different analytical methods as well as more on-site techniques that can be performed straight after the curing process. [2]

The aim of this thesis is to study the curing efficiency of different types of UV curing coatings applied on wood substrates, and how the different application parameters influence the chemical and mechanical resistance. The UV coatings tested in this work are produced by PPG that is a global coatings and specialty materials supplier [3]. The sample series for the testing are prepared by changing the radiation energy (that the coating materials are exposed to) as well as changing the application amount of the coatings. This way samples with different levels of cure and crosslinking density are obtained.

Another purpose for the testing done in this study is to examine different methods for testing of the cure level of UV coatings. Also, the possibility of creating a quick test

method for different types of coatings for the curing level inspection is studied. Currently, basic material properties of UV coatings are tested during development and quality control, but the addition of quick test to the test series could be beneficial.

2. LITERATURE

The main function of coating is to protect the surface that it is applied on. Other purposes for using coatings can be aesthetic, for example the need to hide unwanted surface. Coatings are mainly divided to paints and lacquers by the difference of opacity that the coating provides to the substrate. [2] Properties of the coatings are modified according to what is the substrate that it is applied on, how the coating is applied, how the coating is cured and what is the end use of the coated part. The substrate can be for example of wood, metal, paper, or composite. [4] In this chapter, the components and drying mechanism of coatings are discussed mainly focusing on the 100 % UV curable coatings.

2.1 Coatings

Coatings are used as a multilayer system, there can be one, two or three different coatings on the final surface depending on the substrate, end use of the coated surface, and desired outlook of the coated substrate. If a multilayer system is used, the first layer applied is primer. Primer provides sufficient adhesion between the substrate and topcoat or basecoat and seals the surface of the substrate sufficiently. Basecoat and middle coat provide a smooth surface for the topcoat. Final outlook of sheen and colour is achieved with the topcoat. [4]

Coatings can be divided many ways into different classes. For example, coatings can be divided by the substrate that the coatings are applied to, type of drying mechanism, or by the type of solvent to water-borne, solvent-borne and solventless. By choosing and adjusting the components of the coating different types of properties are obtained for the coating material depending on the end use environment or specific technical requirements set for the coating. [4]

2.1.1 Components of paint and lacquer

Main components in coatings are the solvent and binder component. These are responsible of the film formation of the coating material. Pigments, extenders, and different additives are added to coatings to modify the performance and different properties of the coating. For example, gloss, mechanical properties, and outlook. [5]

For the coating to form a continuous film, it needs a binder that binds the particles in the liquid coating together and to the substrate while drying and thus can be referred as film former component. Binder determines the mechanical and chemical properties of the

coating and is selected to suite the end use of the coated piece. Binders used can be either natural or synthetically derived. Examples of the naturally derived include oils, cellulose derivates and different natural resin that can be modified. Alkyds, acrylics, polyurethanes, and epoxies are examples of synthetic polymers that are common binder chemicals. [5]

Solvent is needed in the formulation to reduce the viscosity of the mixture in order that the coating can be manufactured and applied on the substrate. The most common solvent nowadays is water, but also low molecular weight organic substances are used. Organic solvents used are hydrocarbon solvents and oxygenated solvents. Solubility of the solvent to the binder is an important property. For example, non-polar hydrocarbon solvents dissolve non-polar binders and more polar solvents are used with polar binders. [6]

Pigment is the opacifying and colouring agent in paint. Pigment can be organic or inorganic. Colour that pigment provide is mainly determined by its chemical structure. Light is absorbed and scattered selectively from the pigment surface depending on the chemical structure of the pigment. Also, the crystal structure of the pigment influences on the colour that pigment chemical provides. [4]

The hiding power and opacity are important properties that can be achieved and altered by the amount and choice of pigment. Hiding power describes the ability of coating to obscure the surface underneath. Opacity is affected by the refractive index of the pigment and by the pigment particle size and distribution. Refractive index describes the ability of the substance to bend light. [4] The most used pigment in coatings is titanium dioxide that gives the paint white colour.

Extenders can be classified as pigments, but they do not primarily influence the opacity or colour of the coating film. The main purpose of extenders is to modify certain properties wanted from the coating. These are for example gloss, hardness, and rheological properties. Also, extenders are used to decrease the raw material cost of the product by extending the volume of the product. Most used extenders are different silicates for example talc and kaolin, carbonates like calcium carbonate and dolomite. [5]

Additives in coatings are a large group of different chemicals that are used to improve or modify different properties during manufacturing, storage, and application as well as to improve the performance of the dry coating film. Additives are added to the coating formulation typically in small amounts - for example from 0,01 % to 3 %. Surface active agents are a group of additives that influence the surface tension of the coating. These

include defoamers, wetting and dispersing agents, and substrate-wetting agents. Thickeners and coalescing agents are flow-control additives that influence the viscosity and flow of the wet coating. [7]

Other commonly used additives include waxes, light stabilizers, and preservatives. Waxes influence the gloss and mechanical resistance for example scratch and abrasion resistance. Biocides are preservatives that are used to protect the coating material against microbes during wet state as an in-can preservative and in dried film as a film preservative. Biocides are important in protection also of raw materials used in the coating industry. Biocides are needed especially in waterborne coating that are typically most affected by bacteria and fungi. [7]

2.1.2 UV curable coatings

Components of UV light curable coatings are similar to conventional coatings, but there are some specific components required only for UV coatings. Raw materials that are specific for UV curing coatings include photoinitiators and monomers or oligomers that are polymerized by radicals or cations. One big difference of UV coatings to conventional coatings is that the volatile organic solvent content in UV coating is close to zero because the use of volatile organic substances, VOCs, is not necessary in UV coating. [1]

Monomers or oligomers, called resin, for UV systems can be different acrylates, unsaturated polyesters, epoxides and vinylesters. Resin used determines the curing process and the type of photoinitiator for the coating. For example, radical curing is used with acrylates such as polyester acrylate and epoxy acrylate. Epoxies and vinyl ethers are cured by cationic UV curing. These two most common UV curing processes are descried in more detail in Chapter 2.2.2. Resin is the binder of the UV coating and thus determines mostly the physical properties of the cured film. [2]

Resins used are low molecular weight compared to conventional binders mostly because the viscosity of the mixture needs to be controlled and lowered in the absence of VOCs from the formulation. [1] Typical range of molecular weight for resin is from 300 g/mol to 5000 g/mol. [2] The properties that influence the viscosity of the resin include degree of branching of the molecular chain, intermolecular interactions between the resin molecules and the chain stiffness. [1]

Photoinitiators are responsible for the initiation of the polymerization reaction of UV curable coatings. When exposed to light the photoinitiator molecule absorbs photons leading to forming of reactive species that further initiate curing reactions depending on the type of the photoinitiator. Photoinitiator thus needs to contain a chemical group that can

absorb light at useful wavelengths. Reactive species formed due to light absorption can be radicals, anions, or cations. Most used type is radical photoinitiator that are used in free radical curing process. [2]

Different quantum yields describe the efficiency of a photoinitiator. For example, the quantum yield of photolysis describes the ratio of number of photoinitiators participating in the photochemical reaction to the number of photons absorbed from the radiation. The closer the value of quantum yield of photolysis is one the more efficient the photoinitiator is. This would theoretically mean that almost all photons would initiate one reaction. [1]

Most important properties for photoinitiators include high absorption at the corresponding exposure wavelength, high formation of reactive species and high reactivity of those to the monomer. The photoinitiator for the system also must be selected so that it matches to the spectrum of the UV light source available. [2] It is also important that the photoinitiator is stable in the formulation before exposure to light and the compatibility to other raw materials in the formulation needs to be good. [1]

2.2 Drying mechanism

For the coating to work properly it needs to form solid film on top of the substrate used. The type of drying varies depending on the type of coatings. Most common drying mechanism is physical drying were the solvent used evaporates from the wet film and particles left reconstruct a solid film. UV curable coating on the other hand require exposure to UV light for the wet film to dry, otherwise it will remain in the wet state. [6] The UV curing polymerization process is presented in this chapter, focusing on the two most common UV curing reaction types: free radical UV curing and cationic UV curing.

The level of cure achieved can be tested with different analytical methods as well as with simple inspection methods after the curing process. Different available methods for this are also presented in this chapter.

2.2.1 UV curing

Curing is a polymerization process and has three steps: initiation, propagation, and termination. UV curing process is initiated by light that is absorbed by the photoinitiator. When absorbing UV radiation, photoinitiator goes through chemical modification that leads to forming of active element. An active element then initiates the curing process. [1]

Most common UV curing technologies are free radical curing and cationic UV curing. The difference between the two technologies is in the polymerization mechanism. Free radicals initiate the cure process in free radical UV curing and cations in the cationic UV curing. The formulation of the coating differs by the nature of the binder and photoinitiator depending on which curing system is targeted. Different acrylate polymers are the most used binders for free radical UV curing compositions. In cationic UV curing, binders are often epoxies and vinyl ethers. [1]

Liquid monomers in the formulation form a solid polymer network in the propagation phase of the curing. During termination, chain growth is terminated due to polymerization kinetics, for example by increasing viscosity that affects the chain mobility and thus disables the chain growth. [1]

Within industry, the radiation needed for the initiation of curing is produced with different lamps that emit radiation in correct spectrum for the liquid coating. UV light covers wavelengths from 190 nm to 400 nm that can be further divided to UVA (200 nm – 400 nm), UVB (290 nm – 320 nm) and UVC (190 nm – 290 nm) light ranges. UVV unlike the other UV wavelengths is a visible wavelength and it corresponds to wavelengths from 395 nm to 455 nm. [8] Most used lamps to cure UV coatings are mercury (Hg) medium pressure lamps that can be doped with different traces of other compounds to alter the spectral output of the lamp. Gallium (Ga) is the most used compound to dope UV lamps. Mercury lamp has strong spectral output in 254 nm, 300 nm – 320 nm and 365 nm. With the addition of gallium, the spectral output of the lamp enhances to 390 nm – 410 nm region. [9]

Gallium doping is a requirement when curing pigmented films to obtain through-thickness cure. The pigments reflect, scatter, absorb and transmit light when it hits the surface. This causes problems when curing pigmented films as enough radiation may not get through deep enough to activate initiators and thoroughly cure the film. For example, with titanium dioxide the absorption of light increases rapidly under wavelength of around 390 nm. This also means that the photoinitiator used must be able to absorb light in the higher UVA and lower UVV radiation range. [1]

Gallium lamp has low input on the lower wavelengths including UVB and UVC. Due to this mercury lamp need to be used together with gallium lamp when curing pigmented films. In these situations, gallium is positioned first in the UV line for through cure and after that mercury lamp that will perform surface cure for the film. [1]

Free radical UV curing

The initiation step in the free radical curing is called photolysis. In photolysis, the UV curing is activated by free radicals that are generated from the photoinitiator by UV light. The emission spectrum of the lamps must be in the same spectrum as the absorption spectrum of the photoinitiator for the initiation to occur. Photoinitiators used for free radical curing can be for example benzoin derivatives, α-hydroxyalkylphenones and aromatic ketones like benzophenones. [1]

Free radicals formed in the initiation starts the polymerization reaction by free radical mechanisms by reacting with monomers and oligomers in the coating forming growing polymer chains and polymer network. Examples of monomers and oligomers cured with free radical curing are different acrylates, unsaturated polyester and styrene resins containing carbon-carbon double bonds. [2] The basic of free radical curing process is presented in Figure 1.

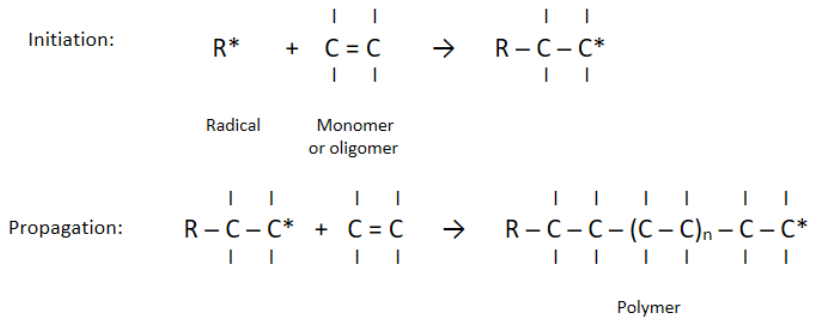

Figure 1. *Free radical UV curing process. [10]*

Chain propagation continues and chain termination starts simultaneously. In chain termination reaction, two radicals combine. The combining radicals can be from growing chains or from the initial photolysis phase. When termination reactions dominate or when the reactive radicals have been consumed the curing reaction is terminated. [2]

Oligomer reactivity, initiation rate and temperature determine the propagation rate of the polymerization. Temperature can increase during the curing due to the heat generated by the lamps and increase the chain mobility and speed up the curing process. During the chain propagation reaction, the viscosity of the coating increase while the chain length increases and thus slows down the reaction. [1]

One of the biggest benefits of using free radical UV curing systems is the speed of the reaction process compared to the cationic UV curing. The free radicals are consumed fast and when the UV light exposure ends the reaction stops. Limitations with the technology are with the shadow areas of the substrate. As light is needed to activate photoinitiator and initiate the polymerization, areas that do not receive sufficient amount of

radiation do not cure properly. This raises limitations with the use of three-dimensional substrates. [1]

With free radical curing one drawback is the oxygen inhibition that can interfere with the curing reaction of the film. During the propagation step the photoinitiator in the presence of air reacts with the oxygen diradical forming peroxy-radicals that act as an inhibitor to the polymerization. This reaction continues until all the oxygen available is consumed influencing the complete polymerization of the film. The layer thickness affected by oxygen is determined by the oxygen diffusivity to the coating film. This is determined by the material polarity and type as well as the viscosity of the coating. With thin films the oxygen inhibition can slow down the polymerization process of the whole film and with thicker films it can affect the air-coating interface polymerization and cause sticky uncured surfaces. This problem can be overcome for example, by increasing the reactivity of the formulation, by increasing the viscosity of the coating or by adding waxes to the formulation that will act as physical barriers for the oxygen. [2]

Cationic UV curing

Light activates the photoinitiator in photolysis similarly as in free radical UV curing. Common photoinitiators used with cationic curing are onium salts like triarylsulphonium and diazonium salts. The organic cation of the ionic compound is the light absorbing component. When exposed to UV light the onium salts form cations and radical cations as well as radicals. These then react further with for example alcohols in the mixture that can donate protons and form Brønsted acids. These acids then initiate the cationic polymerization. Activation of the photoinitiator is the only step in cationic UV curing that requires UV light. [11]

Polymerization then propagates as the proton attacks the electron rich group of the monomers available in the mixture [1]. Monomers used with cationic UV curing include vinyl ethers like di- and triethylene glycol divinyl ethers, and epoxides like cycloaliphatic epoxide. For example, with epoxides the reaction propagates by ring opening polymerization. Curing propagation does not require any more UV light and thus the reaction continues after irradiation and is referred as post-curing. Because of this the curing process also takes more time when compared to free radical UV curing. Post curing can also be accelerated by thermal treatment after UV exposure. Polymerization process is eventually terminated by chain transfer that results in inactive species or when propagating species react with nucleophilic impurities in the mixture for example the anion. [11]

Advantages of the cationic curing process compared to the free radical curing include post-polymerization that does not require UV light, low shrinkage, and better adhesion

to the substrate. There are also limitations with cationic UV curing. Moisture affects the cure by acting as an inhibitor as it can terminate the propagation by chain transfer. Therefore, too high humidity can cause premature termination of the cure and lower material performance. Also, similarly as with the free radical curing, light initiates the curing process and thus shadow areas will not cure properly leading to restrictions in the substrate form. [1]

2.2.2 Evaluation of cure in UV coatings

Level of cure achieved in the UV curing material can be evaluated using different analytical methods by examining the changes in the molecular structure and number of reacting functional groups. Also, more on site techniques for example inspection with finger and fingernail scratch can be used. These methods do not give as much information about the crosslinking density but can be useful as fast tests on production lines. [2]

