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Modification of wood by liquid-precursor thermal spray coating

By

Ganesh Sedhain

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Masters of Science
in Wood Science and Wood Products/ Pulp and Paper Technology
in the Department of Sustainable Bioproducts, College of Forest Resource

Mississippi State, Mississippi

August 2020

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2020

Modification of wood by liquid-precursor thermal spray coating

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This research investigates the efficacy of liquid-precursor thermal spray coating (TSC) as a facile wood modification technique to bring hydrophobicity and UV durability to a wooden surface. The technique was successful in depositing Cu and TiO₂ particles onto southern yellow pine (SYP) veneers by using copper azole, copper quaternary, and titanium tetraisopropoxide as the precursor solutions. Using optimized settings, the average coating surface coverage of > 90% and an average coating thickness of > 5 μm were obtained. The coatings displayed up to 4H rating in the film hardness scale and up to 3B rating in adhesion strength scale, suggesting reasonable mechanical durability under mild mechanical abrasion. TSC-modified wood with TiO₂ created a water repellent layer, yielding a significant increase in hydrophobicity that changed the water contact angle from 57° to 126°. Accelerated weathering test results showed that the TSC-modified wood was more resistant to discoloration compared to unmodified wood.

DEDICATION

To my beloved parents!

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Dr. Yunsang Kim, for his continuous guidance and supervision. He has been a role model to me throughout these couple of years because of his out-of-box thinking and problem-solving capacity. If it weren't for Dr. Kim's knowledge and direction, I would not be at this stage. Moreover, I owe it to Dr. Hassan for letting me access his lab and for his training on various lab equipment. I would like to thank Dr. Xuefeng for providing me insights on my research, not to mention his help on the workshop for preparing the test specimens. I am grateful to Dr. Nicholas for providing me with the necessary chemicals, and the use of the QUV accelerated weathering machine in his lab. I would like to thank Dr. Rubin Shmulsky for providing me veneers for my samples.

I owe it to my colleagues and my close friends, Mr. Bojan Cosovic and Ms. Gulbahar Bhasi Kaya, for their continuous experimental and emotional support throughout my stay at Mississippi State University. I am thankful for having such wonderful colleagues. I would like to thank Mr. David Butler and Mr. Chris McGinnis for their immense contribution towards the invention of the motorized stage, which I honestly thought would not be complete in time. I owe it to them for successful development.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Wood is a very versatile material with uses in construction, furniture, decoration, insulation, and paper industries due to its unique properties such as flexibility, mechanical strength, workability, and affordability. However, as one of the most abundant natural materials, wood is prone to be degraded by weathering (*e.g.*, moisture and ultraviolet rays) and living organisms (*e.g.*, fungi, termites, and insects), which leads to a significant decrease in the mechanical strength and overall value [1,2]. To prevent such degradation, modification of wood is required. Paints, varnishes, and stains are commonly used as protection against moisture and weathering conditions. However, since these methods only react with the surface of wood, they suffer from limited durability, regular maintenance, and brittleness [3]. Chromated copper arsenate (CCA) and creosotes, which can penetrate the cell walls of wood and be fixated there, are among popular wood preservatives. However, the pressure-assisted full- and empty-cell processes used in applying these preservatives need special equipment, which is often capital intensive and potentially dangerous due to significant pressure buildup during the vacuum process [4]. Another disadvantage of the pressure treatment includes its inefficiency towards bleeding and leaching of the toxic chemicals, which lead to the restricted use of some of these wood preservatives [5]. The other reasons that demand the development of a novel wood modification method can be summarized as follows:

- There are increased interests from the scientific community and industries to add extra value to sawn timber and related solid wood products. For example, hydrophilic OH groups in the wood cell wall can be changed into hydrophobic and inert moieties to make wood more water-resistant and ultraviolet (UV)-stable through fluorination and acetylation [6,7].
- The increasing use of wood in construction and structural engineering demands wood to be not only more mechanically strong and flexible to bear a considerable load, but also more durable against moisture, sunlight, and pests to minimize regular maintenance. These properties have not been strictly required for the wood in conventional uses, such as making tools, furniture, and paper.
- Various intergovernmental organizations such as the United Nations (UN) and European Union are bringing out policies supporting a green and sustainable environment, which include the Paris Agreement under the UN convention on climate change [8].

Wood modification is a process (physical, chemical, or biological) that brings desirable properties in wood, such as durability against moisture and UV light. There are two categories of wood modification: bulk and surface modifications. During the bulk modification, properties of wood as a whole, *i.e.*, both inner and outer layers of wood, are modified. In contrast, surface modification is only limited to the first few outer layers of wood. Bulk modification techniques include thermal and chemical methods such as acetylation, furfurylation, Thermowood, Plato, and hot oil process [9]. Since the bulk modification involves more human resources, chemical processes, pretreatments, an ambient environment, and a large amount of power, it can be an expensive, complicated and time-consuming process, which often requires massive treatment facilities along with large and expensive equipment.

Commonly used surface modification techniques include plasma/corona treatment, enzymatic/non-enzymatic grafting onto the wood surface, sol-gel chemistry, deposition of particles on a wood surface, chemical surface modification, surface impregnation, and mechanical and hydro/mechanical methods [10]. Surface modification does not involve complex, time-consuming processes and equipment as in the bulk modification (*e.g.*, acetylation, furofurlation, and thermowood) and is comparatively cheaper. Surface modification of wood can also be carried out in a small operating space within a short time. However, these modification techniques still suffer from some hindrances. For instance, surface modification through the plasma/corona method requires advanced plasma and vacuum chambers and the need for constant reaction environment. The enzymatic grafting technique also requires a coupling agent, which can be extra work that might add to the time and cost of the process [10].

Thermal spray coating (TSC) is regarded as an advanced materials processing technique that has been widely accepted by many industries because of the variety of choices of materials that can be used to produce coatings and ability to recoat worn or damaged coatings without having to replace or remove the part [11]. The coating materials in TSC can be either in a liquid, wire, or powder form. In particular, liquid-precursor TSC is one type of TSC methods in which the material to be coated is in a liquid precursor and is deposited to a substrate by using a flame as a medium under ambient temperature and pressure. During this process, droplets containing a precursor material are transported to a substrate to produce deposition with a very fine (micron-sized) grain structure [12]. Liquid-precursor TSC has already been successfully used in modifying surface wettability and absorption properties of commercial Kraft paper by a thin particle coating in a continuous one-step process [13]. In another publication, a transparent coating based on titanium oxide (TiO₂) nanoparticles was successfully deposited at atmospheric conditions on paperboard to

bring hydrophilic properties [14]. These studies show the successful implementation of the liquid-precursor TSC on lignocellulosic surfaces. The current research ventures to test the efficacy of the liquid-precursor TSC on wood.

The liquid-precursor TSC, which is adopted in this research, can be a unique way to modify the surface of the wood without disturbing the natural integrity of the whole wood. Possible advantages of the TSC over other methods include the ability to operate efficiently under ambient temperature and pressure, a facile process, and flexibility in use (laboratory to industrial scale).

1.2 Rationale and significance

Surface modification is an effective way to enhance the desirable properties of wood. Although many surface modification techniques like plasma/corona treatment, enzymatic grafting on wood and hydro/mechanical methods are in practice, they suffer from complex operating procedures, long processing time, potentially high expenses in equipment and maintenance costs, and high energy consumption. So, there is a need for a novel technique for surface modification of wood, which is simple to apply and does not involve complex processes such as precise control in processing environments (temperature and pressure) and expensive equipment (e.g., plasma-equipped vacuum chamber). It will be significant if the developed wood modification technique can deliver a high-quality surface coating that imparts desirable properties to a wood surface, for instance, wood surface hydrophobic properties. Liquid-precursor TSC can be such a method since it can be conducted under ambient atmospheric temperature and pressure in a less complicated setting. If the liquid-precursor TSC is successful in modifying the surface of wood, an easy-to-implement and straightforward method for the surface modification of wood can be developed.

1.3 Objectives

The research objectives are summarized as below:

- Use the liquid-precursor TSC method to modify the surface of the wood with copper (Cu), and titania (TiO₂) compounds using liquid precursors
- Characterize the morphology, composition, thickness, and overall quality of the Cu and TiO₂ coating on the surface of wood deposited by the liquid-precursor TSC method
- Evaluate weathering durability of wood modified by the liquid-precursor TSC

CHAPTER II

LITERATURE REVIEW

This chapter will review the different categories of wood modification methods and techniques that have been practiced to enhance the properties to wooden surfaces. The surface modification of wood, particularly by the liquid-precursor TSC method, will also be discussed later in the chapter.

2.1 Wood as a material

From the very beginning of human evolution until today, wood has proven to be a vital and versatile naturally occurring material due to its various advantages over other materials in tensile strength, electrical and heat resistance, abundance as well as aesthetic beauty. [7,15]. Wood is easy to work with and has multiple uses in the construction of buildings and other structural infrastructures such as bridges, poles, and monuments. Wood is the primary requisite for pulp and paper production, tools, furniture, and even in arts. Wood is also aesthetically pleasing to look at compared to a metallic surface. It is equally environment friendly, sustainable, and renewable [16]. Due to recently increasing environmental and legislative awareness, wood as a green renewable material is rising to the spotlight as it can be used not only to mitigate the accumulation of greenhouse gases but also to serve as carbon storage in the form of harvested wood products [7,15,16,17]. However, some properties of wood are less desirable than others, *e.g.*, photo and biological degradations. Wood is a bio-material and hence is susceptible to degradation by abiotic

factors such as rain, temperature, and sunlight. Fungi, insects, and termites feed on the lignocellulosic compounds present in wood once they find favorable moisture and weathering conditions [1,2]. Only about 10% of total weight loss of wood due to fungal attack may result in loss of more than 50% strength of the wood [18]. Although wood is a degradable material, it can be seen as a benefit since it is easy to dispose of into the natural environment. However, biodegradation is certainly not preferred if this process is to occur when the wood is used for long-term services [7].

2.2 Wood modification

Wood has to be modified to either reduce or remove unwanted properties such as low tolerance toward moisture, sunlight, and biological attack. Wood modification obtained by the action of a chemical, biological, or physical agents on a wooden material, resulting in improved properties during the service life of the modified wood. The modified wood should itself be non-toxic under or after service conditions. Additionally, there should be no leakage of any toxic substances during service or at the end of life, following disposal or recycling of the modified wood. If the modification is intended for improved resistance to biological attack, then the mode of action should be non-biocidal [7]. Wood modification can be said active where there is an alteration in the chemical properties of wood. In contrast, passive wood modification refers to the case where the alteration is obtained without altering the chemistry of wood [7]. The method and type of wood modification to be used greatly depend on the end-use of the wood product.

Bulk modification and surface modifications

Wood modification is then further categorized mainly as bulk modification and surface modification. Bulk modification changes the properties of the whole wood structure, *i.e.*, the outer and inner surfaces of wood. In contrast, surface modification is limited only to the first few layers of the wood. Bulk modification is applied when the wood is required for underground/underwater purposes, particularly for big constructions and structures, and outdoor climate conditions (exposed to rain and direct sunlight). Compared to bulk modification, surface modification is generally suitable for indoor purposes such as tools, furniture, flooring, and to impart hydrophobic properties in paper/paperboard.

In comparison to bulk modification, surface modification operates in a small space due to the lack of need for heavy machinery/equipment required during the procedure, and demands low energy consumption, which makes it cheaper. Similarly, since the modification takes place only in the first few layers, it takes less time than bulk modification where the entire piece of wood is modified. The process itself is more straightforward than bulk modification because the equipment is basically easy to use, and does not require as much labor.