Fourier transform infra-red (FTIR) spectroscopy can be used to evaluate the cure by studying the changes in the chemical bonds in the material caused by the formation of the crosslinking structure due to the curing process. In IR spectroscopy the energy of different chemical bonds is presented as wavenumbers (of absorbance), and these are expressed as peaks in the spectrum. In this method, the IR absorption spectrum is measured from the sample before and after the UV curing. By comparing the spectral output of the measurements, a degree of conversion can be calculated from the decay in the IR bands caused by the UV exposure. [1]

Differential scanning calorimetry (DCS) can be also used for evaluation of the cure in UV curable coatings. For this purpose, the conventional DCS equipment needs to be equipped with irradiation unit in order that the crosslinking reaction can be monitored by the equipment. Device records the heat (flow) that is generated (for exotherm reaction) during polymerization of the sample. From an already polymerized sample, a heat generated by the UV lamp is determined. This signal is then subtracted from the measured samples signal and the result is presented as a heat flow from the polymerization as a function of irradiation time. From the heat flow curve the number of different reacted functional groups can be evaluated. This way different conditions that equal to different line speeds, lamps and curing temperature can be tested. [1]

The sliding cutting technique can be used to evaluate the level of cure of thin films. In this method thin materials are cut from the specimen surface at inclination angle. The velocity ratio between the vertical and horizontal direction determines the inclination angle. If there is difference on the curing degree inside the material, it can be identified as a change on the shear resistance because the viscous liquid material phase of uncured

region differs from the cured material solid phase. With this method the uncured areas inside the material can be identified even though the material surface is cured. For the testing, the surface and interfacial cutting analysis system (SAICAS) can be used. SAICAS has a diamond cutting blades that slice very thin specimens from the sample surface to the substrate interface. It tests the shear strength of the material as well as the peel strength in a systematic way. [12]

One more on-site technique that can be used to evaluate the cure of the coating after UV oven is rubbing the surface with cloth that is soaked with methyl ethyl ketone (MEK). In this test, the cloth soaked with MEK is wrapped around a ball peen hammer. The hammer is then dragged across the surface and the number of movements back and forth are counted. This is continued until the surface of the coatings breaks. [13]. Damage to the surface for example can be swelling of the coating or detaching of the coating from the substrate. [1] Important is that the hammer is not pressed to the surface but only dragged so that the hammer's own weight determines the pressure applied to surface. Idea is that first baseline count for the rubs is determined for each coating type with sample that is fully cured. After this samples can be compared to that by the number of rubs and classified as pass or fail. Fail means that the count of rubs that the coating can withstand is smaller and the coating is under-cured. [13] This test can also be performed with different solvents for example acetone, butyl acetate and xylene but MEK is the most commonly used. [1]

The most accessible technique to evaluate if the coating has cured or not is simple finger test right after curing. Coating surface after UV oven is pressed with finger to evaluate the softness and stickiness of the film. If the film is not sticky but feels soft, it indicates that the surface has cured but underneath the surface the coating is still not cured. Also, fingernail scratch can be used to evaluate the level of cure. In this the nail of the middle finger is softly dragged on the surface. These techniques are very simple (very qualitative) thus useful, but on the other hand also dependent on the tester as the force used can vary between makers. [1]

3. MATERIALS AND METHODS

In this chapter, the coatings selected for the testing are shortly introduced as well as the application methods and curing equipment. The application methods for the coatings were with single side bar coater film applicators and two different roller coaters. Films were dried with UV line oven available at the laboratory of the company.

The test methods and qualities that were chosen for the testing protocol are potassium permanganate stain, chemical resistance, mechanical resistance, gloss, and pendulum hardness. The principle of these test is presented in this chapter. Pendulum hardness, gloss and potassium permanganate stain tests were chosen as these are easy and fast to do and could also be performed in quality control as a mean to ensure the quality of the production batches. Chemical and mechanical resistance tests could be utilized mainly only in research and development work as the duration of the testing is longer and test protocol is more complex and the results not as explicit when compared to hardness and the stain test.

3.1 Materials

For the tests, two different 100 % UV curing coatings were chosen: matt acrylate lacquer and acrylate paint. Both coatings are cured by the free radical UV curing mechanism.

The curing energy with a Hg-lamp for the acrylate lacquer is recommended to be at a minimum 500 mJ/cm^3. For the acrylate paint same recommendation using both Hg-lamp and Ga-lamp are 400 mJ/cm^3 and 400 mJ/cm^3, respectively. The recommended application amount for the acrylate lacquer is (3 – 30) g/m^2 of wet film and, for the acrylate paint similarly (10 – 40) g/m^2. All the relevant coating properties are presented at Table 1.

Table 1. *Properties of the test coatings in the thesis.*

Property	Lacquer	Paint
Curing energy recommended (Lamp type = mJ/cm3)	Hg = 500	Hg = 400, Ga = 400
Application amount of wet product recommended (g/m2)	3 - 30	10 - 40
Gloss (60 °)	10 - 16	60 - 80
Hardness (number of swings)	60 - 80	30 - 80

The substrates used in the test programme were: two types of glass sheets, birch veneer and high-density fiberboard (HDF). The glass sheets used were a clear one-layer glass sheet and a double glass sheet with black paper between the two sheets. Substrates used in each tests are presented in Table 2.

Table 2. *Different substrates used in different tests with each product as used in this thesis.*

Test	Product	Substrate
Gloss	Lacquer	Black glass sheet
		Birch veneer
	Paint	Black glass sheet
Hardness	Lacquer	Black glass sheet
	Paint	Black glass sheet
KMnO4	Lacquer	Clear glass sheet
	Paint	Black glass sheet
Chemical resistance	Lacquer	Birch veneer
	Paint	Birch veneer
Scratching	Lacquer	HDF
		Birch veneer
	Paint	HDF
		Birch veneer

The main difference between the two glass sheets is that the double layer glass sheet is more even, and the surface quality is better when compared to the one-layer clear glass sheet. As the layer application amount of these products is thin, the double layer glass is required to achieve an even layer of wet paint and lacquer. The HDF used was coated with acid catalyst paint and sanded to provide smooth and even surface.

3.2 Roller coater application

The application of coatings was done with cylinder machine in preparing samples to chemical and mechanical resistance tests. A small (Burkle type BKL) and a larger roller coater (Tomanin type STU-FT/R4) was used depending on the coating type; sealer and acrylate lacquer was applied by using the small roller coater and acrylate top paint was applied with the larger roller coater. Burkle BKL is a smaller roller coater that is intended for laboratory scale use. The Burkle BKL machine used is presented in Figure 2.

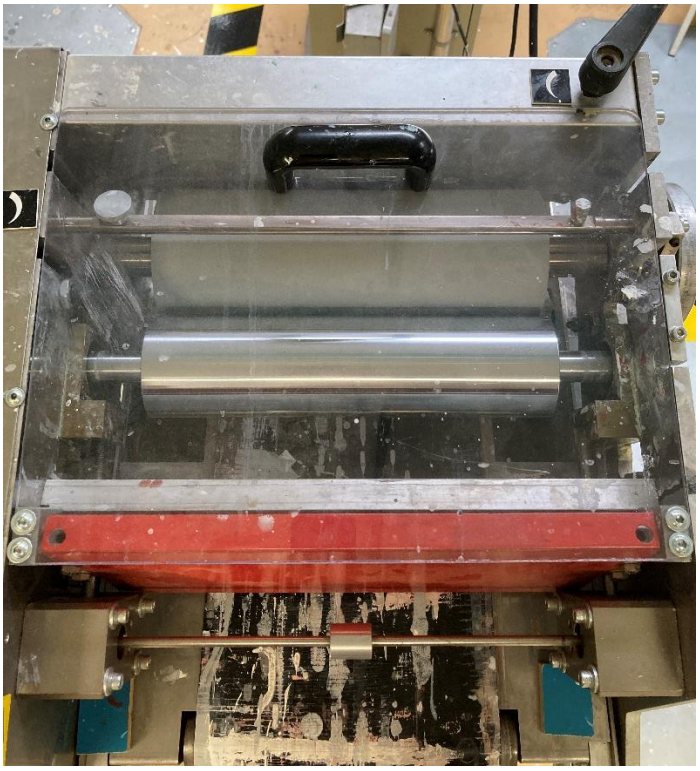

Figure 2. *Small cylinder machine that was used in the application of the coatings of wood substrate.*

Both roller coaters used have the same amount of rolls: dosing roll, spreading roll and conveyor roll and the same working principle. The height between the conveyor and spreading roll is adjusted based on the thickness of the substrate to be coated. Coating material is applied between the dosing and spreading roll. Application amount of the coating to the substrate is determined by the pressure between the dosing and spreading roll. [14] The application amounts are presented later in Chapter 4.

3.3 UV oven

UV oven used in the tests is from the manufacturer Elmag-Superfici and has two lamps, one Ga and one Hg lamp. The power of the lamps can be adjusted to 80 W, 100 W or 120 W. The line speed of the oven can be changed from 3 m/min to 18 m/min. With these parameters the amount of UV dose to the coated sample can be altered.

The UVA and UVV energy achieved with different parameter setting can be measured by running energy recorder through the UV oven. By changing the line speed, lamps (Hg and Ga) and power of the lamps, energy achieved from the UV oven with each setting can be recorded and made into a graph from where energy level with different line speeds can be estimated. The energy recorder used is from EIT and the model is UV

PowerMAP. With this all, UVA, UVB, UVC and UVV total energy densities with each run can be recorded.

3.4 Potassium permanganate stain

Potassium permanganate, $KMnO_4$ can be used to analyse the curing of the coating. Potassium permanganate is strong oxidant, and the stain intensity and colour can indicate the level of cure and the crosslinking density achieved. The test principle is that, with a better cured film, the KMnO4 stain mark is lighter than in film that is not as fully cured. Based on the stain intensity and colour difference, the optimal curing energy for the coating could be defined. [15]

Different testing protocols using $KMnO_4$ to evaluate cure are available from different corporations in the coating business. For example, Coatings & Adhesives Corporation has test method available for this. In this test method, a 1 % $KMnO_4$ solution in water is used to evaluate the cure. A droplet of the test solution is applied to the test surface and, after 5 min, the droplet is cleaned with paper. The results are visually compared to standard, or the relative yellow density is measured with spectrophotometer [15]. This testing principle is used as a starting point for the testing and modified during testing if needed.

Possible ways to evaluate the results of the stain test are visual comparison of the stain marks with different curing energy and colour difference measurement by using spectrophotometer against chosen standard. In the colour measurement by spectrophotometer, the values for L, a and b are obtained (CIE system). With these the colour difference of two measure points can be expressed as dL, da, db and dE. For example, dL indicates the difference in the lightness/darkness from the sample to standard [5]. The further explanation for the spectrophotometric values is presented in Table 3.

Table 3. *Explanation of the meaning of the delta values obtained from spectrophotometric measurements. [5]*

	Explanation of values
dL	- darker / + lighter
da	- greener /+ redder
db	-bluer / + yellower
dE	Total colour difference

The DE value is a calculated based on the values of dL, da and db. It describes the total colour difference between the sample and the standard. [5] In this test most useful delta values presumably are the dL and dE.

3.5 Chemical resistance test

The chemical resistance test is done according to the IKEA specifications, IOS-MAT-0066, Surface coatings and coverings – general requirements, and standards EN 12720 Furniture – Assessment of surface resistance to cold liquids, and EN 12722 Furniture – Assessment of surface resistance to dry heat. Surface resistance is tested using class R2 and R4 requirements described in the IKEA specification for coated wood substrates. The requirements for R2 and R4 classes are described in Table 4.

Table 4. *Requirements for the chemical resistance test specified in IOS-MAT-0066 [16]*

Requirements	R2	R4
Water	24 h	16 h
Paraffin oil	24 h	24 h
Alcohol (48 % aq)	1 h	1 h
Coffee	1 h	1 h
Perspiration (acid + base)	1 h	1 h
Dry heat	70 °C, 20 min	-
Scrathes + paraffin oil	3 N + 24 h	2 N + 24 h

Requirements for the chemicals used are presented in the standard EN 12720 [17]. Water used is distilled or deionized (deionized used here). Coffee is prepared from 40 g of instant coffee in 1 l of hot water. The coffee solution used in this thesis is prepared one day before use. [17]

After the application of coating, the coated pieces according to the standard are conditioned in (23 ± 2) °C temperature and (50 ± 5) % relative humidity at least a week before the test is performed. [17] In this work pieces were aged in 50 °C for 16 h before testing after application.

The testing principle is that paper discs are saturated with each of the test liquid for around 30 s to 60 s and placed on the test surface. The discs are covered with a glass Petri dish, excluding paraffin oil that is left uncovered. After the specific testing time required, the discs are removed from the surface. Excess liquid is removed from the surface by gently pressing the surface with absorbent paper. The testing area is left untouched for 16 h to 24 h. Different testing areas must be marked on the surface. An example of a surface partly under testing is presented in Figure 3. [17]

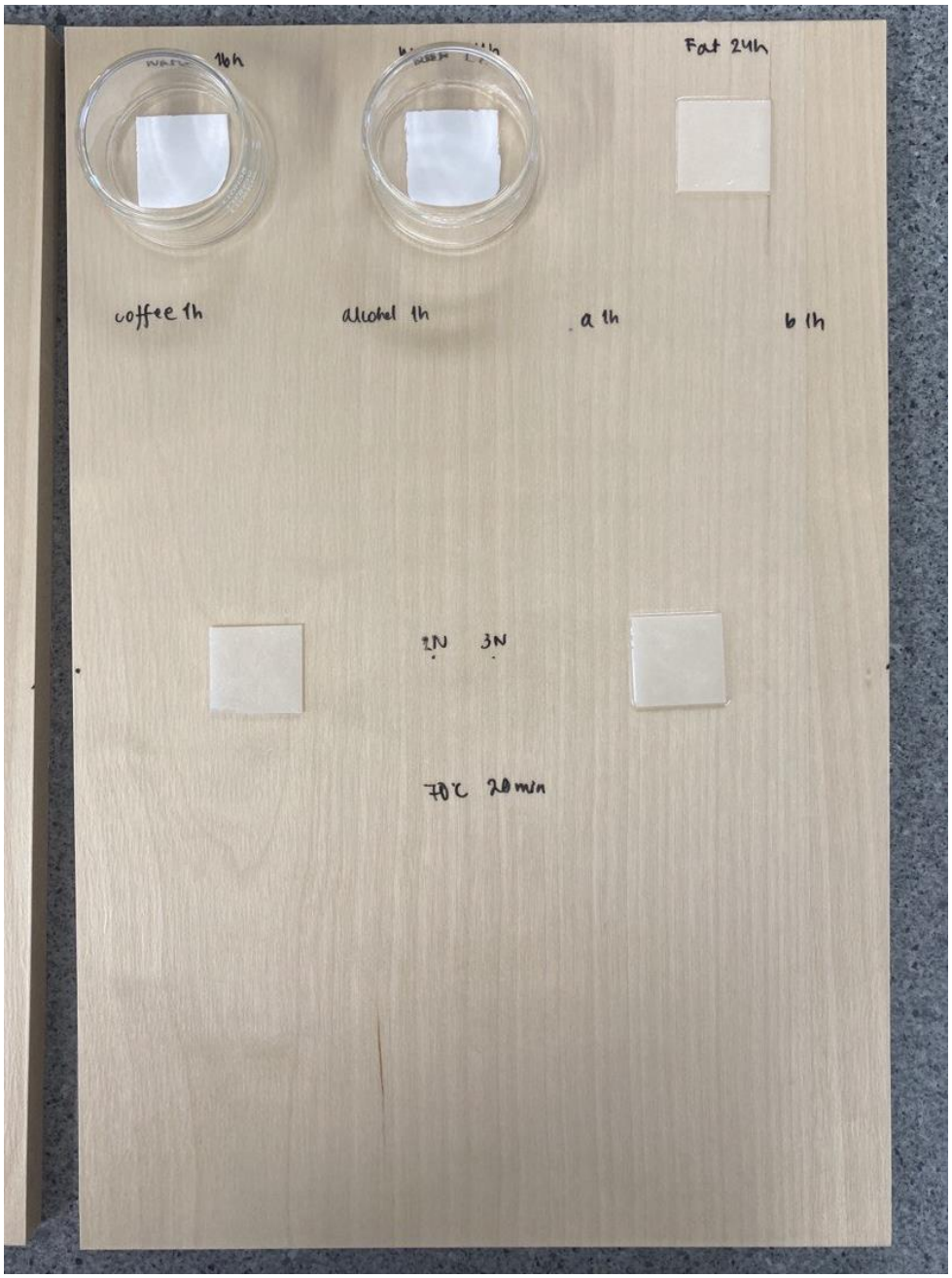

Figure 3. *Chemical resistance test sample under testing. Each of the testing areas are recorded to the sample.*

After the 16 h to 24 h period, the surface is washed by using a cloth immersed in cleansing solution (described in the standard EN 12720) and in the same manner with water. Lastly, the surface is dried with a dry cloth. 30 min after the washing the surface is examined following the numerical rating code presented in the standard EN 12720. The numerical rating code and requirements are presented in Table 5. Test surface is analysed by observing changes in colour or gloss as well as observing other surface defects like swelling and blistering. The test areas are compared to untouched areas from the surface to determine the correct numerical rating. According to the standard the test area

is analysed with a light source that gives the illumination of (1200 ± 400) lx that can be diffused artificial daylight or diffused daylight and from viewing distance of 0,25 m to 1,0 m. Surface is analysed from different angles and by touching the surface to determine the changes in the structure. [17]

Table 5. *Description of the numerical rating code that is used to analyze the results of the chemical resistance test as presented in the standard EN 12720. [17]*

Numerical rating	Description of the requirements
5	No change Test area indistinguishable from adjacent surrounding area.
4	Minor change Test area distinguishable from adjacent surrounding area, only when the light source is minored on the test surface and is reflected towards the observer's eye, e.g. discoloration, change in gloss and colour no change in the surface structure, e.g. swelling, fibre raising, cracking, blistering.
3	Moderate change Test area distinguishable from adjacent surrounding area, visible in several viewing directions, e.g. discoloration, change in gloss and colour no change in the surface structure, e.g. swelling, fibre raising, cracking, blistering.
2	Significant change test area clearly distinguishable from adjacent surrounding area, visible in all viewing directions, e.g. discoloration, change in gloss and colour. and / or structure of the surface slightly changed, e.g. swelling, fibre raising, cracking, blistering
1	Strong change the structure of the surface being distinctly changed and / or discoloration, change in gloss and colour, and / or the surface material being totally or partially removed, and / or the filter paper adhering to the surface.

The dry heat test included in the R2 class requirements is described in the standard EN 12722. In the test, a standard aluminium alloy block (presented in Figure 4) is heated to the testing temperature and placed on top of the test surface for 20 minutes. When 20 min is passed the block is removed from the surface. If moisture is forming on the surface after the block is removed, it needs to be dried with a cloth. Before analyzing the results, the surface is left untouched for 16 h to 24 h. The surface is analyzed in the same manner as with the liquid chemicals and by numerical rating code that is presented in the standard and in Table 6. [18]

Figure 4. *Standard aluminum block used in the dry heat testing.*

Table 6. *Description of the numerical rating code for the analysis of the dry heat test as it is presented in the standard EN 12722. [18]*

Numerical rating	Describtion of the requirements
5	No change test area indistinguishable from adjacent surrounding area
4	Minor change test area distinguishable from adjacent surrounding area, only when the light source is mirrored on the test surface and is reflected towards the observer´s eye, e.g. discoloration, change in gloss and colour no change in the surface structure, e.g. deformation, swelling, fibre raising, cracking, blistering
3	Moderate change test area distinguishable from adjacent surrounding area, visible in several viewing directions, e.g. discoloration, change in gloss and colour, no change in the surface structure, e.g. swelling, fibre raising, cracking, blistering
2	Significant change test area clearly distinguishable from adjacent surrounding area, visible in all viewing directions, e.g. discoloration, change in gloss and colour and / or structure of the surface slightly changed, e.g. swelling, fibre raising, cracking, blistering
1	Strong change the structure of the surface being distinctly changed and / or discoloration, change in gloss and colour, and / or the surface material being totally or partially removed

Paraffin oil on scratch test is presented in the IKEA specification IOS-TM-0002 Surface resistance – test methods. A scratch is made with apparatus that has spherical tip made of polished steel that has hardness HRC 60 – 66. The diameter of the tip is 1 mm. Load-

ing on the surface needs to be adjustable on the apparatus. A scratch can be done manually or with apparatus that has motor. The length of the scratch is approximately 100 mm, and the scratch is done at a speed (50 ± 20) mm/second perpendicular to the wood grain. The scratching apparatus used to perform the test is presented in Figure 5. [19]

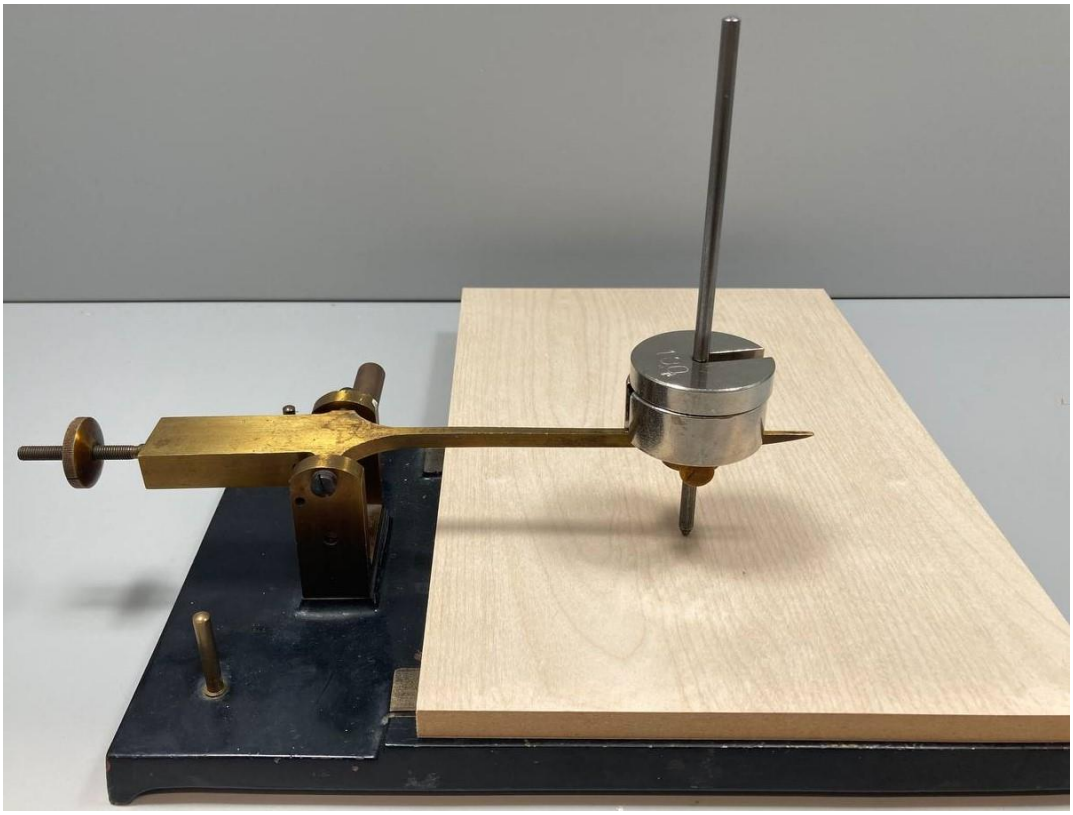

Figure 5. *Apparatus used in the paraffin oil on scratch test with removable weights on top of the scratching needle.*

A Disc is first immersed with paraffin oil for around 30 s and then placed on top of the scratch. Discs are left for testing period of 24 h and then removed. Remaining paraffin oil on the surface is lightly dried with a cloth and then left untouched for 16 h to 24 h. After this, the test area is washed in the same manner as with the liquid chemicals and analysed. In the analysing of the results, the spreading of the paraffin oil into the substrate and coating is examined. The rating criteria is presented in the IKEA specification and shown in Table 7. [19]

Table 7. *Rating criteria for the paraffin oil on scratch test presented in the IKEA specification IOS-TM-0002. [19]*

Numerical rating	Describtion of the requirements
5	Spread only in the sratch where the oil has caused a change in colour up to a total width of maximum 2 mm.
4	Spread to a total widht of maximum 4 mm or to a larger width provided the colour, structure etc. of the test surface is such that only an inspector who is familiar with the type of damage can define the spread.
3	Spread to a total width of maximum 15 mm or a structural change beyond the scratch.
2	Spread to a total width of maximum 40 mm.
1	Spread exceeding a total width of 40 mm.

In evaluating of the test results, the rating 5 and 4 is generally classified as passed in all the R2 and R4 class requirements. The change in the coating surface in the rating 4 is minimal and acceptable. The assumption in this work is that when the curing energy amount is lowered the results from the chemical resistance test would also get worse. From this, it could be determined what is the required energy amount for the coatings properties to be optimal in chemical resistance.

3.6 Mechanical scratching

The mechanical scratching test was performed with Taber Linear Abraser as single scratch test by using scratching tip. The device used is presented in Figure 6.

Figure 6. *Taber Linear Abraser used in the test. On the right is the spline shaft with the scratching tip and weight supporter with two removable weight discs.*

In the single scratch test, the load arm is positioned so that it is furthest away from the device and the cycle amount is set to one. The speed used in the test was 15 cycles/minute. Scratching was performed with three different weights on top of the scratching tip. The weight of the load arm without any extra weight disc is 350 g. For the weight discs, each weigh 250 g. By inserting these discs to the load arm, the force applied to the sample surface by the scratching tip can be adjusted. Example of the testing set up is presented in Figure 7.

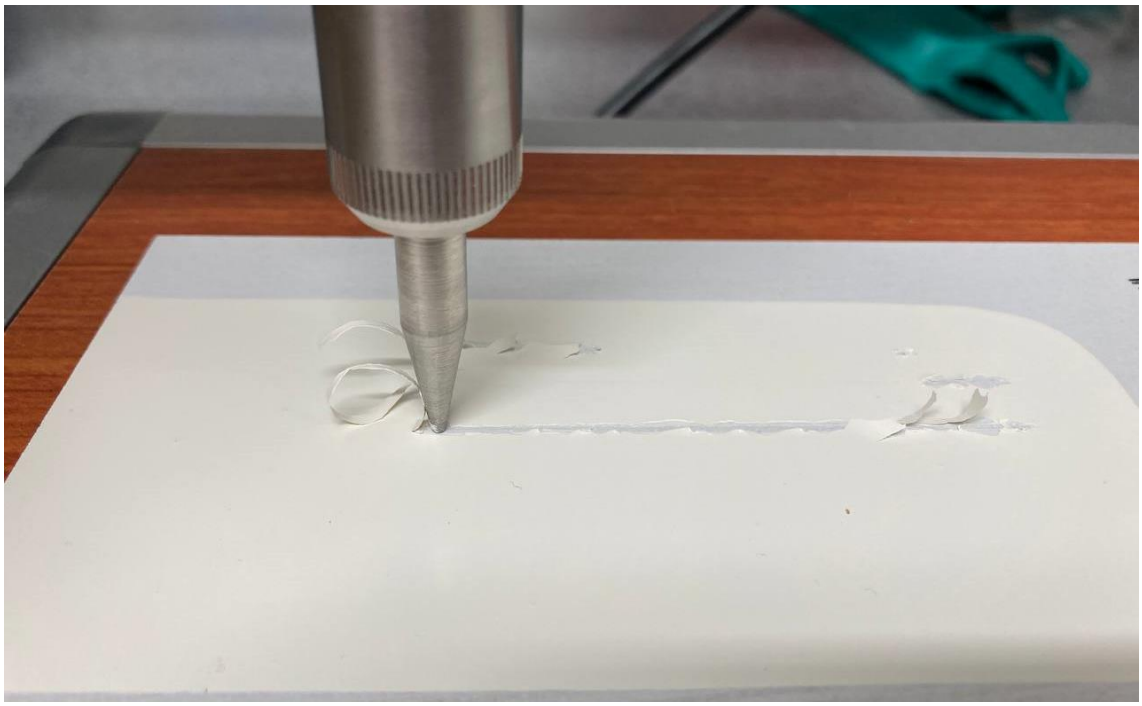

Figure 7. *Sample under testing for the single scratch test.*

Scratches are evaluated by measuring the width of the scratch by using magnifier of 6x and inspecting the state of defect with a microscope.

3.7 Pendulum hardness

The pendulum hardness test is performed according to the standard ISO 1522:2006 – The Pendulum damping test, using BYK Gardner pendulum hardness tester that is presented in Figure 8. Principle in the test is that a pendulum is placed to rest on top of the coated surface. Pendulum is set into oscillation and the hardness of the coating is determined from the time it took for the oscillation amplitude to decrease a specified amount. [20]

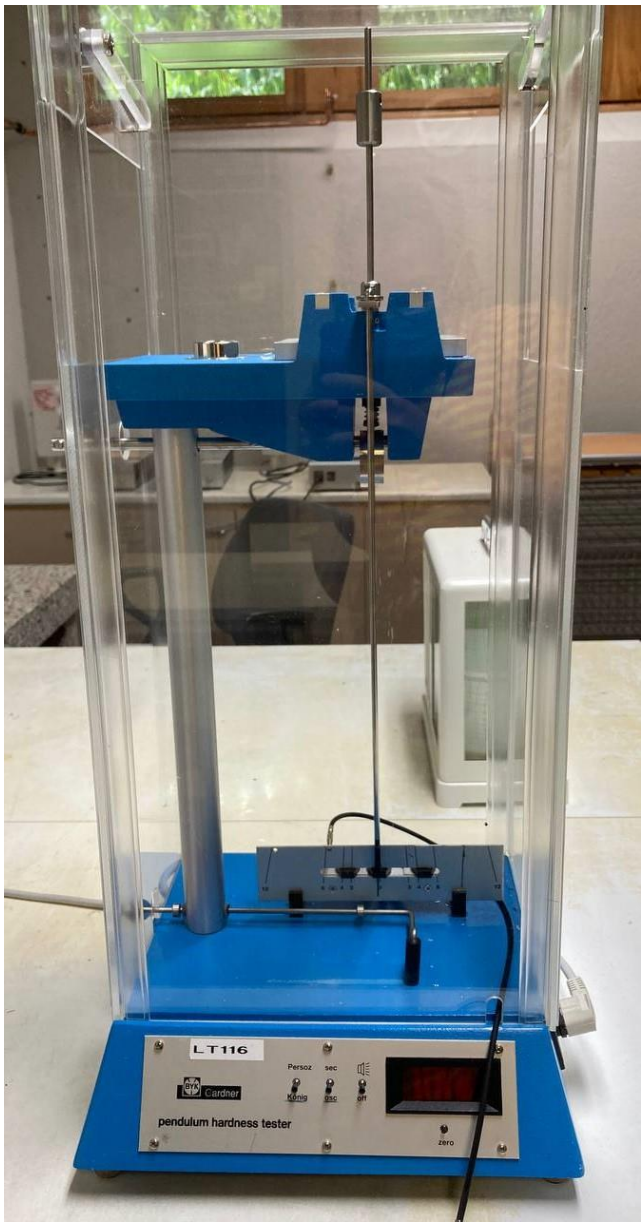

Figure 8. *BYK Gardner pendulum hardness tester used in the measurements.*

In these tests, a Köning pendulum was used. The pendulum consists of two tungsten-carbide balls that has diameter of (5 ± 0,005) mm and hardness of (1600 ± 32) HV 30. The balls are attached to a cross-bar (30 ± 0,2) mm apart from each other. A vertical rod is attached to the cross-bar. The rod is used to counterpoise the pendulum with sliding weight attached to the rod. [20]

The sample is placed below the balls on the sample table. The sample table is raised up so that the balls rest on the sample surface. The pendulum is set to correct angle, 6 ° when using Köning pendulum, and stopped using the mechanisms in the device. Pendulum is released and let to swing. The time for the swing angle to decrease from the 6 ° to 3 ° is the hardness of the sample. This can be recorded using stopwatch or by an automatic system in the measuring device. The result can be either presented as the

time or by the number of swings it took for the amplitude to decrease. In this thesis the results are presented as the number of swings. [20]

4. RESULTS

The testing for the thesis research was started by determining the energies achieved with the UV oven with different line speeds. After this, the testing procedure for each test method was planned. The aim was that with each test method, same curing energies would be used to be able to compare results and find limits for the curing energy needed.