2.3 Bulk modification methods

2.3.1 Acylation and Acetylation

During this process, hydroxyl groups in the cell wall that are more susceptible to moisture are replaced with larger and more hydrophobic chemical groups. Acetylation is the chemical reaction between acetic anhydride with the hydroxyl groups present in cell wall polymers. With the substantial increase of these acetylated hydroxyl groups over the wood cell wall surface, the durability and dimensional stability of wood increases accordingly [19].

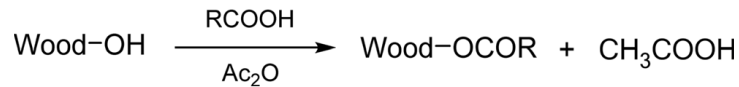


Figure 2.1 Acylation of wood with mixed acetic-fatty esters [9].

2.3.2 Furfurylation

Furfurylation is considered to be a non-toxic substitute for conventional wood preservation techniques with heavy metals. It is based on the principle that low-molecular-weight furfuryl alcohol can penetrate into wood cell walls and polymerize in-situ [20]. The characteristics of the furfurylated wood greatly depend on the retention level of the polymerized furfuryl alcohol present in the wood cell walls [9].

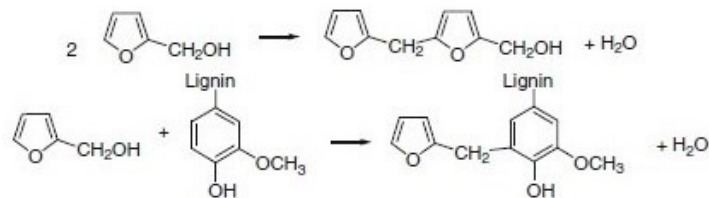


Figure 2.2 Main reactions involved in the polymerization of furfuryl alcohol [9].

2.3.3 Modification with thermosetting resins

Wood modification with thermosetting resins involves the impregnation of phenolic resins inside the wood cell structure. This impregnated wood, when cured at a high temperature (either with/without compression), greatly increases the resistance of wood to decay, termite, and other biological agents [9].

Apart from these dominant techniques, several industrial processes use heat treatment to modify wood. Examples can be further categorized as the Thermowood process, the Plato process, the oil heat treatment process, and the pressurized conditions, which involve creating high steam pressure to increase relative humidity which ultimately results in physical and chemical changes of wood [9]. These methods are primarily limited to a particular geographical area or company profile.

2.4 Surface modification methods

2.4.1 Plasma treatments

Plasma contains a high density of excited ionized particles that can be further used to modify surface properties of various materials like wood, metal, polymer, glass, elastomer, and ceramic. For wood, plasma treatment is mostly used to create a hydrophobic surface on wood products, to activate the wood surface for adhesion, and to improve pest resistance. Exposure to the highly excited particles of plasma affects the orientation and density of the substrate. It polarizes the surface molecules of wood by oxidation, thus increasing the polar character in a surface, which creates strong covalent bonding between substrate and coating/adhesives [21]. However, the main drawback of this process is high operation and maintenance costs. To generate thermal plasmas, a controlled and constant environment with ambient temperature, inert gases, and a high vacuum (below 10^2 Pa) is required [10]. Furthermore, most of these processes are usually batch operations, which is favorable mostly for large-scale production [14].

2.4.2 Enzymatic or enzyme-assisted grafting on a wooden surface

Enzymatic or enzyme-assisted grafting uses enzymes like laccases, lipases, and peroxidases to graft foreign molecules to the substrate surface. It is based on the covalent bonding

of functional groups with substrate surface having anchor groups, which is facilitated by an enzyme-based reaction. This method is mainly used for the functionalization of wood for enhancing wettability, hydrophobicity, weathering resistance, and antibacterial properties. The main issue with the grafting method, however, is the need for a coupling agent to provide a suitable link between functional groups of the wood surface and external molecules to be grafted with desired properties. [22]. This process can also be plasma-assisted, which can be expensive.

2.4.3 Mechanical treatments

Mechanical treatment methods like sanding and planing use linear vibration friction to increase surface density and hardness and can be used as alternatives to surface densification. The linear vibration friction also brings chemical changes in wood that occur mainly due to changes in extractives coverage. Sanding and planing can be used primarily to change pH value, surface roughness, and adhesive wettability of a wooden surface [23,24]. Besides this, properties like wettability, resistance to biological organisms, and fire retardancy can also be achieved through mechanical treatments [10].

2.4.4 Thermo-hydro-mechanical surface treatment

This method is used for densifying solid wood to reduce empty voids in wood by compression in combination with steam treatment [10]. The modification results in the densification of the surface, which provides hardness and abrasion resistance to the treated wood. However, to obtain hydrophobicity and improved resistance to biological organisms, the densified wood needs to be further treated.

2.4.5 Thermal spray coating

Thermal spray coating (TSC) implements a thermal source and a mechanical spray to create a distinct coating on a variety of materials to either enhance their rigidity, surface properties, or aesthetic value. During this process, particles are sprayed through a heating source, resulting in the deposition of molten or semi-molten particles on a surface (Figure 2.3). TSC is flexible in use and does not require complex operations to coat or recoat substrate if the old coating is damaged or worn off [11]. The wide choice of feeding stock (in the form of either solid wire, grains, liquid, or even powder) that is used as the raw material for the TSC method further adds up to its flexibility. As a result, TSC has gained increasing popularity among the leading material processing companies lately.

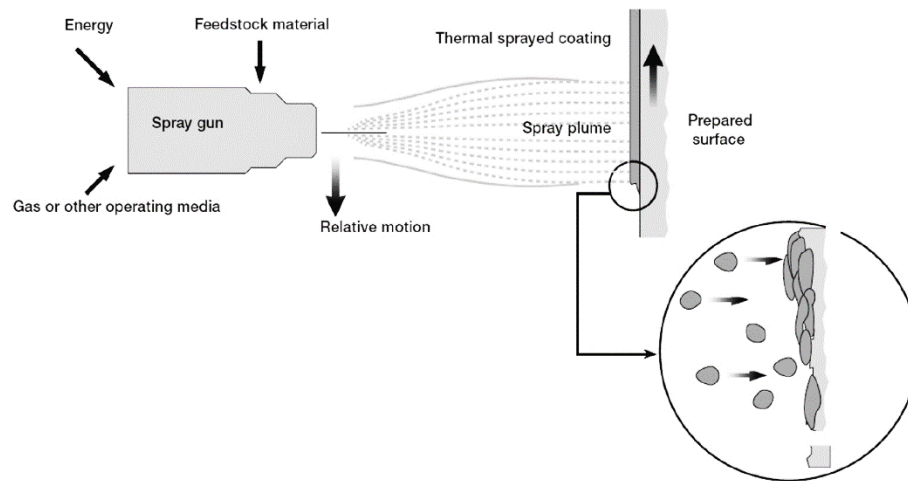


Figure 2.3 The schematic diagram for the thermal spray coating method [5].

Liquid-precursor thermal spray coating method

In the liquid-precursor TSC method, a precursor solution is used as the feeding stock. The precursor solution is atomized to micro-droplets by high-velocity airflow, which in the presence of flame leads to the deposition of particles on the surface of wood [25]. The deposition obtained by this process has a significantly large amount of minute inorganic particles, which can be increased to cover a reasonably large surface area to increase the efficiency of the coating [26,27]. The liquid-precursor TSC method is simple, economical, and fast because it does not require expensive equipment and chambers, rigorous and complex chemical treatment processes, pretreatments, and a large amount of energy. Since it can be carried out with a one-step linear process under ambient temperature and pressure, TSC has the flexibility to be scaled up to an industrial level [14]. Figure 2.4 shows the basic principle of how the liquid-precursor TSC works. The spray or coating material is prepared in a solution form, which is then brought in contact with a flame source. The high temperature present in the flame, along with the pressure from compressed air, melts the precursor material in solution, thereby breaking the material into fine atomized particles, which is further transferred to the substrate placed in the direction of the incoming particles to create a coating on the substrate surface.



Figure 2.4 Schematic representation of thermal spray coating [28].

CHAPTER III

MATERIALS AND METHODS

The materials and methods chapter provides information on the liquid-precursor TSC method, preparation of test specimens, coating parameters, and tests and methods used to determine the overall properties of the coating and TSC-modified wood. The details on the determination of coating hardness, adhesive strength, contact angle measurement, and QUV accelerated weathering test are described as well.

3.1 Preparation of test specimens

Three different precursor solutions were prepared by diluting copper azole (25% content, Viance LLC) and copper quaternary (9.6% content, Viance LLC) in distilled water, and titanium tetraisopropoxide (>98% purity, Acros organics) in isopropyl alcohol, respectively. TiO₂ and copper oxide were chosen as the coating materials because they were already well known for their superior hydrophobic, UV absorption, and biological protection properties [29,30,31]. These precursor solutions were further processed to deposit copper and TiO₂ particles directly on:

a) A glass slide (as a proof-of-concept)

The dimension of the slide: 1" x 3" (Fisherbrand™ Economy Plain Glass Micro Slides)

b) A wooden slab

Veneers from a southern yellow pine (SYP) were used to create the wood substrate for applying surface coating (Figure 3.1 a). The veneers were cut tangentially into 1" x 5" dimensions by using a table saw, and radial arm saw stationed at woodshop laboratory at the Department of Sustainable Bioproducts, Mississippi State University (Figure 3.1b). All of the wooden samples were oven dried at 104 °C for 24 hours and then stored securely on a desiccator prior to liquid-precursor TSC (Figure 3.1c and d). The pre-conditioning was performed to maintain uniform moisture content across all samples.

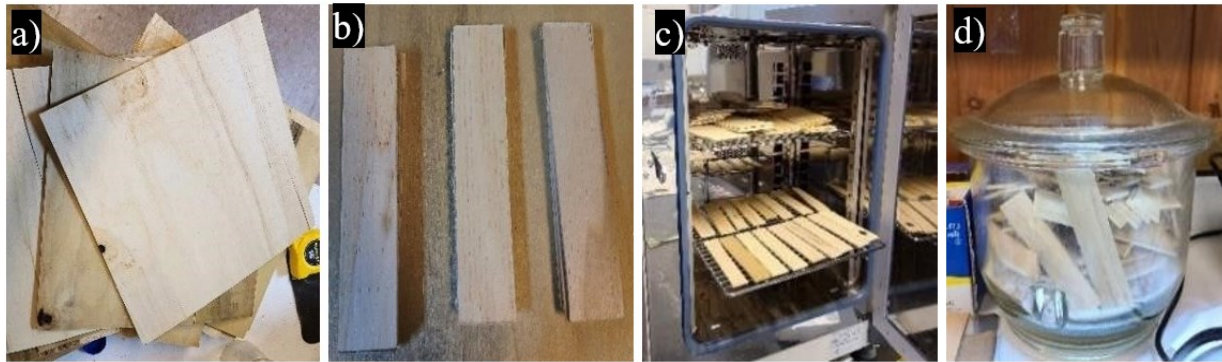


Figure 3.1 Images a) to d): various processes associated with test specimen preparation.