In this chapter, the test results from the different test are presented. Also, the substrates and sample preparation method are presented with each test method.

4.1 UV oven

To determine the line oven parameters for the tests, the UVA and UVV energies with different oven settings were evaluated using running energy recorder as previously presented in Chapter 3.3. In Figure 9, the UVA energies achieved with different line speeds and lamp intensities is presented when using both Hg and Ga lamp.

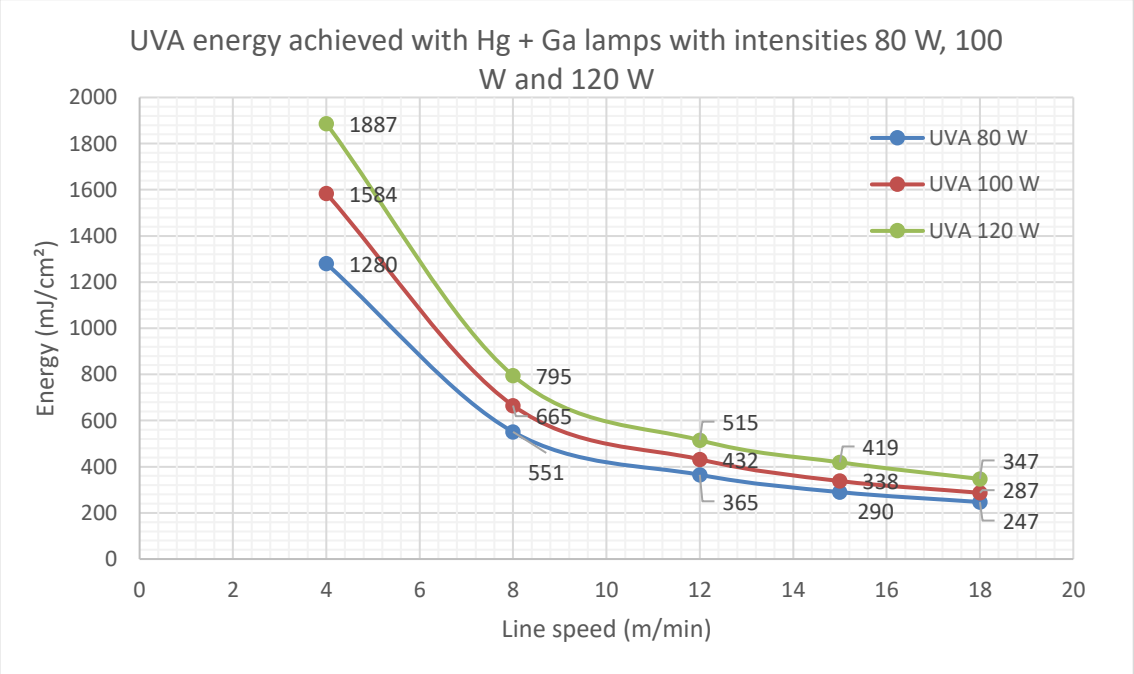

Figure 9. *UVA energy achieved with the UV oven at different line speeds when using halogen and gallium lamps at intensities 80 W, 100 W and 120 W.*

From the figure it can be noticed that the UVA energy increases when increasing the lamps intensities with same line speeds. When the line speed is increased the amount of energy the piece is exposed to is lower.

The difference between the three possible lamp intensity is not big but lower energy levels are easier to obtain when using a lamp intensity of 80 W. The recommended energy doses for the coatings chosen were from 400 to 500 mJ/cm^2. With a lamp intensity of 80 W, it is easier to test energy amounts below these by altering only the line speed. In Figures 10, 11 and 12 the energy achieved with different lamp combinations are presented while using 80 W lamp power.

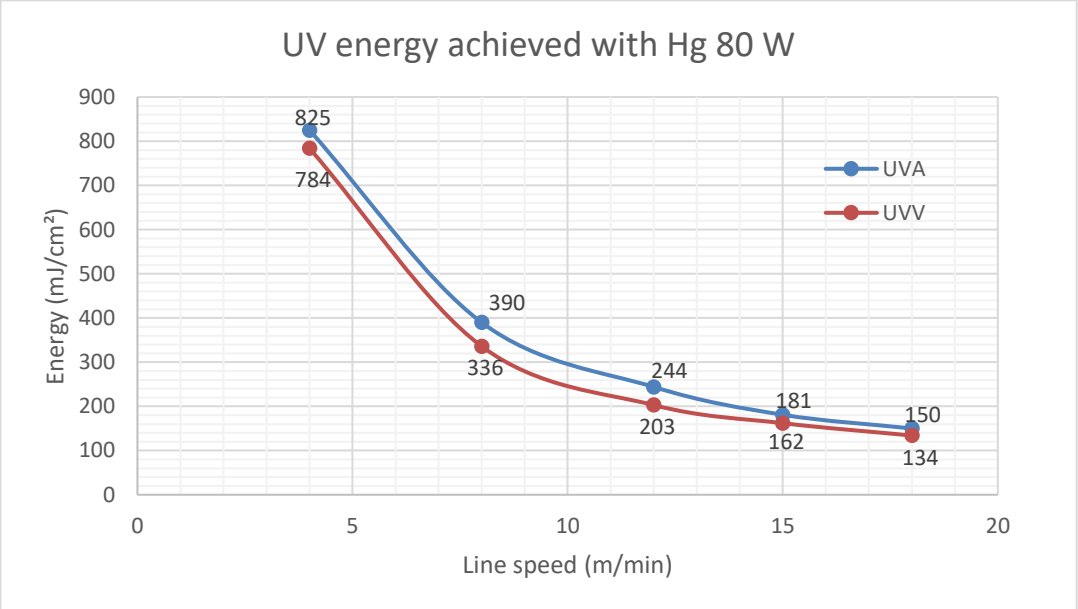

Figure 10. *UV energy achieved with the UV oven at different line speeds when using halogen lamps at 80 W.*

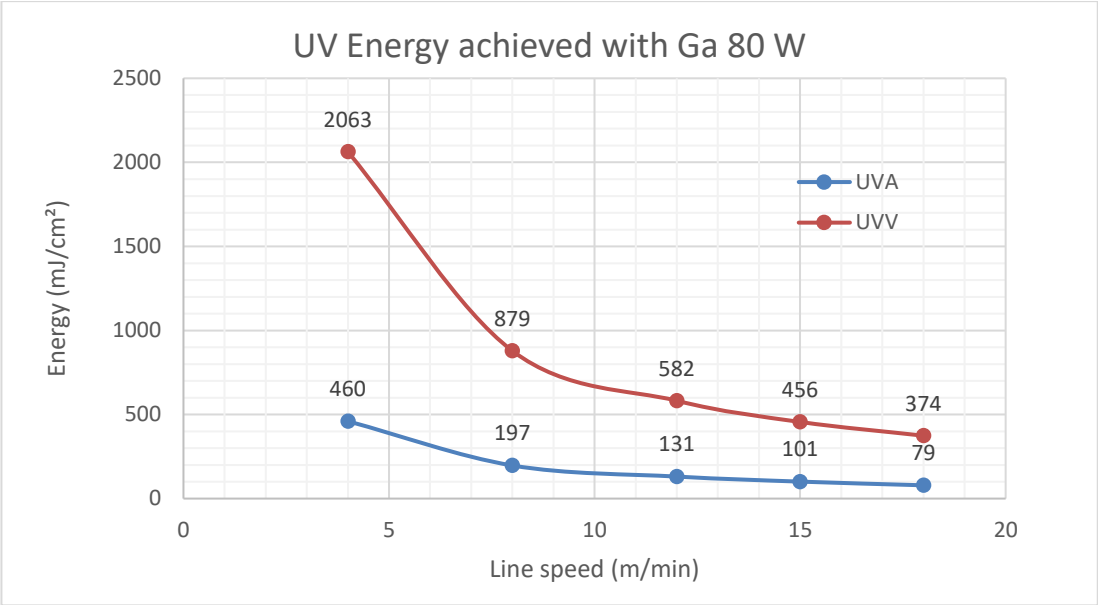

Figure 11. *UV energy achieved with the UV oven at different line speeds When using gallium lamps at 80 W.*

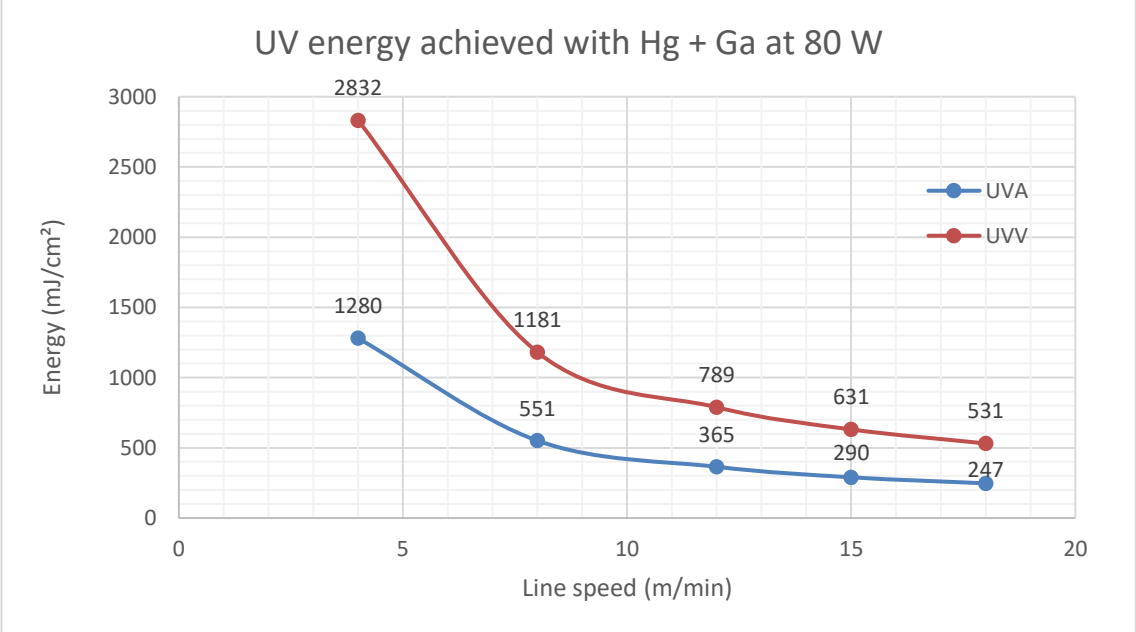

Figure 12. *UV energy achieved with the UV oven at different line speeds when using both halogen and gallium lamps at 80 W.*

From the figures the amount of UV energy with different line speeds can be evaluated for the testing of this thesis. For the acrylate lacquer, 500 mJ/cm^2 UV dose was recommended. This can be achieved approximately with line speed of 6,8 m/min when using Hg-lamp at 80 W. This can be evaluated from Figure 10.

The recommended UV dose for the acrylate paint was 400 mJ/cm^2 from both Hg and Ga lamps. The limiting factor for this is the Ga-lamp that has much lower UVA energy levels

compared with Hg-lamp at same line speeds. With the UV oven used the recommended energy for the paint is acquired with line speed of 5 m/min. This can be evaluated from the Figure 11.

4.2 Gloss and hardness

The testing was started with application of chosen coatings on glass sheet and testing different curing energies to determine what could be the testing parameters for other tests and to understand how through is the cure of the coatings with each energy levels. Application was done with 30 µm and 15 µm single side bar coater film applicators to black glass sheet and the UV oven's lamp power set to 80 W. 30 µm layer thickness was chosen for the lacquer because with the same thickness samples could also be prepared for the $KMnO_4$ stain test. With 15 µm applicator available it was not possible to prepare samples for the clear glass sheet that was needed for the stain test. When converting the µm to g/m^2 using the specific gravities of the products, 30 µm of lacquer is equal to approximately 35 g/m^2 of wet lacquer and similarly with the paint 15 µm is equal to approximately 26 g/m^2 of wet paint.

Two different batches from both products were tested and line speed of the UV line oven was changed to obtain different curing energies. Test with these samples included observation by fingertip if the coating was cured, measuring pendulum hardness and gloss. Gloss was measured from 60° angle by using glossmeter. Results from these tests are presented in Table 8.

Table 8. *Curing energy testing with 30 µm layer of acrylate lacquer and 15 µm layer of acrylate paint on glass sheet.*

	Line speed (m/min)	Lamp used = energy approx. (mJ/cm3)	Touch dry	Gloss (60°)		Hardness	
				#1	#2	#1	#2
Lacquer	4	Hg = 825	yes	21	16	82	80
	5	Hg = 700	yes	25	16	49	69
	6	Hg = 600	yes	29	16	69	67
	7	Hg = 470	yes	35	24	52	85
	8	Hg = 390	yes	36	29	54	81
	9	Hg = 340	yes	42	28	44	81
	10	Hg = 300	yes	40	35	50	65
	11	Hg = 270	yes	27	36	47	47
	12	Hg = 244	yes	34	35	42	45
Paint	4	Ga = 460, Hg = 784	yes	69	65	33	32
	5	Ga = 400, Hg = 700	yes	71	65	25	31
	6	Ga = 300, Hg = 540	yes	69	65	33	30
	7	Ga = 250, Hg = 470	yes	71	65	29	22
	8	Ga = 197, Hg = 390	yes	71	soft	32	soft
	9	Ga = 170, Hg = 340	no	-	-	-	-

Acrylate lacquer dried to ‘touch dry’ with all the energy levels tested. However, from the gloss and hardness results it can be noticed that there is variation between the samples. When the curing energy decreases the gloss of the coating increases. For this product, the normal gloss level is from 10 to 16 when measured with 60 °. Overall, with the batch #2 the results are more linear but the gloss of the batch #2 is more stable with the lower line speeds than with batch #1 that has more variation. With line speed of 7 m/min (470 mJ/cm^3) the gloss increases with both batches quite much when compared to 6 m/min (600 mJ/cm^3) result. This could indicate that the minimum radiation energy level to obtain correct gloss level is between 470 mJ/cm^3 and 600 mJ/cm^3.

Pendulum hardness values in the Table 8 are presented as mean from several measurements from same sample surface. With the lacquer samples hardness decreases when the curing energy decreases, and this indicates that the curing is not complete.

Gloss was also measured from birch veneers prepared for the chemical resistance test, top coated with the lacquer. The pieces were primed with two layers of UV curing sealer, sanded and top coated with the acrylate lacquer. Two different application amounts were used for the lacquer and the pieces were dried using with different line speeds. The systems tested and gloss are presented in Table 9.

Table 9. *Gloss of birch veneers coated with the acrylate lacquer with different application amount of lacquer and different curing parameters.*

Application amount (g/m2)	Drying speed (m/min)	Lamp used = energy approx. (mJ/cm3)	Gloss 60 °
9	5	Hg = 700	10
9	6,8	Hg = 500	12
9	8	Hg = 390	14
9	10	Hg = 300	13
27,5	5	Hg = 700	11
27,5	6,8	Hg = 500	10
27,5	8	Hg = 390	13
27,5	10	Hg = 300	15

Gloss of the lacquered surface is at acceptable range with the birch substrates. Noticeable is that when the curing energy is lowered, the gloss increases. This is in line with the test that were done to the glass sheet. But, in the films on glass, the gloss increased more rapidly, and the differences are much bigger when - in these samples - the gloss level overall is much lower. The application amount could cause the difference between these samples.

Acrylate paint sample cured with line speed 9 m/min surface was noticeably soft after oven and is marked as not touch dry, because of this no further test were made for these. With line speed of 8 m/min there were variation between the two batches tested. With batch #1 the surface felt dry and hard but with sample from batch #2 the surface felt dry, but the film was soft that was identified by pressing with fingertip. From this can be concluded that the amount of UV radiation (197 mJ/cm^3) from the Ga-lamp was too low as the ‘deep cure’ is not sufficient.

The gloss and pendulum hardness results for the paint samples are more stable than those with the lacquer. The hardness in the batch #2 decreases with line speed 7 m/min from 30 to 22 that indicates that there is difference in the level of cure. Similar drop is not visible in results from the batch #1 that has more variation in the hardness with different line speeds.

4.3 Potassium permanganate stain

The level of cure was also analysed by using potassium permanganate, $KMnO_4$, water solution. To understand the effect of $KMnO_4$ for the cured surface, samples were prepared with different curing energy. 0,5 % and 1 % water solution of $KMnO_4$ were used in the testing to understand the type and strength of the stain mark left on the surface.

Solutions were applied on the surface of the cured coatings and left for 1 and 5 minutes. After this the surface was cleaned by using cloth damped with water or solvent. The result of this test is presented on Figure 13.

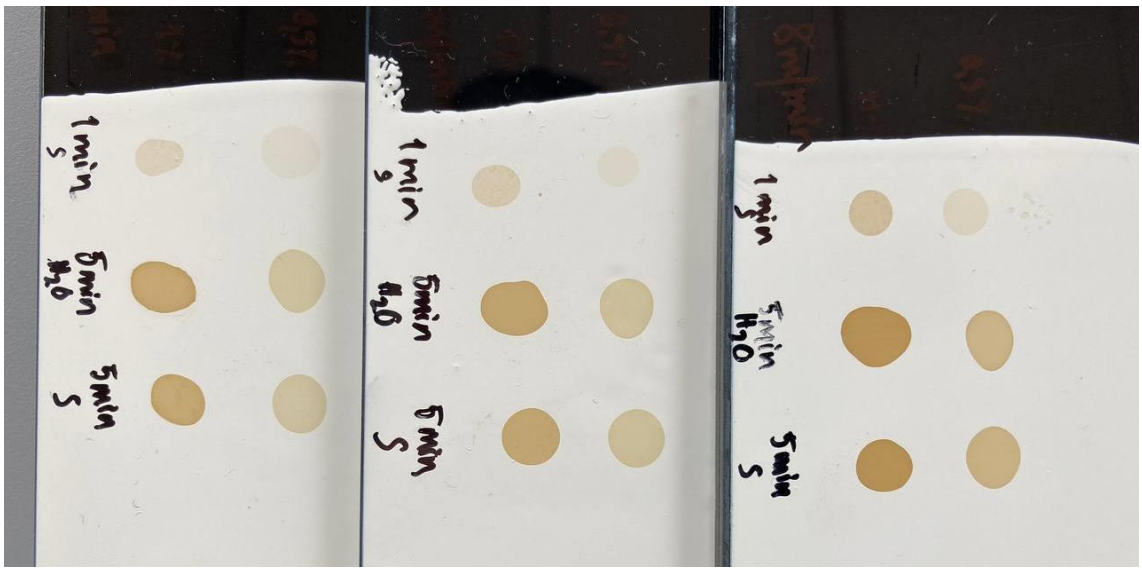

Figure 13. *Acrylate paint cured with line speeds of 4 m/min, 5 m/min and 8 m/min in order from left to right. In each film 1 % (left column) and 0,5 % (right column) solution of KMno₄ was tested with exposure times from 1 min to 5 min. First stain row in each sample is for 1 min exposure that was cleaned with solvent, second stain row for 5 min exposure cleaned with water and third stain row cleaned with solvent.*

Based on the first tests, it was noticed that the evaluation of the cure based on the stain is hard as the difference between colour of the stains at the sample surfaces were minor. Stains in the film cured by using speed 8 m/min are slightly darker than for the 4 m/min and 5 m/min speeds indicating that the level of cure between the films is different. Based on this the 1 % $KMnO_4$ solution was chosen for further testing since the stain mark is darker and differences between the samples could be easier to notice with visual evaluation.

For further testing samples with 1 min and 5 min exposure time to 1 % $KMnO_4$, samples were prepared onto glass sheets. Acrylate lacquer was applied with 30 µm applicator to clear glass and paint with 15 µm applicator to black glass sheet. From the paint, same samples were used as for the gloss and hardness test presented earlier. A Clear glass sheet was chosen for the lacquer because on the black glass sheet the stain marks would not have been visible. Two different production batches from both products were used in the evaluation to see if there are much variation between them. The samples were visually evaluated, and the stains were measured with spectrophotometer to determine the colour difference between the stain marks. Images of the stain marks on cured

lacquer surfaces are presented in Figures 14 and 15 and on paint surfaces in Figure 16, 17 and 18.

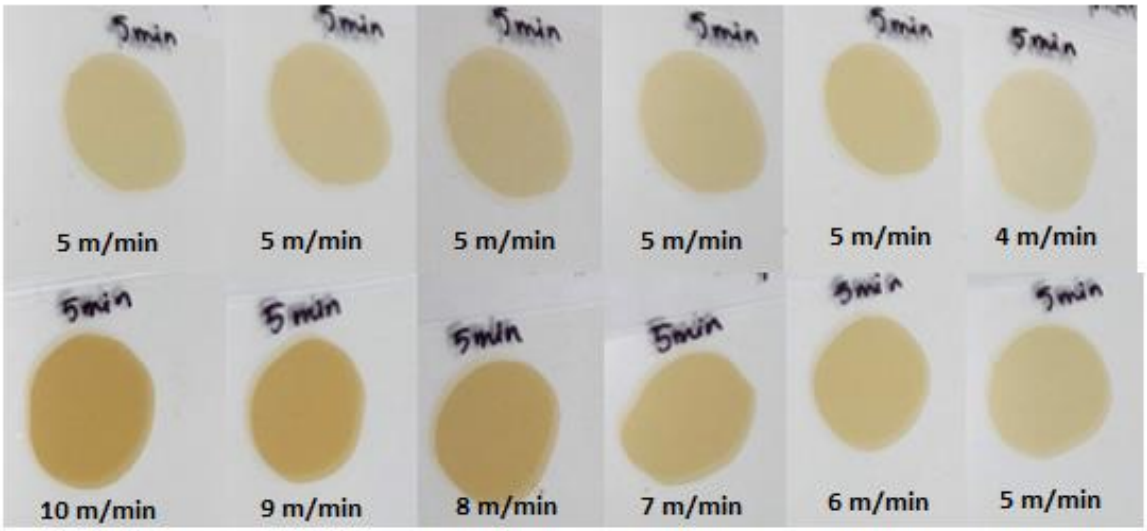

Figure 14. *Stain marks from the lacquer film. Each stain is presented with the same 5 m/min stain on the upside as a standard taken in the same image to minimize the effect of lighting on the shade.*

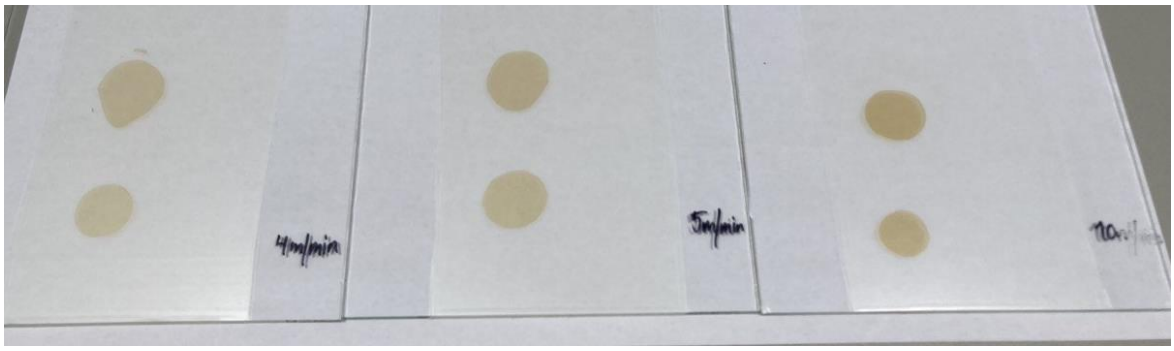

Figure 15. *Example of acrylate lacquer samples cured with different line speeds of 4 m/min, 5 m/min and 10 m/min. $KMnO_4$ exposure of 5 min cleaned with water for colour difference measurement.*

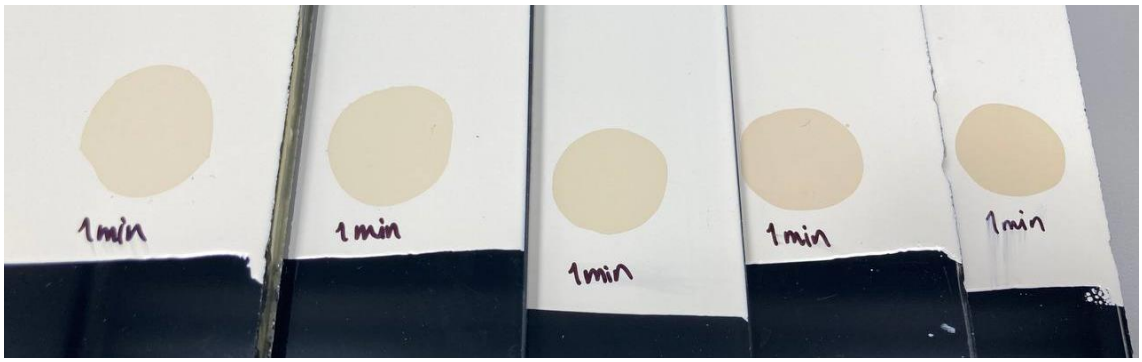

Figure 16. *$KMnO_4$ stain marks left to the paint film with 1 min exposure time. Films are cured with line speeds from left to right: 4 m/min, 5 m/min, 6 m/min, 7 m/min and 8 m/min.*

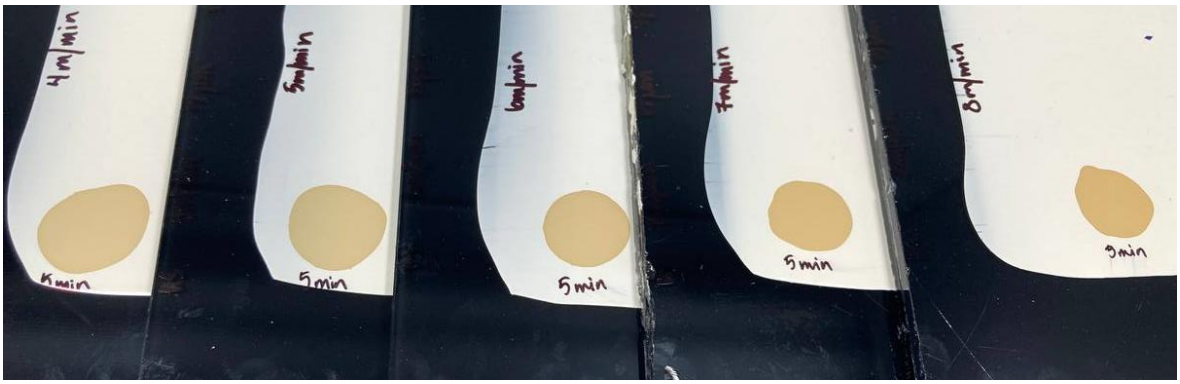

Figure 17. *$KMnO_4$ stain marks left to the paint film with 5 min exposure time.*

Figure 18. *Comparison of $KMnO_4$ stain marks left to paint films cured when using a 4 m/min, 5 m/min and 8 m/min line speed from left to right.*

Visual comparison of the stain marks leads to conclusion that when the line speed of the oven is increased the stain mark is darker and thus the film not cured fully as suspected. The differences are quite subtle but still noticeable. The darkness of the stain increases

steadily when the line speed is increased and curing energy is lower. This is most noticeable from the Figure 14 where the difference between the stain marks is illustrated with several line speed.

To obtain more data from the stains they were also measured with spectrophotometer. The colour difference was measured from the same samples with 5 min $KMnO_4$ exposure by using the stains obtained with line speed 5 m/min as standards. With the lacquer samples white paper board was placed behind the clear glass sheet to provide base shade due to the transparency of the substrate. The results are presented in Tables 10 and 11.

Table 10. *Colour difference measured with spectrophotometer from the $KMnO_4$ stain from two different lacquer batches using 5 m/min stain as standard.*

	Linespeed (m/min)	Lamp used = energy approx. (mJ/cm3)	Colour difference				
			dL	da	db	dE	dev.
Lacquer #1	4	Hg = 825	1,09	-0,55	-3,97	4,16	0,51
	5	Hg = 700	**STD**	**STD**	**STD**	**STD**	0,77
	6	Hg = 600	-1,37	0,56	2,05	2,53	0,35
	7	Hg = 470	-1,82	0,85	3,46	4	0,92
	8	Hg = 390	-2,26	1,15	4,5	5,17	0,78
	9	Hg = 340	-3,14	1,74	6,36	7,3	0,42
	10	Hg = 300	-3,54	2,1	7,4	8,46	0,51
Lacquer #2	4	Hg = 825	2,24	-0,49	-7,18	7,54	0,6
	5	Hg = 700	**STD**	**STD**	**STD**	**STD**	0,09
	6	Hg = 600	-1,58	0,75	3,62	4,03	0,1
	7	Hg = 470	-3,42	1,55	6,22	7,27	0,05
	8	Hg = 390	-5,19	2,64	10,16	11,71	0,33
	9	Hg = 340	-6,77	4,11	12,37	14,69	0,02
	10	Hg = 300	-8,42	4,65	13,12	16,27	0,03

Table 11. *Colour difference measured with spectrophotometer from the $KMnO_4$ stain from two different paint batches using the 5 m/min stain as standard.*

	Linespeed (m/min)	Lamp used = energy approx. (mJ/cm3)	Colour difference				
			dL	da	db	dE	dev.
Paint #1	4	Ga = 460, Hg = 784	2,13	0,89	1,1	2,56	0,26
	5	Ga = 400, Hg = 700	**STD**	**STD**	**STD**	**STD**	1,04
	6	Ga = 300, Hg = 540	-0,71	0,92	1,68	2,04	0,24
	7	Ga = 250, Hg = 470	-1,75	2,51	4,43	5,39	0
	8	Ga = 197, Hg = 390	-4,24	3,83	5,31	7,8	0,05
Paint #2	4	Ga = 460, Hg = 784	0,41	0,1	0,02	0,42	0,04
	5	Ga = 400, Hg = 700	**STD**	**STD**	**STD**	**STD**	0,08
	6	Ga = 300, Hg = 540	-0,35	0,22	0,45	0,62	0,01
	7	Ga = 250, Hg = 470	-1,87	1,14	2,12	3,05	0,16
	8	Ga = 197, Hg = 390	soft	soft	soft	soft	soft

From one stain the colour was measured from three spots and the “dev.” in the Tables 10 and 11 represent the deviation in the colour between these three measurements. The deviation varies between the measurements quite much. Different factors that cause higher deviation to the measurements are the uniformity of the colour in the stain area and the spot where the measurement was made. Also placing of the sample surface to the correct spot on the device was quite hard. It could be possible that in some measurement the area measured contains both stained and unstained surface.

The results from the spectrophotometer measurements are logical with the dL and dE values. When the curing energy is lower the stain mark is darker and the total colour difference increases when compared to the 5 m/min stain that was used as standard. The stains obtained with 4 m/min line speed are also lighter on the shade when comparing to standards. This indicates that the level of cure of the film is lower with higher line speeds. But when comparing the results from the two different batches of same product it can be noticed that the variation with the same line speeds is quite high. For this reason, the measurements from different batches were also compared so that with each line speed batch #2 measurement data was compared to batch #1 data. These colour differences are presented in Table 12.