3.2 Liquid-precursor TSC process

The precursor solutions were fed through an airbrush by a constant rate of compressed air of 3 psi. A butane lab torch was used as a thermal source to generate sufficient flame and heat to react with the precursor solution. As the precursor solution is sprayed through the flame from a butane torch, the precursor is atomized and sequentially deposited on the substrate [12,32]. The setup of the process is shown in Figure 3.2a. The airbrush and the butane torch are placed close to each other in a certain angle in a way that when both are switched on, the droplets from the

precursor solution get exposed to the flame and then pushed to the substrate surface placed in a certain distance (Figure 3.2b).

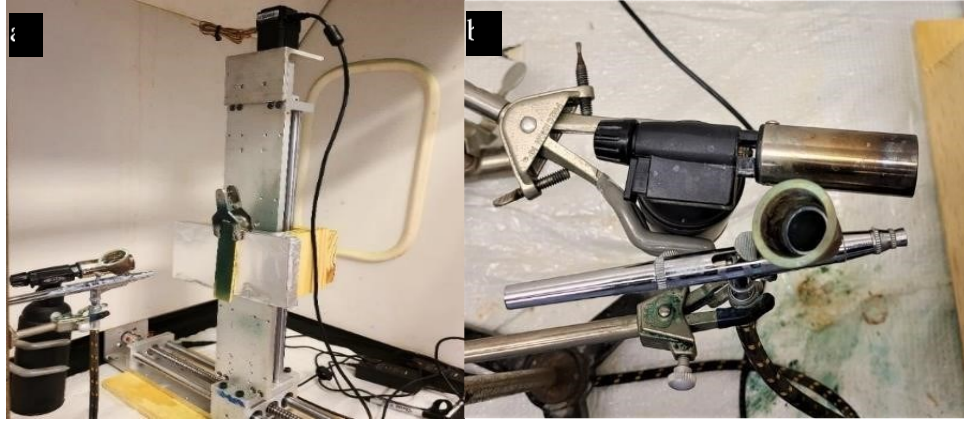


Figure 3.2 Image a) Liquid-precursor thermal spray method setup used in the research, and b) angle between air brush and butane torch in the liquid-precursor TSC setup used in the research.

3.3 Process parameters

Various process parameters were systematically varied to examine their effects on the quality of the deposition made by the liquid-precursor TSC, which included:

3.3.1 The angle between the flame source and the precursor solution

Three different angles between the flame source and precursor solution was used (10° , 45° and 90°). The logic behind this was to find a suitable angle that provides better deposition.

3.3.2 Distance between the flame source and the substrate

Six different distances (5 cm, 7.5 cm, 10 cm, 12.5 cm, 15 cm and 20 cm) was used to find the best setting to get maximum deposition without any thermal degradation of the wood substrate used.

3.3.3 Concentration and feeding rate of precursor solutions

The concentration (1 - 15 wt%) and feeding rate of precursor solutions (3-5 cc/min) were varied to find the optimal conditions to obtain maximum coating coverage with uniform deposition.

3.4 Methods of spraying

In TSC, either the spraying component or the specimen to be coated needs to be in motion. We decided to set the specimen in motion while leaving the sprayer stationary. We note that when treating a large wood specimen, setting the spraying part in motion is also produces good results. In this thesis, three different spraying methods were attempted regarding how to control the movement of a specimen to be coated while precursor materials were sprayed through flame from a butane torch. The differences in coating quality and the time required were compared. These methods were:

3.4.1 Hand-held method

This technique was used at the beginning of the project when the motorized stage was still under development. The wood samples were held by a tong facing the direction of incoming inorganic particles, at a specified distance from the source. The samples were moved along x and y-axis in a predetermined pattern to maintain the same spray pattern across all coated samples (Figure 3.3). The wood samples were exposed to the liquid-precursor TSC for a total of 3 spray periods. Each spray period lasted 60 seconds, followed by a rest period of 20 seconds to cool down the sample, which minimized thermal degradation.

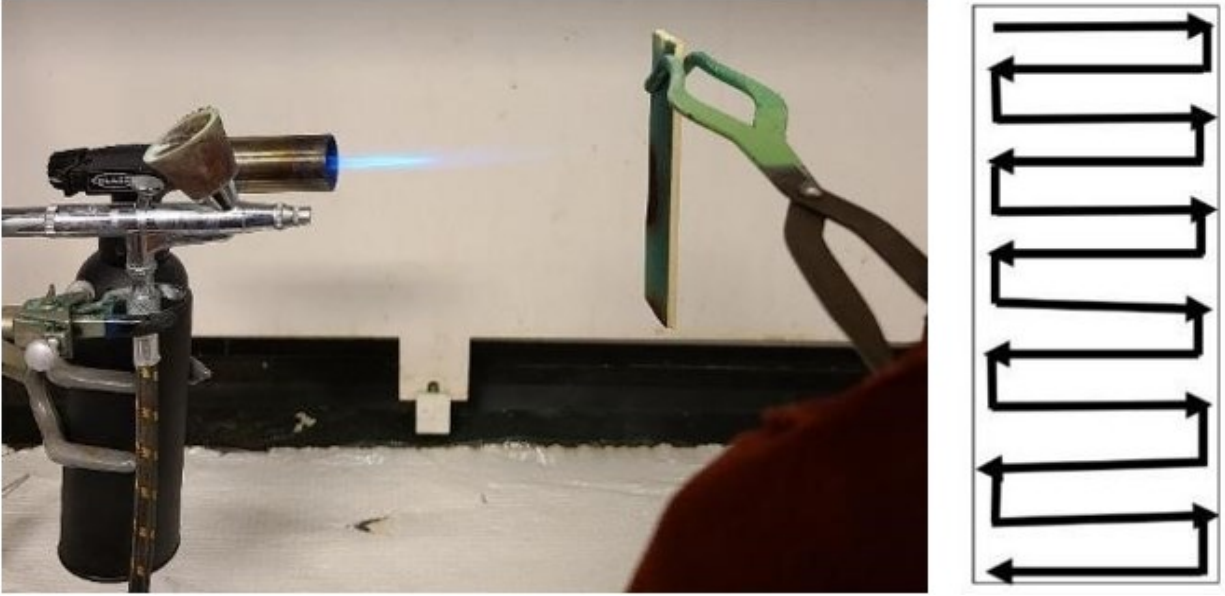


Figure 3.3 Experimental setup and the spray pattern created for the hand-held method.

3.4.2 Motorized stage method

A motorized stage that can move the wooden samples in any desirable pattern was developed to avoid human error while moving the samples in front of thermal spray. The 2-axis (XY) motorized stage was made out of two linear stage actuators based on a manual sliding table ball screw with a stroke of 400 mm (Model no: SFU1605), welded on top of another, as shown in Figure 3.4. Each linear stage weighed 12.17 pounds and had a dimension of 26 x 8.25 x 5.3 inches, which was heavy enough to minimize vibrations from the motor as well as to avoid tipping over of the stage itself. The repeat positioning accuracy of the stage was ± 0.02 mm and had a load bearing capacity of up to 25 pounds. The travel range of the stage was 18 inches along both (XY) axis and could hold sample with dimensions up to 1 ft square. The sliding ball screws were then replaced and welded with two NEMA 17 stepper motors (DMX-J-SA-17, Arcus Technology, USA). The stepper motors were equipped with 16 micro step, USB 2.0 communication and control

via a BASIC-like programming language, and required a 12 to 24 DC voltage input and a recommended driver current of 1.6 A (2.0 A max). The motors were then connected and controlled via Windows graphical user interface (GUI) program to test, program, compile, download, and debug spray patterns to perform TSC on wood specimens mounted on the motorized stage (Figure 3.4). A speed of 1.5 cm/s was employed for the TSC method. Higher speeds can also be achieved if desirable.

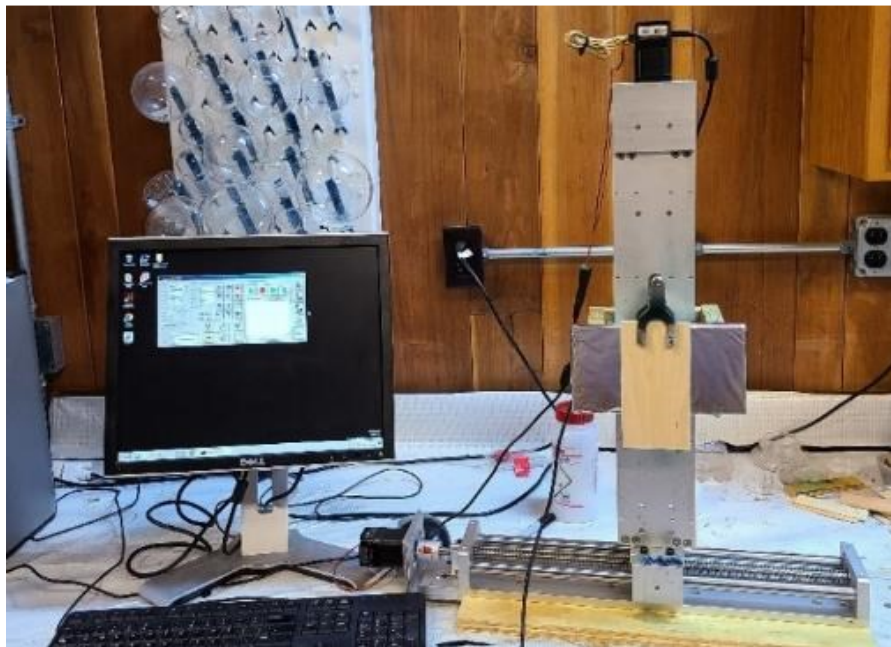


Figure 3.4 Motorized stage setup with the integrated GUI program software.

Two methods of TSC deposition were attempted using the motorized stage method.

Method 1 (consecutive coatings with resting): The substrate was exposed to the liquid-precursor TSC for a total of 3 spray cycles, which included a spray for 60 seconds, followed by a 20-seconds

rest period after each spray to minimize thermal damage. The method followed the spray pattern, as shown in Figure 3.5.

Method 2 (single coating): The substrate was exposed to the liquid-precursor TSC in a single spray cycle, which lasted for 180 seconds without any rest period, following the identical spray pattern to Method 1 as shown in Figure 3.5, throughout the entire period. The distance between the torch and the substrate was increased from 7.5 cm to 10 cm to remedy thermal damage. Method 2 was approximately 45 - 50 seconds faster than method 1 to complete one cycle.

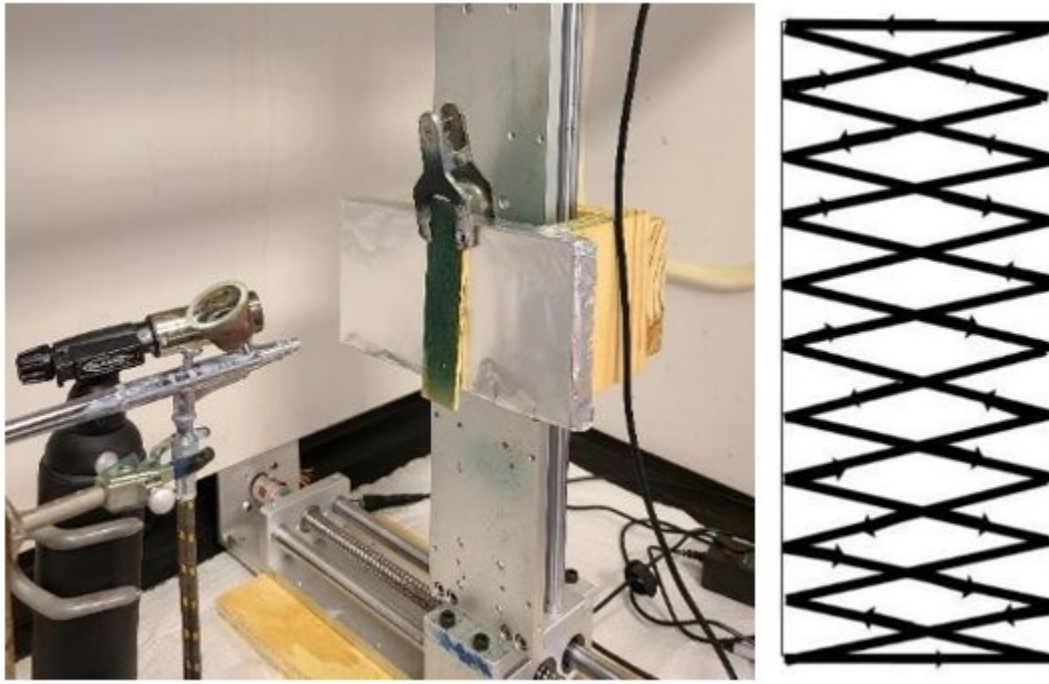


Figure 3.5 Experimental setup and the spray pattern created for the motorized stage method.