Table 12. *Colour difference of the stains between the two batches with each line speed. The data from batch #1 is used as a standard.*

	Linespeed (m/min)	Lamp used = energy approx (mJ/cm3)	Colour difference			
			dL	da	db	dE
Lacquer #1 (STD) vs. #2	4	Hg = 825	+2,31	+0,04	-5,47	5,94
	5	Hg = 700	+1,16	-0,02	-2,26	2,54
	6	Hg = 600	+0,95	+0,18	-0,68	1,19
	7	Hg = 470	-0,43	+0,68	+0,51	0,96
	8	Hg = 390	-1,76	+1,74	+3,41	4,11
	9	Hg = 340	-2,47	+2,38	+3,61	4,98
	10	Hg = 300	-3,72	+2,54	+3,46	5,68
Paint #1 (STD) vs. #2	4	Ga = 460, Hg = 784	-0,08	+0,66	+0,36	0,76
	5	Ga = 400, Hg = 700	+1,65	+1,46	+1,43	2,62
	6	Ga = 300, Hg = 540	+2,01	+0,77	+0,20	2,16
	7	Ga = 250, Hg = 470	+1,57	+0,08	-0,89	1,76
	8	Ga = 197, Hg = 390	-	-	-	-

The difference between the two batches in both products are quite big as suspected based on the data from Tables 10 and 11. With the lacquer the difference between the two batches is smallest with samples prepared with line speeds of 6 m/min and 7 m/min.

With the paint the samples prepared with 4 m/min line speed have similar stain reaction, but when the line speed is increased the batch #2 has lighter shade when compared to #1. This could mean that the batch #1 is not as fully cured as the #2.

4.4 Chemical resistance test

The chemical resistance test was done for test pieces with different topcoats, application amounts and curing parameters. Same primer was used in all the samples, UV-curing epoxy-acrylate sealer. Topcoat used in the systems was the same UV-curing acrylate lacquer and UV-curing paint as used in the other tests.

Systems, application amounts and curing conditions are presented in Table 13. The substrate in all the pieces was birch plywood. All the samples have the same amount of UV sealer as primer. Primer application was done with small cylinder coating machine and the pieces were coated two times with approximately 20 g/m^2 of sealer. Layers were dried with Hg-lamp at speed 5 m/min. Pieces were also sanded with P320 after each sealer layer. Lacquer topcoat was also applied with small cylinder coating machine but with the paint larger coating machine was used.

Table 13. *Coating systems for chemical resistance test pieces. Birch plywood was used as substrate in all systems.*

		Top Coat		
Number of sample	**Product**	**Application amount (g/m^2)**	**Drying speed (m/min)**	**Lamp used = Curing energy approx. (mJ/cm^3)**
1.1	Lacquer	9	5	Hg = 700
1.2	Lacquer	9	6,8	Hg = 500
1.3	Lacquer	9	8	Hg = 390
1.4	Lacquer	9	10	Hg = 300
2.1	Lacquer	27,5	5	Hg = 700
2.2	Lacquer	27,5	6,8	Hg = 500
2.3	Lacquer	27,5	8	Hg = 390
2.4	Lacquer	27,5	10	Hg = 300
3.1	Paint	9,6	4	Ga = 460, Hg = 784
3.2	Paint	9,6	5	Ga = 400, Hg = 700
3.3.	Paint	9,6	6	Ga = 300, Hg = 540
3.4	Paint	9,6	7	Ga = 250, Hg = 470
3.5	Paint	9,6	8	Ga = 197, Hg = 390
4.1	Paint	36,5	5	Ga = 400, Hg = 700
4.2	Paint	36,5	6	Ga = 300, Hg = 540
4.3	Paint	36,5	7	Ga = 250, Hg = 470
4.4	Paint	36,5	8	Ga = 197, Hg = 390
5	Paint	15,6	5	Ga = 400, Hg = 700

Pieces were scratched with fingernail after oven to see if the curing of the topcoat varied. With paint samples 3.2, 3.3, 3.4, a fingernail touch left noticeable scratch that indicated that the coating was not fully cured. Also sample 3.5 was not cured and the surface was soft. Due to this, paint samples numbers 3.1 and 5 was also prepared. Sample 3.1 with same application amount but higher curing energy and sample 5 with slightly higher application amount of the paint to see if the layer thickness was the problem. With the sample 5 the scratching after oven result was better implying that the 9,6 g/m^2 is slightly too thin layer of this paint. Also, in all other paint samples a small scratch was visible, but the coating appeared to be fully cured. In the lacquer samples, on surfaces, no scratches were visible.

The chemical resistance test was performed for the pieces after ageing of 16 h at 50 °C according to the method presented in Chapter 3.5. Results from this test are presented in Table 14. Sample number 3.5 was left out of the testing as it was not fully cured.

Table 14. *Results from the chemical resistance test. Samples were rated according to criteria presented in chapter 3.5.*

	Water 16 h	Water 24 h	Fat 24 h	Coffee 1 h	Alcohol 1h	Acid 1 h	Base 1h	2N + fat 24 h	3N + fat 24 h	70 C 20 min
1.1	5	5	5	5	5	5	5	5	5	5
1.2	5	5	5	5	5	5	5	5	5	5
1.3	5	5	5	4	4	5	5	5	5	5
1.4	5	5	5	4	4	4	4	5	5	5
2.1	5	5	5	5	5	5	5	5	5	5
2.2	5	5	5	5	5	5	5	5	5	5
2.3	5	5	5	4	5	5	5	5	5	5
2.4	5	5	5	4	4	5	5	5	5	5
3.1	5	5	5	4	5	5	5	5	5	5
3.2	5	5	5	4	4	4	4	5	5	5
3.3	5	5	5	4	4	4	4	5	5	5
3.4	5	5	5	4	3	3	3	5	5	5
4.1	5	5	5	4	5	5	5	5	5	5
4.2	5	5	5	4	5	5	5	5	5	5
4.3	5	5	5	4	5	5	5	5	5	5
4.4	5	5	5	3	4	5	5	5	5	5
5	5	5	5	4	5	5	5	5	5	5

The results from the samples with the lacquer topcoat (1.1 – 2.4) are good. Samples with the lower application amount (1.1 – 1.4) have small differences in the coffee, alcohol, acid, and base exposure as samples with lowest curing energy have slightly poorer durability against these. The change in the sample surface from 5 to 4 is minor and can be

observed only from certain angle and thus the rating 4 can be classified as acceptable change. Same can be noticed with the thicker application amount samples with lower energy curing. The clearly observed change in these series is only with coffee and alcohol. The layer thickness has an impact on the chemical resistance with this lacquer based on the results of this testing.

The results with the paint samples are similar as with the lacquer, but the changes are more apparent. The layer thickness influences the chemical resistance so that thicker layer samples have slightly better chemical resistance. When the sample is exposed to lower curing energy the results are also slightly worse, but still good as with the lacquer. Between samples 3.3 and 3.4, the significant change can be noticed as alcohol, acid and base resistance drop from 4 to 3. In rating 3, the surface defect is already quite distinct. Similar change is not visible in the samples with thicker layer. Example of the difference between rating 4 and 3 in 1 h coffee exposure is presented in Figure 19.

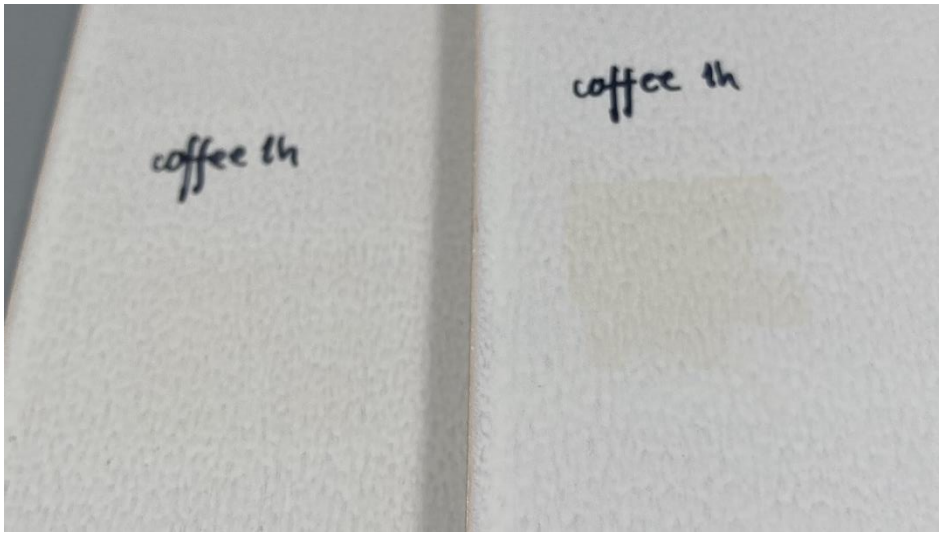

Figure 19. *Difference of result 4 and 3 with 1 h coffee. Samples are paint with the higher application amount. On the left side coffee mark is rated as 4 and the samples is cured with 5 m/min line speed. The right side is rated as 3 and the line speed used in curing is 8 m/min.*

Overall, the results of the test imply that the chemical resistance is better when the coating is subjected to higher curing energy. Also, with same radiation energy better resistance can be achieved with higher film thickness.

4.5 Mechanical scratching

The testing was started with the HDF panel as a substrate to understand the effect of the single scratch. HDF panel was painted and sanded smooth by the supplier. The chosen coatings were applied with 30 µm applicator to the panel surface and dried in the UV

oven with different line speeds. Two parallel samples from same batches of product were prepared with each line speed. Scratching was performed with three different weights (mass) from the load arm: 350 g, 600 g, and 850 g.

The lacquer sample was cured with five different line speeds (for five separate series). After the scratching, the pieces were evaluated using a small magnifying glass of 10x with a measuring scale. With the lacquer samples, the coating film mostly cracked due to the scratching, but the coating did not detach from the substrate completely. The width of the defected area due to scratching could be measured with the magnifiers measuring scale. These results are presented in Table 15.

Table 15. *Width of the scratches done as a single scratch with three different weights for lacquer samples cured with different line speeds.*

	line speed (m/min)	widht of the defect on coating (mm)		
		350 g	600 g	850 g
Lacquer 30 µm	4	0,3	0,5	0,8
	5	0,4	0,5 - 0,8	1
	8	0,3	0,5 - 0,8	0,6 - 1,4
	10	0,5 - 1	0,6 - 1	1 - 1,3
	12	0,5 - 0,6	1	1 - 1,4

From the table, it can be noticed that with each weight used the response in the width of the defect is similar when the line speed is increased. With the highest level of curing energy used, the scratch width is smallest and when the amount of energy used is lowered the width of the defected area increases quite proportionally. Also, it was noticed that when the amount of curing energy was lowered the width of the defect varied more inside the single scratch which can also be noticed from the results. For example, with the lowest weight 350 g when using 10 m/min line speed in UV oven the width of the defected area varied from 0,5 mm to 1 mm. This could indicate that the film is unevenly cured and there might be parts in the film that were not cured as well as other parts. In Figures 20, 21 and 22 the lacquer surfaces after testing are presented for samples prepared with 5 m/min, 8 m/min and 10 m/min line speeds.