3.5 Determination of coating coverage on a wooden sample through ImageJ

ImageJ is an image processing software that is used widely in image editing and analysis.

ImageJ was used to find the approximate coverage of Cu and TiO₂ coatings on the wood surface.

A set of microscopic images of the samples at different magnification levels was taken, and the one that represented the overall sample coating was selected and opened via ImageJ (Figure 3.6a). By using the “adjust” function from the “image” menu bar, light adjustments were made on the image so that ImageJ can appropriately distinguish between the colors of the coating and wood surface (Figure 3.6b). After slight editing, the image was converted into 8-bit or 16-bit by using the “type” function from the “image” menu bar (Figure 3.6c). This was necessary as the “threshold” function to calculate the coverage of the coating only works with an 8-bit or 16-bit image. The “threshold” function, which can be accessed from the “adjust” tool in the “image” menu bar, was carefully adjusted so that it covered the entire coating area leaving the uncoated areas exposed. The coverage percent of the coating was then recorded from the threshold bar (Figure 3.6d).

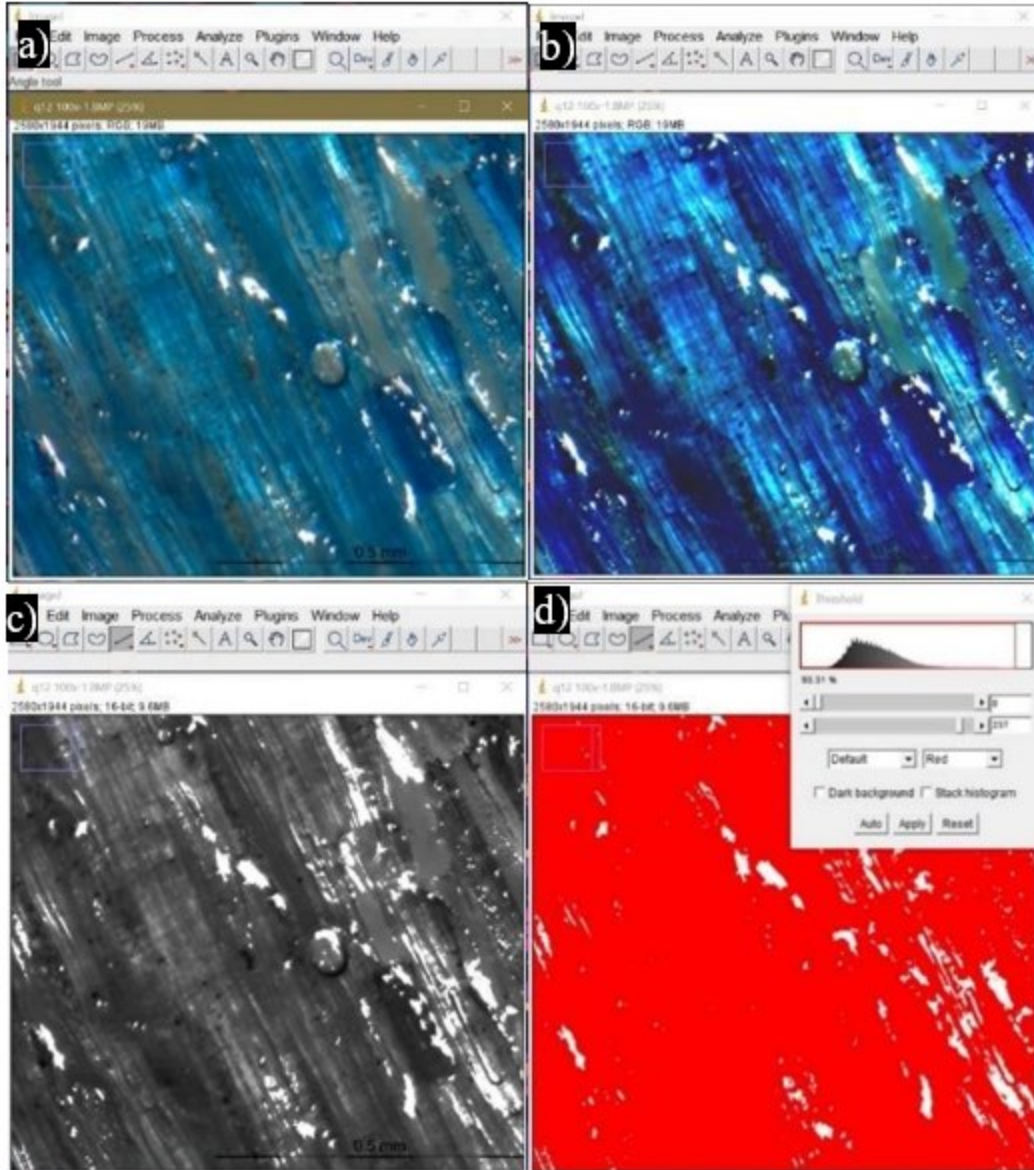


Figure 3.6 Images a) to d): different steps involved in coating area coverage calculation from Image J.

3.6 Thickness estimation of Cu and TiO₂ coatings by TSC

The thickness of Cu and TiO₂ was estimated using a weight gain after TSC and density of the coating materials. Three sets of data were used to obtain the average thickness and standard deviation. The mean values of weight before and after TSC was calculated for all 3 sets. The

difference in weight before and after TSC was calculated and converted into wt% change, as shown in Figure 3.7. Change in wt% for the control samples was assumed to be the same as for the treated samples since the difference in the rate of moisture loss among wood samples made from the same veneer would be negligible. The weight gain and/or loss by the control sample was then subtracted from that of treated samples to obtain a normalized wt% change, which was further converted to actual weight gained during the TSC process. Using the formula, density = mass / (sample dimension x coating thickness) derived from for density ($\rho = m/V$ where ρ is density, m weight gain, and V sample volume), the coating thickness was estimated with the assumption that the used wood slab was conformal. The density used for Cu and TiO₂ were 6.31 g/cm³ and 4.23 g/cm³, respectively.

Set	Sample Name	Weight before TSC (g)	Mean Wt. before TSC	Weight after TSC (g)	Mean Wt. after TSC	Weight loss/gain	S.d.	C.v.	Weight change (percent)	Remarks	Normalized weight change	Weight gained (g)	Thickness estimate (cm)	Thickness (micrometer)
1	Control	7.406	6.120	7.407	6.122	0.001	0.01	0.001	0.02	Gain				
2	Control	4.846		4.856		0.010								
3	Control	6.109		6.102		-0.007								
1	Cu azole	6.840	5.838	6.887	5.881	0.047	0.01	0.002	0.73	Gain	0.71	0.041	0.000253	2.530
2	Cu azole	6.329		6.381		0.053								
3	Cu azole	4.347		4.375		0.028								
1	Cu quats	8.398	8.370	8.428	8.412	0.030	0.01	0.002	0.51	Gain	0.49	0.041	0.000249	2.494
2	Cu quats	8.551		8.609		0.058								
3	Cu quats	8.160		8.199		0.040								

Figure 3.7 An example of thickness estimation calculation for Cu coatings by TSC.

3.7 Characterization of Cu and TiO₂ coatings by TSC

The quality of Cu and TiO₂ coating made on wood by TSC was characterized by hardness and adhesive strength tests, as well as the water contact angle of TSC-modified wood. Accelerated weathering testing of TSC-modified wood and pristine wood was also performed to evaluate the

impact of Cu and TiO₂ coatings on dimensional stability and weathering durability of wood. The pre-conditioned wood samples that were modified by the TSC method were further dried and stored inside a fume hood under ambient temperature for 24 - 48 hours before the characterization tests.

3.7.1 Morphological characteristics

The coating coverage and the morphology of the Cu and TiO₂ coatings were studied under an optical microscope (OM). OM images were processed and analyzed by using ImageJ to estimate the percentage coverage area of the coating to the wood substrate.

3.7.2 Film hardness pencil test

An ASTM 3363 standard film hardness pencil test was employed to evaluate the hardness level of the Cu and TiO₂ coatings by the liquid-precursor TSC method. The coated wood panel was placed on a sturdy horizontal surface. The pencil was then brought in contact with the coated surface at a 45° angle, which was just polished on an abrasive paper to maintain a smooth circular cross-section free of chips and nicks at the edge (Figure 3.8). The testing started first with the hardest pencil and continued until the pencil can no longer gouge or cut into the coatings.



Figure 3.8 Pencil hardness kit used for ASTM 3363 standard film hardness pencil test (hardness gradually increases from 7B to 6H scale).

3.7.3 Adhesion tape test

It is essential to know how well the coating adheres to the wood substrate to estimate the durability and efficiency of the applied coating by TSC. ASTM D3359 measuring adhesion by tape test method B was used to calculate the adhesive strength of the coating. A lattice pattern with 5 – 11 lines on each side was marked in the coating of the substrate (Figure 3.9). A 3M pressure-sensitive tape was then applied to the previously cut lattice and then removed after 90 +/- 30 seconds of application. Judging by the type and amount of the failure acquired, a corresponding scale was given to the adhesive strength of each sample.



Figure 3.9 Tape test kit used and lattice pattern created on the wood substrate during ASTM D3359 measuring adhesion by tape test.

3.7.4 Contact angle measurement

The water contact angle of the Cu and TiO₂ coated samples was measured to assess the surface properties of the samples treated with the liquid-precursor TSC method. A water contact angle less than 45° represents a hydrophilic surface. An increase in water contact angle above 90°

represents a hydrophobic surface. A water contact angle above 150° signifies a superhydrophobic surface. A pipette was used to dispense a single droplet (about 3-5 µl) of high-purity distilled water on the coated surface. The picture of the droplet was taken from a distance of 1 – 2 cm using a macro lens in a Samsung S20 plus version 1.0 smartphone. All water contact angles were estimated using the drop-test plugin in ImageJ software.

3.8 Weathering test

The effects of Cu and TiO₂ coatings of wood by TSC on dimensional stability and UV resistance of wood upon weathering was studied using a QUV® accelerated weathering tester.

3.8.1 QUV accelerated weathering test

To evaluate the weathering durability of TSC-modified wood samples, an accelerated weathering test (ASTM G154: QUV accelerated weathering) was carried out. The weathering chamber simulated the real-time sunlight, moisture, and UV exposure conditions (Figure 3.10). UVB- 313 bulbs (Q-panel products) were used for the weathering test which consisted of a 4-hour UV cycle at 140 °F, followed by a 4-hour condensation cycle to simulate dew and moisture conditions. A total of 120 cycles over 20 days was used. A total of 13 veneer samples including 4 untreated control samples along with 9 TSC-modified samples of 1" x 5" each were placed inside the weathering chamber. Temperature and relative humidity of the room, in which the QUV accelerated weather machine was located, were maintained at 72 °F and 60 - 70%, respectively, for up to 20 days.



Figure 3.10 QUV accelerated weathering machine and room climate used for the test.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the efficacy of the liquid-precursor TSC method in modifying wood will be discussed. The effects of varying process parameters of TSC on the quality of Cu and TiO₂ coatings will be presented first. The results from characterizations of Cu and TiO₂ coatings will presented includes surface coverage, coating thickness, morphology, surface tests such as film hardness, adhesive strength, and water contact angle. The influence of TSC modification on the resistance of wood to UV light and moisture was tested with an QUV accelerated weathering machine.

4.1 Varying TSC process parameters

4.1.1 The angle between a flame source and an airbrush (10 to 90 degrees)

The angle between the flame source and the airbrush was systematically varied to find an optimal angle to obtain more deposit in less time as the time duration of the precursor solution exposed to the flame would be directly proportional to the number of atomized particles deposited on the substrate. The angle between the sources of flame and the precursor (*i.e.*, the directions of the flame and the airbrush) was varied from 10° to 90° (Figure 4.1a to c). Studying the images d to f from Figure 4.1, it can be observed that image d, which was made from a 10° angle, has the most vibrant greenish tint (the color of copper azole) among all three of them for both glass and wood substrates. Since the green color comes from copper azole depositions, it is assumed that more greenish color in a substrate translates to more Cu particle deposition. Comparing image d

and e, image e, which was made at a 45° angle, has less coloring for both glass and wood substrate. This could be attributed to less deposition because more color contrast would be visible if there were a larger deposition, which makes sense for the reason that at 10° angle, the precursor solution was exposed the longest in the flame, among all angle variations. Similarly, for a 90° angle (Figure 4.1f), the substrates suffered from major fire damage. This might have occurred because there was not sufficient injection of liquid (water and IPA) to cool down the flame, causing severe fire burns. Based on these observations and conclusions, a 10° angle was selected for the TSC method.

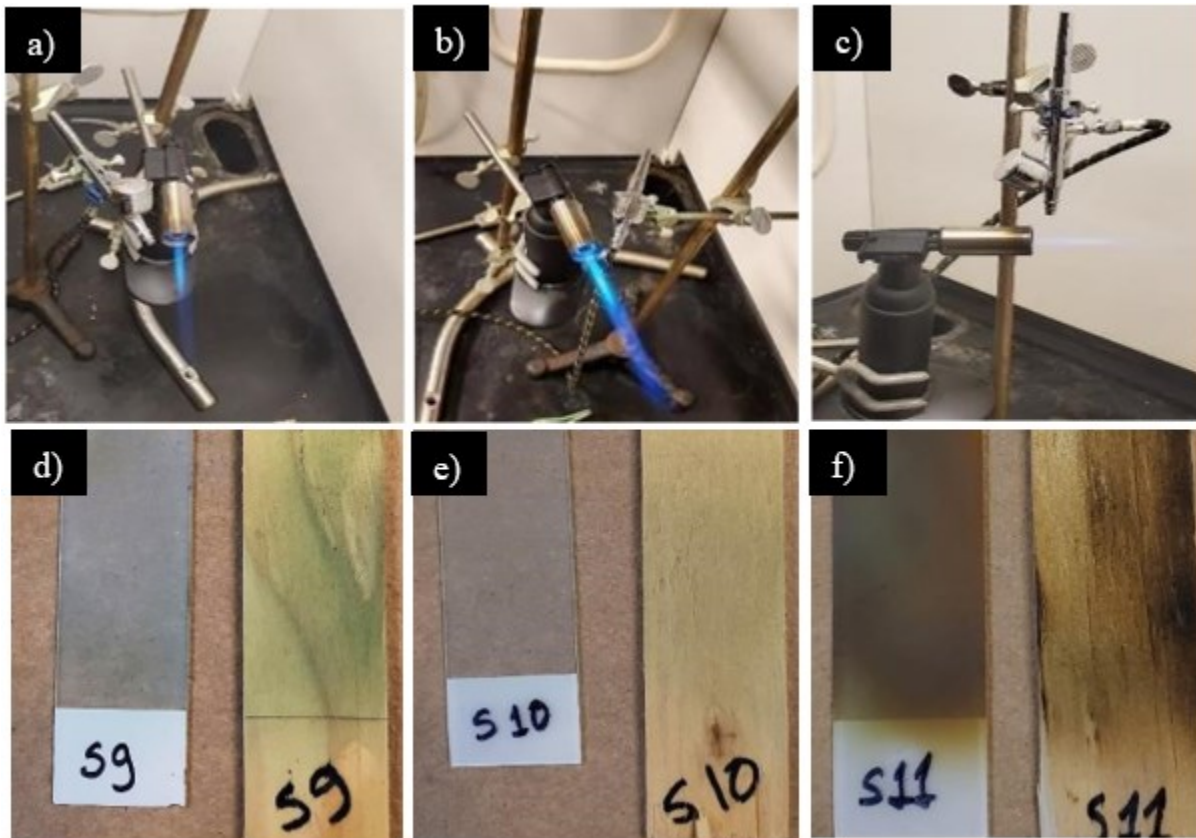


Figure 4.1 Images showing angles between the flame source and the airbrush, ranging from (a) 10° to (b) 45° and to (c) 90° and the visual difference of samples prepared on a glass and wood substrate by using these angle variations, images d), e), f), respectively.

4.1.2 The distance between a flame source and a substrate (5 to 20 cm)

The distance between the flame source and substrate was systematically varied to observe the change in coating quality as the intensity of spray will be different at different distances. The intensity of spray and flame are inversely proportional to the distance between them and the substrate. However, an increase in coating coverage can be expected with increasing distance. The quality of coating deposited by TSC was determined by comparing the OM images of samples made at different distances. Starting from 5 cm, the distance was increased to 20 cm by moving either the flame source or the substrate, based on which option was convenient at that time (Figure 4.2a to e). Comparing the OM images for Cu quats coating at distances of 5, 7.5, 10, 12.5 and 15 cm from Figure 4.2f to j, at the distance of 5 cm, the substrate developed a dark brownish color, which was obviously caused by thermal damage from the flame (Figure 4.2f). As the distance was increased to 12.5 cm, the fire burns disappeared, and the wood substrate gradually developed a bluish color tint covering a large portion of the substrate surface (Figure 4.2g - i). Since the blue tint primarily came from Cu quats, it is safe to assume that the increase in bluish tint would correlate to an increase in the deposited Cu particles. As the distance was further increased to 15 cm (Figure 4.2j), the surface coverage and the contrast of the tint decreased, signifying less deposition of Cu particles. Based on these observations, the best results were obtained between 7.5 cm to 12.5 cm. However, the samples occasionally suffered fire burns at 7.5 cm distance. Thus the 10 cm distance has been chosen to be employed for further TSC experiments to deposit more particles without burning the wood substrate.

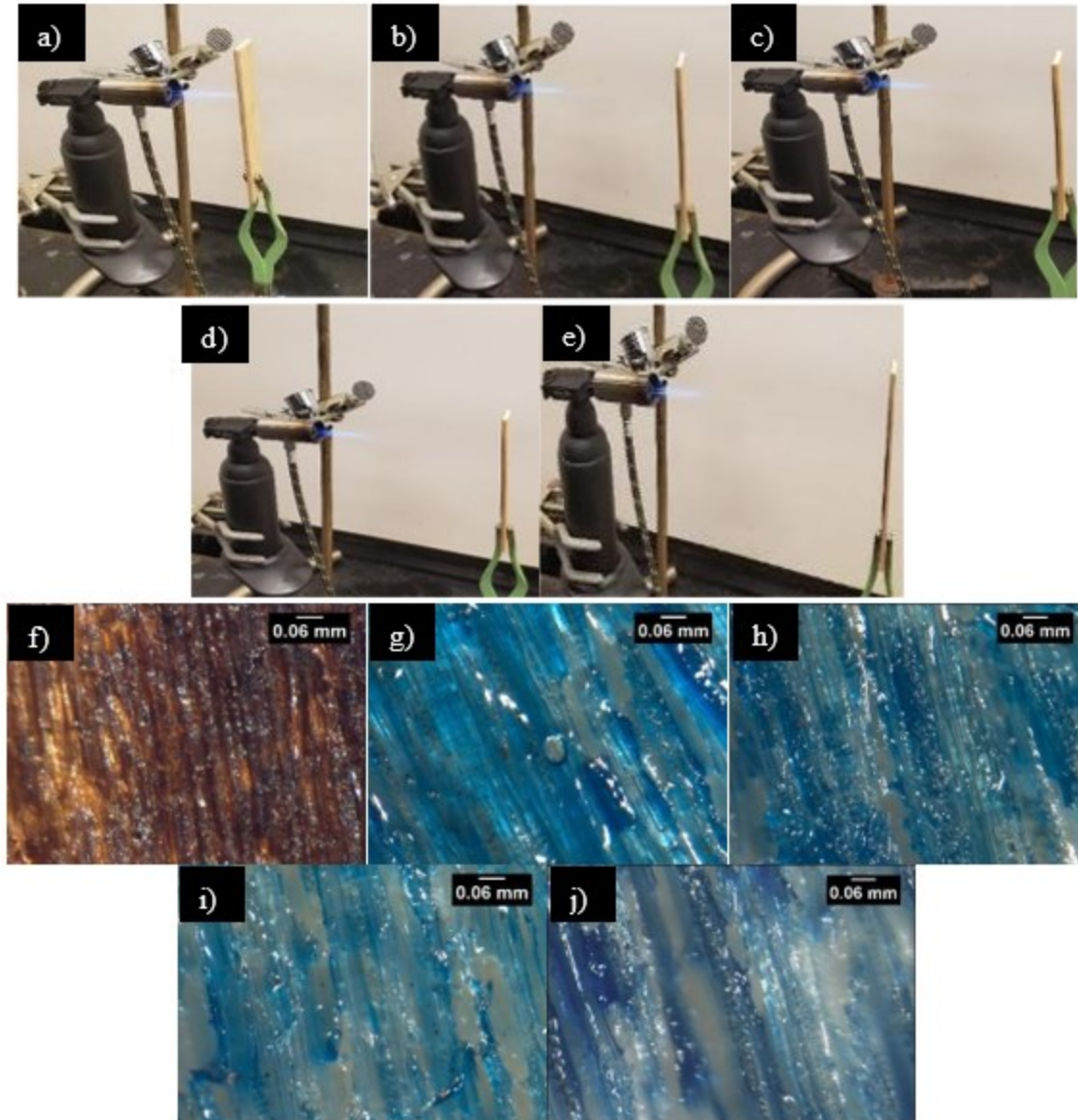


Figure 4.2 Photos a) to e) showing varying flame-to-sample distance of 5, 7.5, 10, 12.5, and 15 cm, respectively. OM images f) to j): the Cu quats coatings achieved by the respective settings.