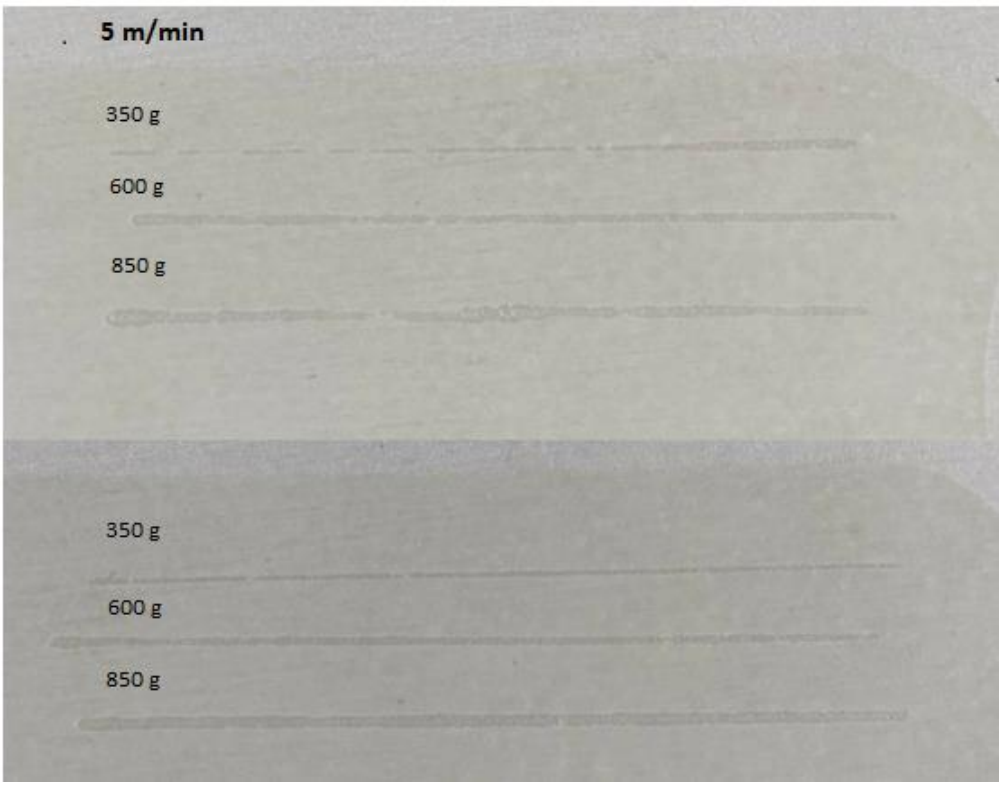

Figure 20. *Parallel lacquer samples cured with line speed of 5 m/min*

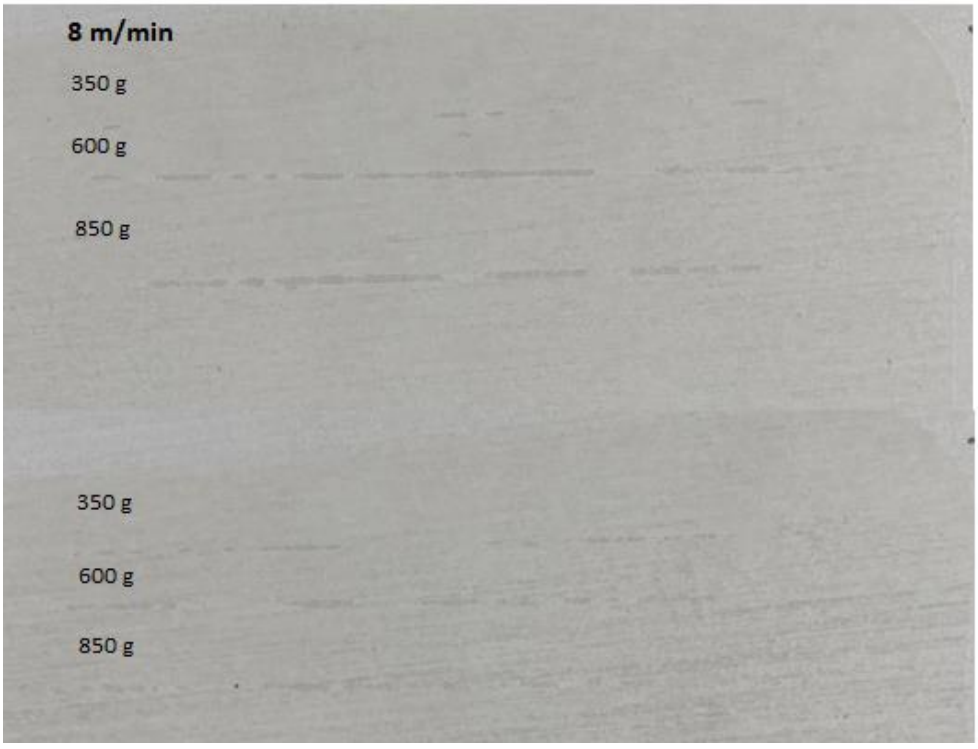

Figure 21. *Parallel lacquer samples cured with line speed of 8 m/min*

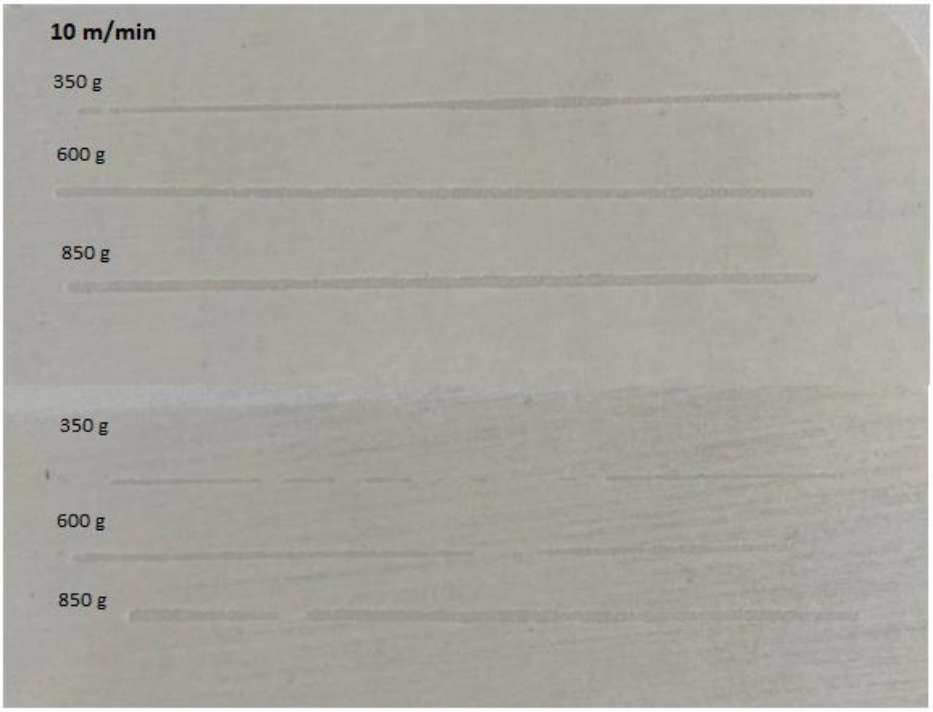

Figure 22. *Parallel lacquer samples cured with line speed of 10 m/min.*

In the lacquer samples, the defect of the scratch does not always continue through the whole scratching length as can be seen from Figures 20, 21 and 22. Especially when comparing samples prepared with 5 m/min and 8 m/min the difference is noticeable. In the samples prepared with 5 m/min the defect from the scratch is visible in the whole scratching length, but in the sample prepared with 8 m/min the defect left by the scratching tip is nearly visible. The width of the defected area with the highest load (mass = 850 g) is also smaller is some parts in the 8 m/min sample (0,6 mm – 1,4 mm) when compared to the 5 m/min sample (1 mm) as presented in Table 15. The hardness of the lacquer surface when cured with 8 m/min line speed can be optimal to withstand the force of the scratching tip.

The paint samples were prepared with only two different line speeds (5 m/min and 7 m/min) for the HDF panel. The application amount was also 30 µm with these samples. The amount is slightly too high but the 15 µm applicator used earlier was not possible to use due to the small warping of the HDF panel. Application direction with the HDF panel could only be from the short size down due to the small warpage of the panels and short enough 15 µm applicator was not available.

Similar evaluation for the paint sample was not possible to make as for the lacquer samples because the products behaved differently. If the coating was not ripped from the surface the width of the scratch (or any defect) was not possible to evaluate as the

scratch mark in the paint surface is polished line rather than a visible scratch. In Figure 23 and 24 the defects due to the scratching are presented in the paint samples.

Figure 23. *Scratching done to paint sample cured with 5 m/min line speed on HDF panel. Weights used for the scratching are 350 g, 600 g and 850 g starting from left to right.*

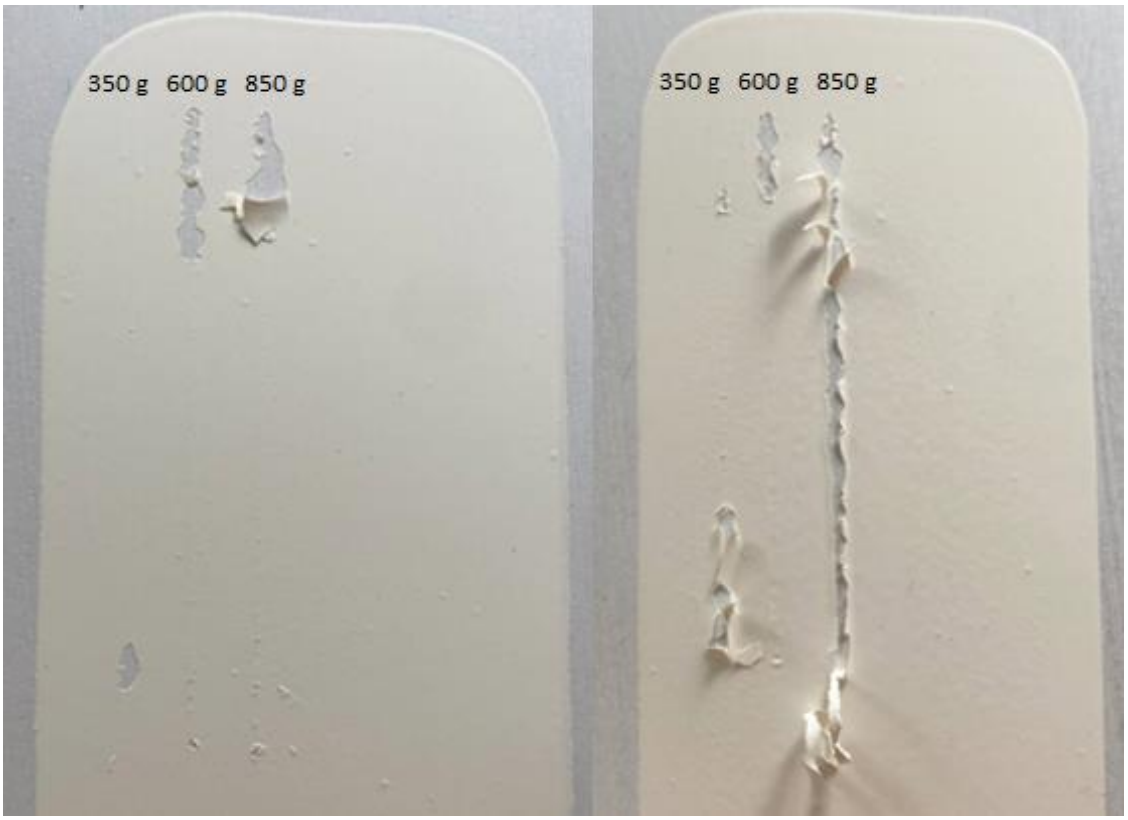

Figure 24. *Three single scratches with different weights done to paint samples cured with 7 m/min line speed.*

From the Figures 23 and 24 it is noticeable that the type and degree of defect varies between line speeds and also between the two parallel samples. With the 7 m/min line speed, the samples prepared the difference between the parallel samples is big as seen in Figure 24. Especially with the highest load of 850 g as in the other sample the surface is pealed from the substrate completely while in the parallel sample (left side) similar effect is visible only in the beginning of the scratch. It was also noticed that under the cured surface the paint was still partly in liquid state with the sample on the right side. Similar was not noticed with the sample on the left side. The surfaces in both felt hard and not soft when pressing them with finger right after the curing. As the samples were prepared from the same batch of paint during the same day the difference for these could come from the UV oven.

Scratching was also done to same pieces that were used in the chemical resistance testing. The application amounts and curing parameters are presented in Chapter 4.4 in Table 13. Scratching was done in same manner as with the HDF panels and the direction of the scratch was perpendicular to the wood grain. Scratch marks were evaluated by using microscope to determine the type of defect in the surface. Example of the defects caused by the single scratching in two lacquer surfaces with same application amount of 27,5 g/m^2 and different curing energies are presented in Figures 25 and 26.

Figure 25. *Image taken with microscope from the lacquer sample 2.2 (27,5 g/m^2, curing 6,8 m/min) scratched with Taber Linear Abraser. Weights of the load arm 350 g, 600 g and 850 g in order from left to right*

Figure 26. *Image taken with micrscope from the lacquer sample 2.4 (27,5 g/m^2, curing 10 m/min) scratched with Taber Linear Abraser. Weights of the load arm 350 g, 600 g and 850 g in order from left to right.*

From the microscopic images, it can be noticed that the scratch tip causes a groove on the surface. In some of the scratches, there are cracks on the lacquer film on the sides of grooves. This type of behaviour of the lacquer film is visible on the Figure 25 on the scratch performed with 850 g load and in Figure 26 in scratches performed with 600 g and 850 g load. By visual inspection, it looks like the sample prepared with higher line speed with 10 m/min has more cracking on the sides of the grooves even with lower loads from the scratching tip. The cracking of the lacquer is small, and it is not fully visible without enlargement of the scratched area.

Similar microscopic images of the paint samples are presented in Figures 27 and 28. Application amount of paint in these both is 36,5 g/m^2 and the line speed used for the curing is 5 m/min and 8 m/min.

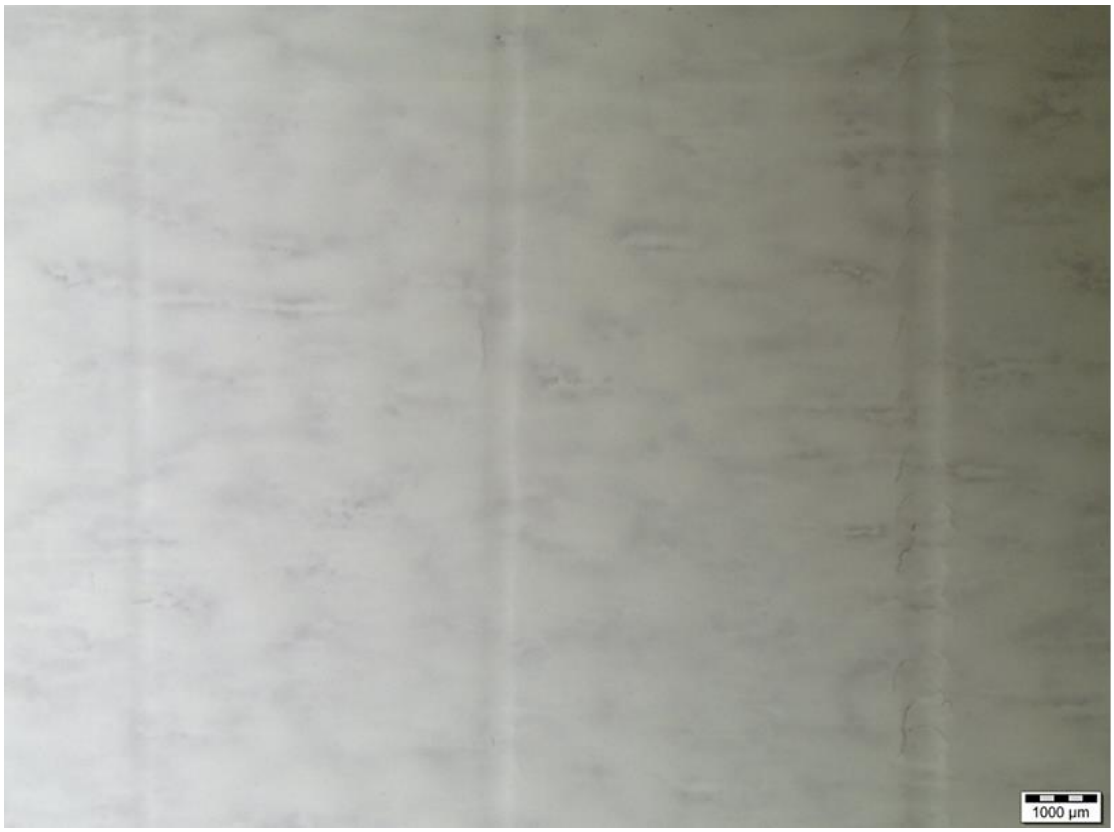

Figure 27. *Image taken with microscope from the scratched paint sample 4.1 (36,5 g/m^2, curing 5 m/min). Weights of the load arm in order from left to right 350 g, 600 g and 850 g.*

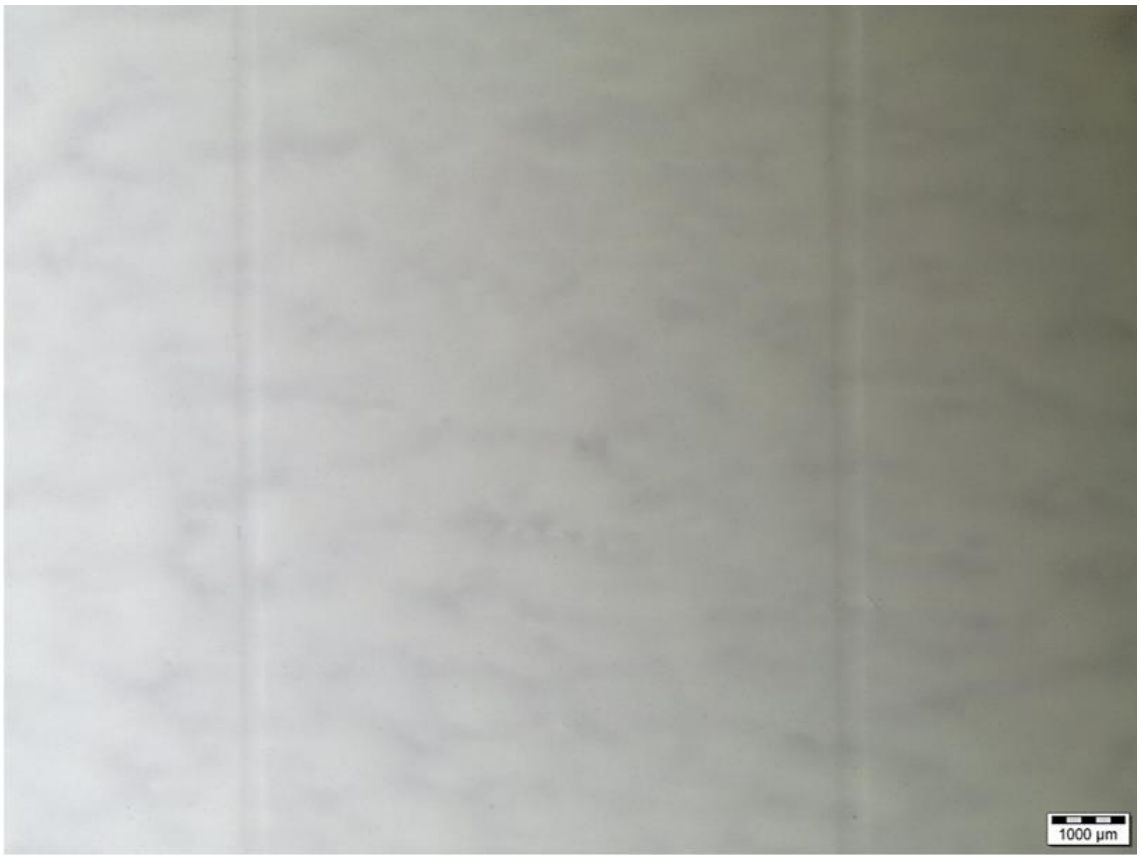

Figure 28. *Image taken with microscope from the scratched paint sample 4.4 (36,5 g/m^2, curing 8 m/min). Weights of the load arm in order from left to right 350 g and 600g.*

The grooves left by the scratching tip are visible in the microscopic images similarly as with the lacquer. There is also some cracking of the paint film visible on the side of the grooves as well as on the groove itself. The cracking in the scratches performed in the sample 4.4 is minimal when compared to the scratches in the sample 4.1. Especially the scratch made with 850 g load in the sample 4.1 is cracking quite heavily from the grooves. Unfortunately, the three scratches made to the sample 4.4 were too far apart so that all three scratches could be fitted in the same image. The scratch made with the 850 g load arm was visually similar as the 600 g.

The degree of cracking due to scratching varies in both lacquer and paint samples between the different curing energies. This indicates that the level of cure varies between the samples prepared with different curing energies.