4.1.3 The concentration of precursor solutions

Three precursor solutions were used: a) copper azole, b) copper quaternary, also known as copper quats, and c) titanium tetraisopropoxide. The OM images of Cu and TiO₂ TSC coatings

prepared on a glass substrate by using identical process parameters (10 cm distance at 10° angle and 3 wt% concentration) were compared in Figure 4.3. The surface coverage of Cu and TiO₂ coatings estimated by ImageJ analysis using the OM images is summarized in Table 4.1. The coating images were taken on a glass substrate as the TiO₂ coating was not visible through OM in a wood surface at low concentration (3 wt%). Observing the OM image for the control sample, it seems it has nothing on it except for some tiny dust particles. Comparing Cu and TiO₂ coating images at the same concentration (Figure 4.3b to d), it seems that Cu particles are more readily and uniformly deposited than TiO₂.

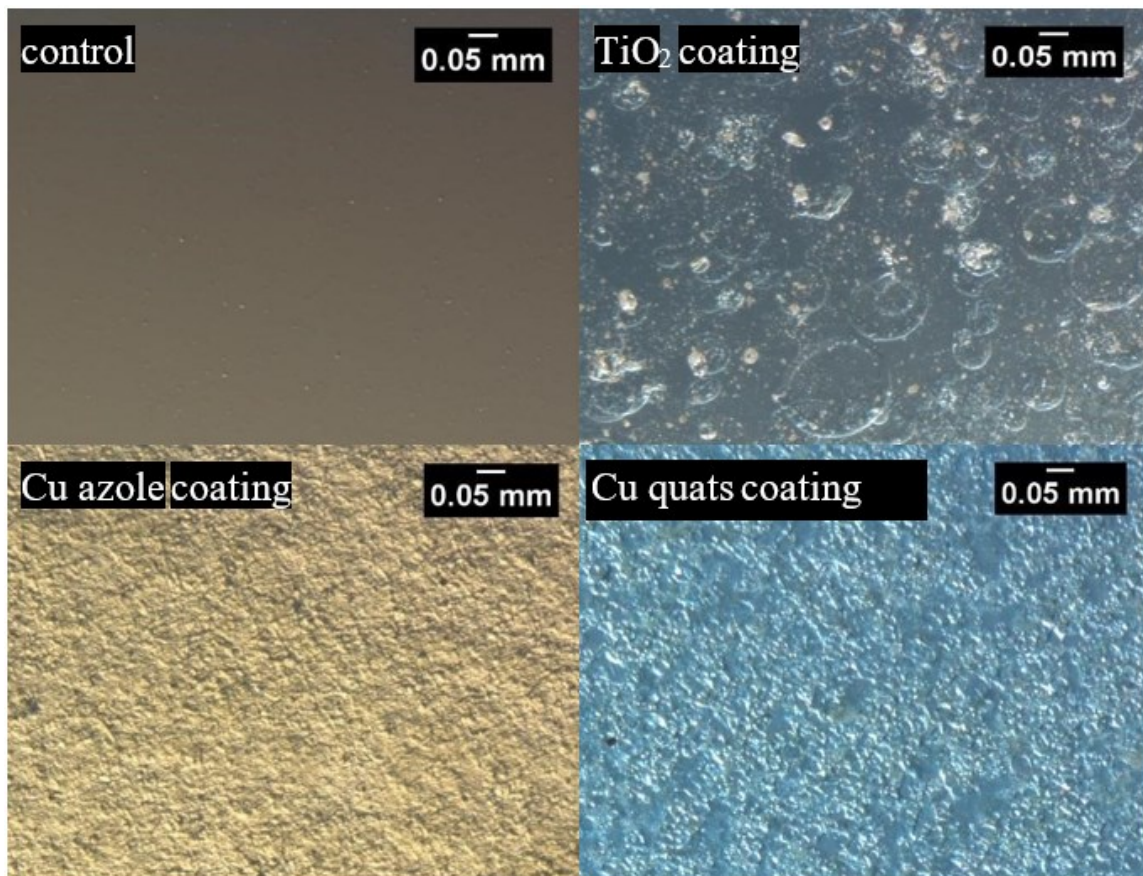


Figure 4.3 Comparison of OM images between Cu and TiO₂ coatings made with the same process parameters (10 cm distance at 10° angle) at 3 wt% concentration of the precursor solutions on a glass substrate.

Table 4.1 Evolution of surface coverage depending on the concentration of precursor solutions on a glass substrate.

Precursor Solution	Concentration (wt%)	Avg. surface coverage (%)	Standard deviation
Cu azole	1	45.4	3.0
Cu Quats	1	47.8	2.6
Tetraisopropoxide	1	27.3	2.2
Cu azole	3	75.2	1.6
Cu Quats	3	76.8	1.1
Tetraisopropoxide	3	48.7	2.5
Cu azole	5	97.83	0.1
Cu Quats	5	98.6	0.5
Tetraisopropoxide	5	69.2	2.5
Tetraisopropoxide	15	95.76	1.1

To find the concentration of precursor solutions that can achieve more than 90% of surface coverage on a wood substrate, the precursor concentration was increased from 1% and higher. It was found that Cu precursor solutions were able to achieve over 90% coverage at 5 wt%, whereas the concentration had to be increased to 15% for TiO₂ precursor, as shown in Table 4.1. As a result, concentrations of 5 wt% and 15 wt% were employed for Cu and TiO₂ precursor solutions, respectively, for further TSC experiments.

4.2 Surface coverage and thickness of Cu and TiO₂ coatings

4.2.1 Surface coverage and thickness

Surface coverage was estimated by analyzing OM images of TSC-modified wood with ImageJ. Low concentration (< 5% for Cu and < 15% for TiO₂), short distance (< 10 cm), and high angle (> 10°) conditions all resulted in less than 85% surface coverage for the wood samples. However, surface coverage of more than 90% was recorded for all wooden samples prepared with

5 wt% of Cu and 15 wt% Ti precursor solutions at a 10 cm distance with an angle of 10° as shown in Table 4.2.

Table 4.2 Surface coverage of TSC-modified wood using Cu and TiO₂ liquid precursors.

Sample	Distance (cm)	Concentration (wt.%)	Air pressure (psi)	Set	Area Coverage (%)	Mean area coverage (%)	Std. deviation	Coeff. of variance
Control	10 cm		3	a)	2.92	2.87	0.38	0.13
				b)	2.47			
				c)	3.22			
Cu Azole	10 cm	5	3	a)	90.85	91.31	1.88	0.02
				b)	89.70			
				c)	93.38			
Cu Quats	10 cm	5	3	a)	95.35	94.75	0.71	0.01
				b)	94.93			
				c)	93.97			
TiO ₂	10 cm	15	3	a)	90.08	90.08	1.77	0.02
				b)	88.23			
				c)	86.54			

4.2.2 Coating thickness

Numerous experiments were conducted by varying different process parameters, as discussed in Chapter 4.1, and surface coverage of Cu and TiO₂ coatings was estimated as examined in Chapter 4.2.1. Considering the resulting OM images and surface results, an experimental setting for liquid-precursor TSC was developed (process parameters were: a distance of 10 cm apart, an angle of 10° between airbrush and torch, and a concentration of 5 and 15 wt% for Cu and Ti precursors, respectively), for optimal particle deposition and surface coverage. Several Cu and TiO₂ coatings were produced using this setting, and their thickness was estimated by the method

explained in Chapter 3.5. An average coating thickness of $> 5 \mu\text{m}$ was recorded for the coatings produced from both handheld and motorized stage TSC (Table 4.3).

Table 4.3 Estimated coating thickness from TSC with various spray methods.

	Motorized stage						Handheld		
	3 coat spray			1 coat spray			3 coat spray		
	Cu quats	Cuazole	TiO ₂	Cu quats	Cuazole	TiO ₂	Cu quats	Cuazole	TiO ₂
thickness (μm)	6.5	6.3	5.3	6.6	6.5	5.4	6.3	4.9	4.7
standard deviation	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
coefficient of variance	0.002	0.001	0.001	0.002	0.002	0.001	0.002	0.02	0.02

4.3 Morphology of TSC-modified wood

4.3.1 Comparison of OM images in terms of their thickness measured

OM images of the samples were taken after each coating cycle, and their thickness was estimated for all precursor solutions and spray methods. TSC seemed to deposit inorganic particles sparsely at first and then gradually increased the surface coverage of particles as the process continued, as shown in (Figure 4.4 - 4.6) [25]. Comparing the images and data from Table 4.4, it is interesting to note that the most of the thickness deposition occurs at the 1st coating for the motorized stage method (Figure 4.4a – c to Figure 4.6a - c). This may be because, in the beginning, the wood substrate is very porous with a large surface area for the Cu and TiO₂ particles to adhere to, which gradually decreases with increasing deposited particles. However, this was not true for the handheld method, which gained the maximum thickness at the 3rd coating cycle (Figure 4.4d – f and Figure 4.6d - f). This could be the result of either the different spray patterns employed for

the motorized and handheld methods or because of the inconsistent spray pattern caused by human error during the handheld method. Comparing the OM images for Cu and TiO₂ in Figure 4.4 - 4.7, it is observed that Cu particles comparatively cover more surface than the TiO₂ particles, which agrees with the results from the surface coverage from the previous chapter. Comparing the images for Cu and TiO₂ made by the single coating spray method and multiple coating spray produced by the motorized movement (Fig 4.7), the coatings produced by single coating spray appear to have more particle deposition than those for the multiple coating spray. This conclusion was drawn from the difference in color richness and texture of the coating observed on the OM images for spray methods, which is further supported by the data from Table 4.4.

Table 4.4 Thickness comparison for each coating cycle using motorized stage and handheld methods.

Method	Precursor solution	Thickness (μm)			Total thickness (μm)
		1 st coating	2 nd coating	3 rd coating	
Motorized stage (3 coat spray)	Cu azole	2.5	1.9	1.9	6.3
	Cu quats	2.5	2.0	1.9	6.5
	Titanium tetraisopropoxide	2.2	1.9	1.2	5.3
Handheld (3 coat spray)	Cu azole	1.5	1.3	2.1	5.0
	Cu quats	1.7	1.7	2.8	6.3
	Titanium tetraisopropoxide	1.6	1.5	1.6	4.8

Three coating spray:

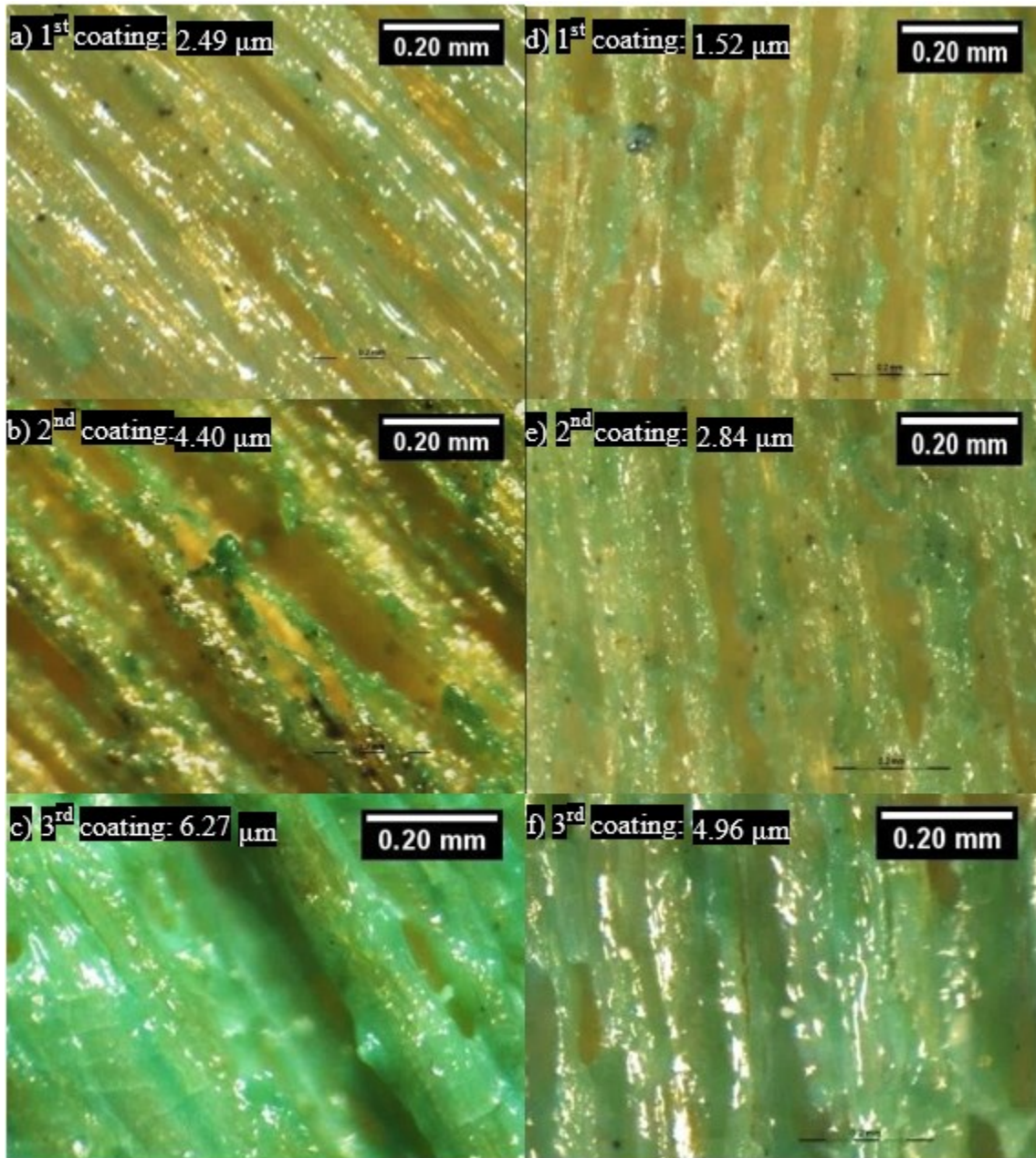


Figure 4.4 Images a) to f): side by side comparison of morphology of Cu coating from copper azole after each coating cycle using motorized stage (image a to c) and handheld methods (image d to f).

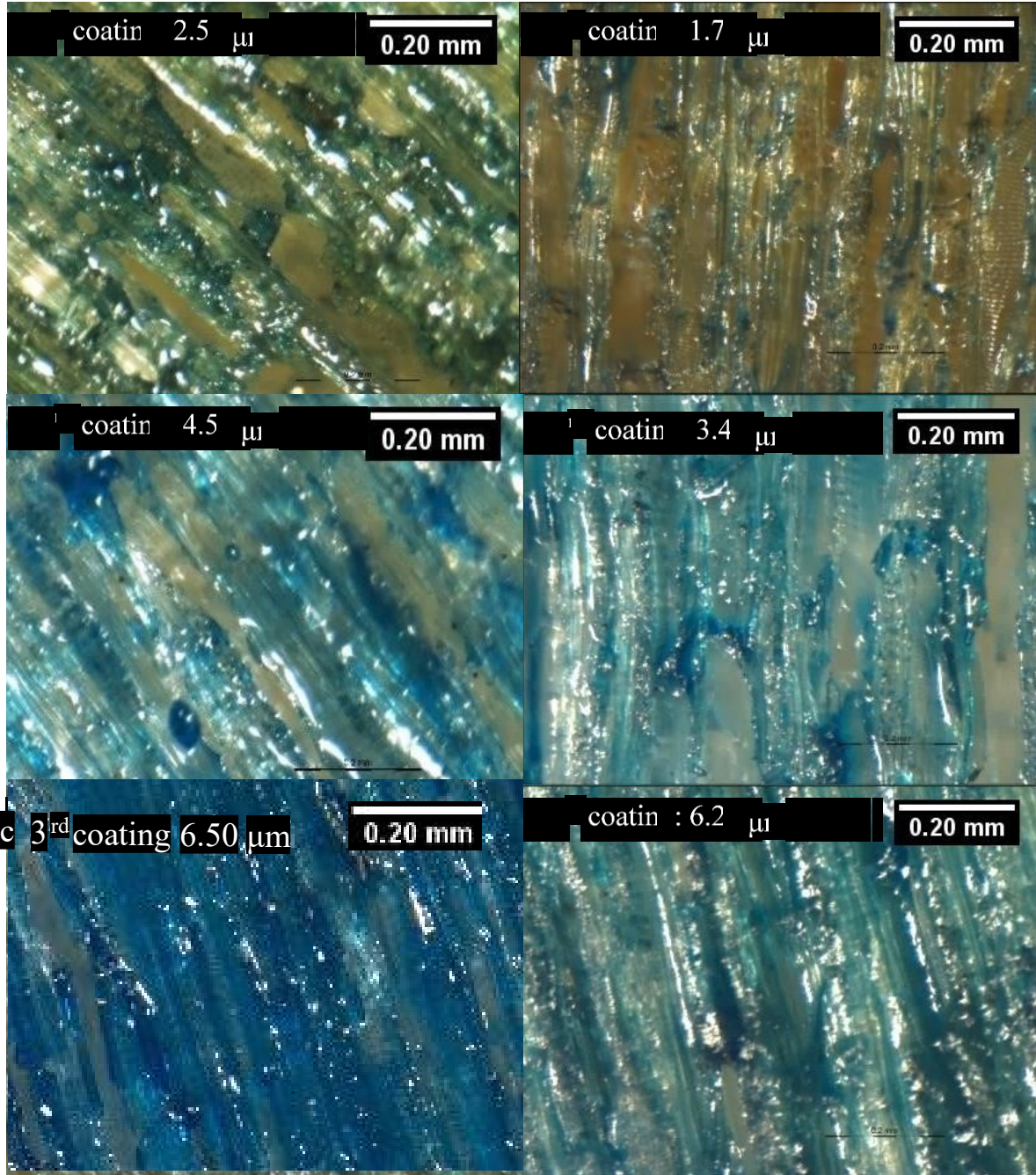


Figure 4.5 Images a) to f): side by side comparison of morphology of Cu coating from copper quats after each coating cycle using motorized stage (image a to c) and handheld methods (image d to f).

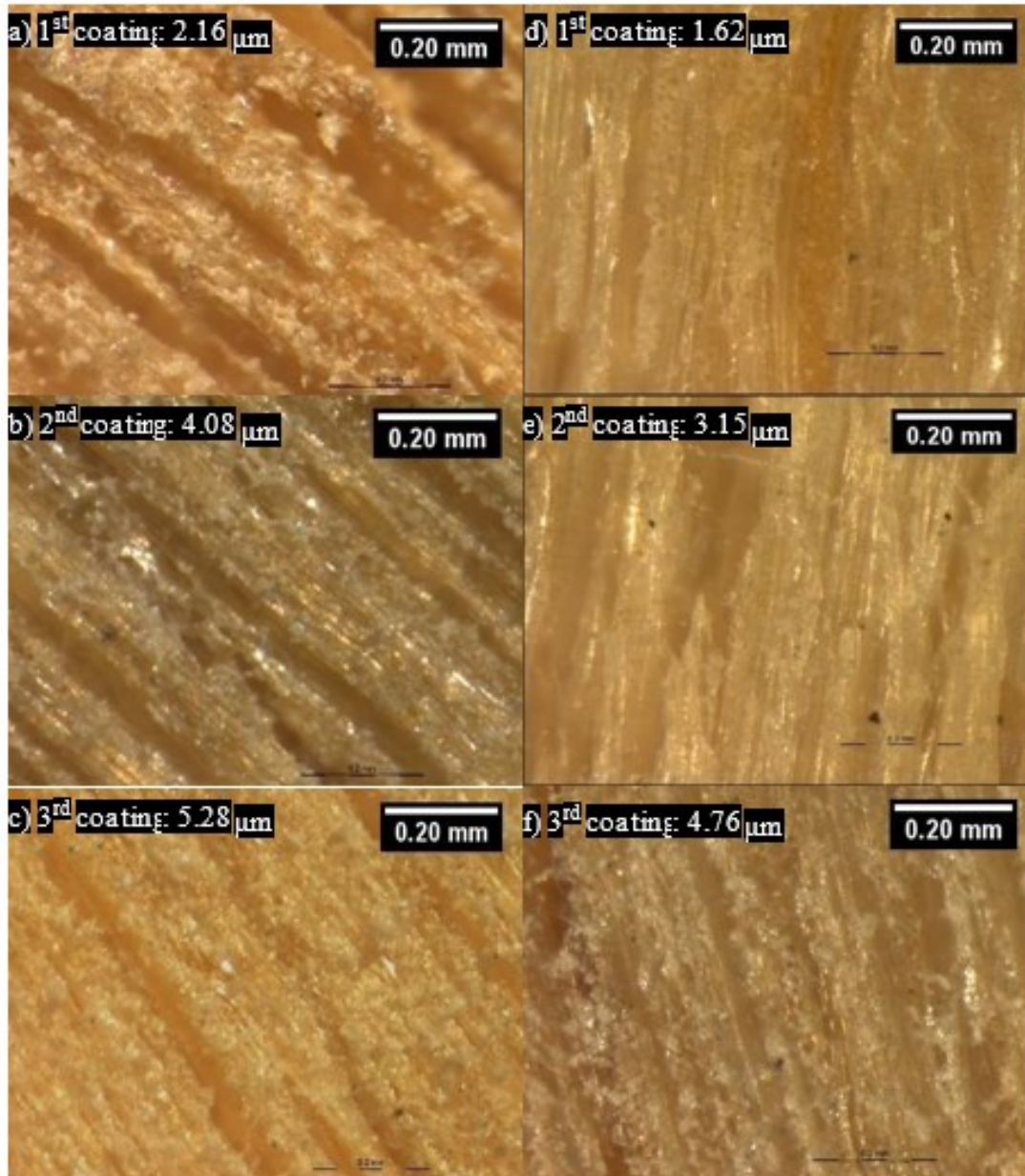


Figure 4.6 Images a) to f): side by side comparison of morphology of TiO_2 coating from titanium tetraisopropoxide after each coating cycle using motorized stage (image a to c) and handheld methods (image d to f).