5. ANALYSIS AND COMPARISON OF THE TEST RESULTS

There is noticeable variation in the test results between the two different coatings in same tests and between the different test performed. All of the test performed give good data about how the coatings behave with different curing energies, but the difficulty is in the grading of the results. In most of the tests (methods), visual inspection is the best way of grading and analysing the results. This leaves possibility for the influence of the opinion of different operators.

The test results are not showing a linear relation when certain effect or exertion is varied. The coatings have been accepted usually when they fulfil given specification, for example by gloss and hardness. The test results here show that the difference between acceptable and non-acceptable material is small. In some tests, the difference between the results from parallel samples were relatively big thus the accuracy and repeatability of the test performed can be questioned.

In this chapter, the results of the tests are first analysed and then compared with each other. Also, the possible error sources and the repeatability of the test is evaluated.

5.1 Gloss and pendulum hardness

The gloss and hardness tests are a good and simple methods to achieve quantitative and comparable information on the cured films performance. It is also relatively easy to set limits on what is acceptable result and what is not based on what is the desired material property. The level of cure for the paint and lacquer is hard to analyse based solely on these tests, but they provide valuable information on how the coatings behave when the curing energy is changed.

As discussed earlier in Chapter 4.2, the energy levels to achieve correct gloss results with the lacquer were between 470 mJ/cm^3 and 600 mJ/cm^3. With the hardness test, similar energy limits were not identified as the hardness did not behave linearly. Nevertheless, the hardness test method is a good test to perform together with the gloss measurements as it still provides added value and information about the cure level of the film.

With paints, the usefulness of the test is opposite to the lacquer. The gloss test did not provide any clear limits for the curing energy as the gloss results with different curing energies did not have any clear variation implying that the surface cured well with all

tested (UV) energies. The hardness test on the other hand provided some information about the behaviour of paint. It was noticed that, with 250 mJ/cm^3, from the Ga-lamp the hardness dropped with the other batch indicating that the film was not fully cured. With 300 mJ/cm^3, the hardness result was still on the same level as with higher energy levels.

In the results, there were differences between the two different batches tested with both products. Differences between the results from the two batches of the same product can be caused by the age of the samples. Also, with matt products such as the lacquer, insufficient mixing of the product can cause higher gloss as some of the matting agents can be left at the sedimentation at the bottom of the can. The used film thickness of 30 µm is high for both products and this also affects the gloss and hardness results. Lastly, the condition of the glass surface also has an impact on the hardness results as well as any contamination and impurities on the cured film. If there are scratches or other defects on the surface, it can lower the hardness results of the tested film.

5.2 Potassium permanganate stain

The $KMnO_4$ stain test results were logical here, the stain mark left on the surface becomes darker when the curing energy is lowered, but the differences between two batches are quite big as presented in Chapter 4.3. Based on the colour measurement data from the stains it is hard to analyse or determine any limits on what enough curing energy is for the products tested.

From the difference in the colour measurements between the two batches, a limit for the curing energy could be determined based on how big the difference in the spectrophotometer results is according to the Table 12. With the lacquer the difference between the two different batches was smallest with line speeds 6 m/min and 7 m/min with dL and db. This could indicate that the curing reaction is similar with the energy levels from 470 mJ/cm^3 to 600 mJ/cm^3. With higher and lower energy, the difference in dL and db increases above 1. With the higher energy levels, the difference could be caused by over curing effect.

With the paint samples, only with line speed of 4 m/min and energy of 460 mJ/cm^3 from the Ga-lamp, the difference between the two batches was small. Already when increasing the line speed to 5 m/min the difference in the dL and db increased significantly. The limiting factor with the paint is the energy reached from gallium doped lamp that is required for the through cure of the paint due to titanium dioxide pigments in the product. With this product the energy of 400 mJ/cm^3 achieved with 5 m/min seems to be already too low.

With these determined energy levels, the difference in the stain darkness with each batch (Table 10 and 11) can be calculated. For example, with the lacquer batch 1 the difference in the stain darkness, dL, between the line speeds 6 m/min and 7 m/min is 0,5. With batch 2 the same difference is already bigger at 1,84.

Visual inspection of the stains with the help of the colour measurement could be possible. For example, with the lacquer, if the 470 mJ/cm^3 and 600 mJ/cm^3 were classified as acceptable result then these could act as standards for the visual inspection. During testing it was noticed that the stain intensity and colour start to fade during time. For this reason, the measurements and images of the stain marks were taken during the same day of the stain exposure. For the visual inspection a standard would be needed and creating that is problematic due to the fading colour of the stain. One option would be image taken from the stain difference, but images do not replicate the colours identically. The differences in the stain shade and intensity were small and transferring these into digital standards is not easy.

In this work only the shade of the stain was measured and the colour difference between the stains with different curing energies were analysed. Another possible option for the evaluation could be to measure the colour difference between the regular coating film and the stain. This type of evaluation considers the possible change in the shade of the coating film as well. The colour changes of the coatings film while changing the curing energy could also be followed with this type of analysis.

Stain test could be useful when studying the curing efficiency and difference of version with slight differences in the formulation. For quality control purposes, this test does not offer enough precise results as the differences between the batches were quite big and overall, the results are too ambiguous. This creates problem when trying to determine correct acceptance limits on what could be an acceptable result and what is not. To use this test method to analyse the cure of UV curing products, multiple different batches and samples from those should be prepared and measured with the spectrophotometer to understand better the scatter between the samples (evaluations).

5.3 Chemical resistance test

The chemical resistance test was performed as it is presented in the standards IOS-MATT-0066, EN 12720 and EN 12722. The rating criteria for the results are clearly presented in the standards and this makes the evaluation of the results more straight forward when comparing to some of the other test performed.

Based on the results the prepared samples have good chemical resistance. All the lacquer samples fulfil the requirement for acceptable result. Only noticeable difference in the results was the difference between the two different application amounts. With the lower curing energies of 300 mJ/cm^3 to 390 mJ/cm^3, the higher application amount of 27,5 g/m^2 has slightly better resistance than the samples with the lower application amount of 9 g/m^2.

With the paint sample, similar effect of the application amount to the curing properties was visible already in the sample preparation phase as more samples were needed after noticing that the samples with the lower application amount of 9,6 g/m^2 were not curing properly. Also, the chemical resistance of the samples prepared with lower application amount became worser when the curing energy was lowered. Problem with the curing of the thinner layer of the coatings could be caused by oxygen inhibition.

With the higher application amount of 36,5 g/m^2, the paint layer cured better and drop on the chemical resistance can be noticed in the sample cured with 197 mJ/cm^3 from the Ga-lamp and 390 mJ/cm^3 from Hg-lamp. The energy amount from the Ga-lamp is low when compared to the energy levels that could be recommended based on the other test performed. The reason for this can be that the curing energy received from the Hg-lamp has sufficiently cured the surface of the film and thus there is no big change in the resistance for the chemicals.

Previously the UV curable wood coatings have been tested by the R2 and R4 requirements. Based on the testing here, the samples prepared fulfil the requirements of these well. This raises question that is the classification to the R2 and R4 classes correct for these types of coatings. Chemical resistance test is good test that can be executed in research and development laboratory, but it is not useful in quality control purposes as the testing time including the sample preparation and testing is long. If there would have been clear differences in the 1-hour chemical exposures like coffee and alcohol, those could have been useful to be performed as quick test similarly as the $KMnO_4$ stain on glass sheet to check if the result is normal or not.

5.4 Mechanical scratching

The main difficulty in the mechanical scratching test is in the evaluation of the results. Already during testing, the first samples prepared on HDF board it was noticed that the two chosen coatings behaved differently. This creates a problem when trying to make evaluation criteria for the test results that takes in to account the different behaviour of different coating types. The HDF lacquer samples were compared by the width of the

defect left by the scratching tip. This type of evaluation was not possible for the paint samples as the type of defect was different as stated in Chapter 4.5.

Between the two different types of samples prepared for the mechanical scratching test the drawdown on the HDF panel provides results that are easier to interpret as the effect of the change on the curing energy is visible especially with the lacquer samples. The samples prepared on birch veneer provide more information about the mechanical performance of the coating but the difference between different curing energies is not as distinct.

With lacquer, it was noticed that with the highest load of 850 g used there were more cracks on the scratch area when increasing the line speed of the UV oven. This indicates that the lacquer surface is more brittle with lower curing energy. With higher curing energy the surface is harder and can withstand the force of the scratching tip better. This was visible in the samples prepared for birch veneer. With the paint the behaviour of the cured film was opposite in the birch samples. The scratch area has more cracks when the curing energy is higher. This indicates that the surface is softer with the lower curing energies. The amount of energy from the Ga-lamp can be too low and thus the through cure for the film is not achieved with the lower levels. The surface of all the paint samples felt hard and cured and this implies that the energy from the Hg-lamp was sufficient with all tested line speeds.

For lacquer, a limit for the curing energy could be determined from the scratching test done for the HDF panels based on the variation on the width of the defect caused by the scratching tip. With the lowest weight used (350 g) the width of the defect is quite stable with line speeds 4 m/min, 5 m/min and 8 m/min. When the line speed is increased to 10 m/min the variation of the width of the defect increases inside the single scratch as presented in Table 15. With higher loads the width of the defect is stable mostly only with the 4 m/min and 5 m/min line speeds. Based on this test the limit for the curing energy of the lacquer is between the line speeds 5 m/min and 8 m/min so in range from 390 mJ/cm^3 to 700 mJ/cm^3 likely being closer to the 390 mJ/cm^3.

Similar evaluation of sufficient curing energy for the paint is difficult to make based on the scratching tests done. For the HDF panels, all samples prepared had similar tearing of the coating due to the single scratch as presented in Chapter 4.5. In the samples prepared with higher curing energies the tearing is smaller in the full length of the scratch. From this it can be evaluated that the 5 m/min line speed provides the minimum energy amount (Ga = 400 mJ/cm3 and Hg = 700 mJ/cm^3) required for curing of the paint film.

During testing here, it was noticed that there were differences in the results between the parallel samples, especially with the paint samples prepared on the HDF panels. This could be caused by the uneven cure of the film or by the overheating of the UV oven. Samples were prepared so that the curing was started with the slowest line speed samples and the line speed was increased during testing. Ga-lamp generates more heat during use than the Hg-lamp. With the paint samples this could mean that the heat generated by the Ga-lamp has fastened the curing reaction in the later prepared samples as the temperature has increased during the test run.

5.5 Comparison of the results

All testing performed provided information on the curing efficiency of the chosen products but there are differences on the required curing energy to achieve good material performance. With each test some recommendation on sufficient curing energy needed for these products were made excluding the chemical resistance test. Chemical resistance test provided the best results from the test performed and the differences between different curing energies were quite minimal. With the lacquer a limit for the curing energy was not possible to determine. In Table 16 the recommendations on the minimal curing energy needed for the tested products based on the performed test is presented.

Table 16. *Different minimum energy levels obtained from the different tests performed*

	Test	Minimum curing energy according to test (mJ/cm^3)
Lacquer	Gloss and hardness	Hg =470
	KMnO4 stain	Hg =470
	Chemical resistance	-
	Mechanical scratching	Hg = 390
Paint	Gloss and hardness	Hg = 540, Ga = 300
	KMnO4 stain	Hg = 784, Ga = 460
	Chemical resistance	Hg = 390, Ga = 197
	Mechanical scratching	Hg = 700, Ga = 400

The lacquer product performed quite similarly in the test and the variation on the energy required between the test is small. With the gloss, hardness and $KMnO_4$ stain test the energy level is slightly higher at 470 mJ/cm^3 than with the mechanical scratching. In all these tests the film thickness was slightly too high, and this can cause poorer results from the test. In the birch veneer samples prepared the film thickness is in the currently recommended range and in these samples the results from gloss and chemical resistance were good. Around 400 mJ/cm^3 energy from the Hg-lamp is good recommendation for the lacquer tested. The current recommendations given for the film thickness

are correct as the 35 g/m^2 (equals to the 30 µm) is already too high application amount for this product.

There is more variation in the recommendations for the paint tested. The highest energy value was needed in the $KMnO_4$ stain test. The stain test was quite ambiguous and creating rating criteria for the results was also hard. The higher energy need can imply that the chosen approach for the evaluation is too strict or false all together. The lowest energy recommendation on the other hand came from the chemical resistance test and as discussed already earlier the R2 and R4 requirement might be too easy for the 100 % UV curing products. The recommendation from the gloss and hardness test is most probably closest to the reality. In these tests, the film thickness was on the recommended range. In the scratching test, the recommendation is based on the performance in the HDF panels and in those the film thickness used can be too high. This affects the results and the energy required to cure these is also much higher. The birch veneer samples performed better in the scratching test and in these the application amount was in the range recommended.

With paint, it is evident that tests that invade the cured surface harder, like pendulum hardness and scratching, require higher curing energy to get good results. With testing that require only that the surface of the film is properly cured, the energy need is much smaller. This is explained by the fact that the energy gain from the Hg-lamp is always higher with the same line speed than with the Ga-lamp. When pigmented coatings are cured, the Hg is responsible for the curing of the surface of the film as the radiation generated with the Hg-lamp cannot penetrate to the pigmented film unlike the radiation generated form the Ga-lamp. This is evident in the chemical resistance and gloss test but based on the results the $KMnO_4$ can penetrate the cured surface of the film and expose the uncured material beneath the cured surface.

The tests chosen for this work provide good observations on the curing efficiency of the coatings but to get more information about the effect of different curing energy levels also a more analytical test should have been included in the testing procedure. For example, analysing the cured material with FTIR could have provided valuable information about the degree of cure of the material. By using FTIR also the repeatability of the tests could have been evaluated better as the differences between the parallel samples prepared would have been more evident. Also, the effect of application amount could have been studied more clearly. The sliding cutting technique that was also presented in Chapter 2.2.2. could also have been interesting addition to the testing procedure as it could have exposed the uncured material underneath the cured surface. Comparing this technique to the pendulum hardness and scratching tests could have been beneficial.

None of the tests provide individually enough information about the curing of the coatings so that it could be used solely to test the cure level of the film. By performing different test to the coating an understanding about the cure and coating properties as well as the effect of film thickness can be achieved. From the test performed most useful are still the gloss and pendulum hardness measurements. Also, simple fingernail scratching and finger pressing after the UV oven proved to be beneficial during the sample preparation. The other test performed were not useless, but more testing would be needed to create usable rating criteria for the results.

6. CONCLUSIONS

The aim of this thesis was to study that how can the necessary amount of curing energy be determined for UV curing products so that the film would be fully cured, and the properties achieved optimal. This was executed by preparing samples with different curing energies and application amount from two different UV curing products. Samples were tested with different test method to understand how the difference on the curing level effects to the material properties.

Determining the optimal curing energy for 100 % UV curable coatings is difficult, but the differences in the curing level of the coating films caused by the different application parameters are visible based on the tests performed in this thesis. The problem is in the interpretation of the results as most of the test are evaluated mainly by visual inspection. Quantitative results were provided only in the gloss and hardness test.

During testing it was noticed that the film thickness of the coating is one of the most determining application property for the tested coatings. Correct film thickness is required from the product in order that “correct” material properties are achieved. If the film thickness is too low, there is a risk that the film does not cure due to oxygen inhibition. Comparably if the film is too thick the through cure of the film may not be achieved. In both cases the normal material properties are not achieved as the film is not fully cured.

All around test that would be suitable for different types of 100 % UV curing product was not found. Usefulness of each test performed in this thesis depends on the type of coating and on the wanted properties from this coating. For example, elastic coating films behave differently than harder and tougher films. Testing methods for these types of coatings and the rating criteria for the results should be different. This demonstrates that the decision to choose two different types of coatings for the testing was correct.

Potassium permanganate stain test has potential to be used as a quick test method to evaluate the cure level achieved with UV coatings. In this work the difficulty was in creating of rating criteria for the results. To overcome this issue more tests with several different batches of one product should be tested. Also, combining analytical method such as FTIR with the testing could be beneficial as more information about the changes in the molecular level could be obtained to support the decision-making process.

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