Single coating spray:

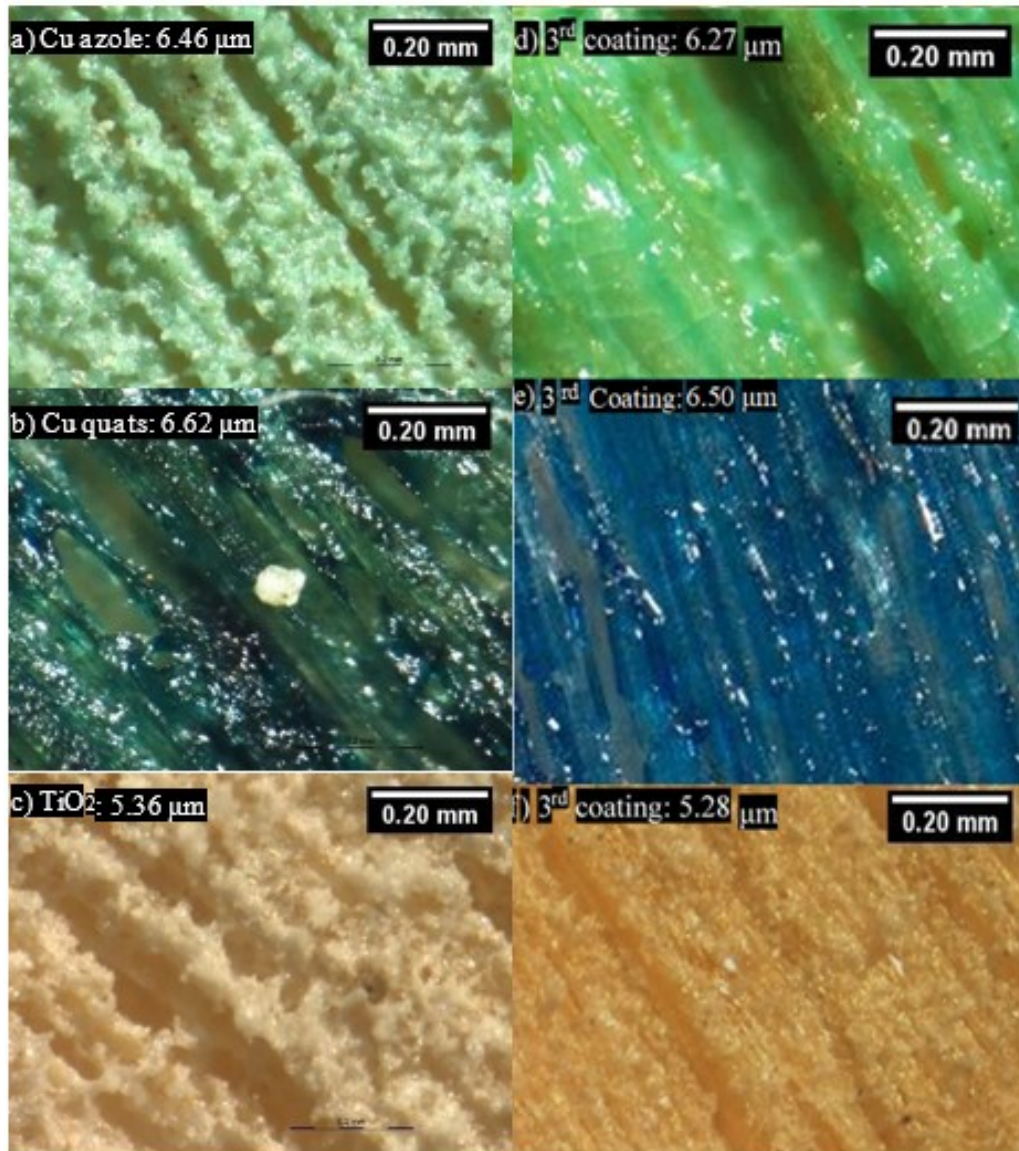


Figure 4.7 Images a) to f): Side by side comparison of thickness for each precursor solution used for a single coating spray process using motorized stage (image a to c) and multiple coating spray using motorized stage (image d to f).

4.4 Surface coating tests

4.4.1 Film-hardness pencil test

The film-hardness test is a way to evaluate the resistance of wood coating towards wearing, tearing, and physical abrasion, which is vital for coatings of specific uses, for example, thermal barrier coatings. Harder coatings usually have more durability. A set of hardness pencils for the ASTM 3363 standard film hardness pencil test was used to create dent and scratches on the coated wood surface, which was later analyzed to provide a hardness level. Figures 4.8 and 4.9 show the dents made by these pencils along with their respective hardness level on Cu and TiO₂ coated wood samples.

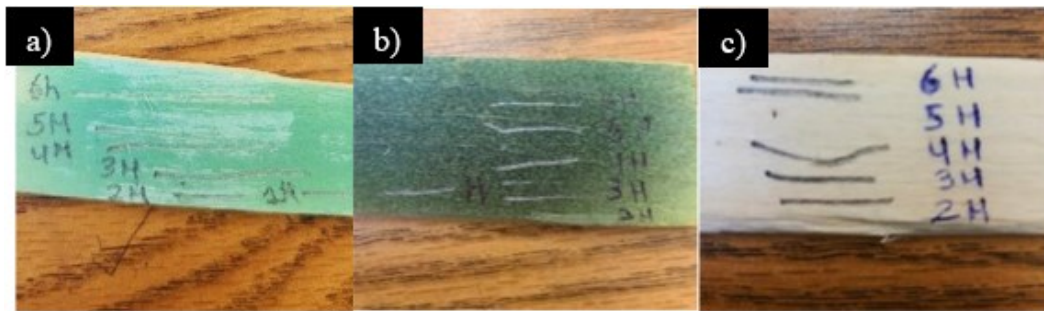


Figure 4.8 Hardness test images for coatings made by the handheld method with (a) copper azole, (b) copper quats, and (c) titanium tetraisopropoxide as their precursor solutions.

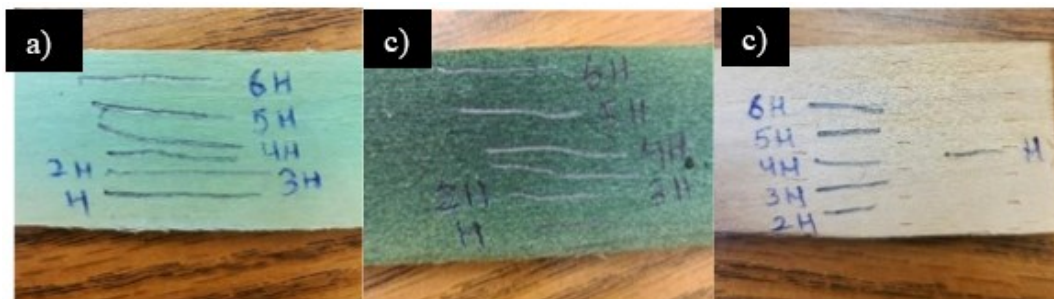


Figure 4.9 Hardness test images for coating made by the motorized stage method with (a) copper azole, (b) copper quats, and (c) titanium tetraisopropoxide as their precursor solutions.

Table 4.5 Film hardness pencil test results (hardness increases gradually from B to 4H).

Spray method	Precursor solution	Hardness level
Control		B
Hand-held	Copper azole	2H
	Copper quats	2H
	Titanium tetraisopopoxide	3H
Motorized stage (single coat)	Copper azole	3H
	Copper quats	3H
	Titanium tetraisopopoxide	4H
Motorized stage (3 coats)	Copper azole	3H
	Copper quats	3H
	Titanium tetraisopopoxide	4H

The pencil-hardness test results show that the coating obtained from the motorized stage method had higher hardness strength than the coating obtained from the hand-held process, recording the highest hardness level of 4H in the hardness scale (Table 4.5). The reason for the motorized method depositions being superior to the handheld movement is most certainly because of the high repetition accuracy of the motorized stage, i.e., ± 0.02 mm which creates a uniform, consistent and smooth movement, compared to the shaky and uneven movement produced by the handheld movement method. Similarly, the possible difference in thickness and morphology of coatings achieved by employing these two different movement methods could also be another reason for the difference in hardness level. Comparing the hardness level between the three different liquid precursors used, TiO₂ coating had the hardest surface, recording 4H and 3H in the hardness scale for the motorized stage and handheld movement, respectively. The average hardness level of Cu coating, i.e., 3H, achieved from the TSC method closely relates to the hardness level of 4H in Cu coating, achieved by a patented method that involved preparing a copper ion mixed solution, dipping the substrate in the solution and sintering the substrate [33]. In

this study a copper oxide coating was deposited on a ceramic substrate through the thermochemical reactions achieved by sintering the target material at 900° C. Another publication claims a hardness level of 5H hardness level for Cu coatings, created by a patented method of electrodepositing particles on the substrate surface [34]. A Cu coating was produced by using different metal/polymer substrates as a part of a cathode and placing an anode in an electrolyte mixture to electrodeposit the textured layer on the substrate. Similarly, the average hardness level of TiO₂ coatings, i.e., 4H, achieved from the TSC method are quite comparable to the hardness level of 6H, and 4H for TiO₂ found on other studies which used the sol-gel process [35, 36]. Although the hardness levels were quite comparable, the difference observed could be the result of the difference in Cu coating finishes, i.e., TSC coating, sol-gel coating, electroplating, produced as a result of different methods employed in the preparation and could also be related to the difference in coating thickness achieved by these methods. Another study that generated self-cleaning TiO₂ coatings by dipping, spray and flow coating methods, which could be potentially more laborious than the TSC method due to the additional dipping and flow coating process along with spraying, claimed the same hardness level of 4H for TiO₂ coating which highlights the easiness and efficiency of the TSC method [37].

4.4.2 Adhesion tape test

The adhesive strength for Cu and TiO₂ coatings were evaluated by creating a lattice pattern on the coating, removing the coating around the lattice pattern using a 3M tape (Figure 4.10), and then studying the types of cracks and defects created on the coated surface. Table 4.6 shows the results from the adhesion tape test. Percent area removed translates to the percentage of coating removed as chips and flakes around the lattice grid area after applying and removing the adhesive tape. A lower percent area removed corresponds to better adhesive strength.

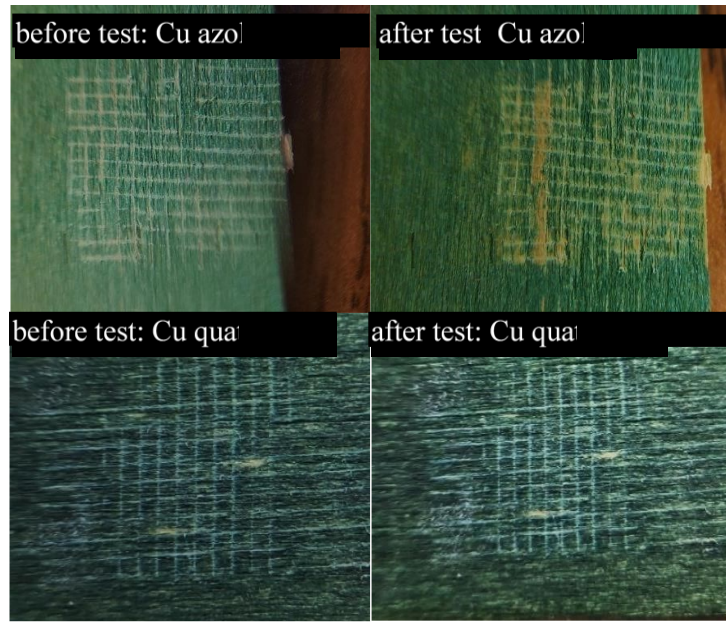


Figure 4.10 Photographic images of Cu coatings before and after the adhesion tape test.

Table 4.6 Adhesion tape test results (adhesion strength increases from 0B to 4B).

Method	Precursor solution	Percent area removed	Adhesion strength
Handheld	copper azole	> 65%	0B
	copper quats	15 - 35%	2B
	TiO ₂	35 - 65%	1B
Motorized stage (single spray)	copper azole	15 - 35%	2B
	copper quats	< 5%	4B
	TiO ₂	5 - 15%	3B
Motorized stage (3 times spray)	copper azole	15 - 35%	2B
	copper quats	5 - 15%	3B
	TiO ₂	5 - 35%	Between 2B and 3B

Similar to the hardness test results, the adhesive strength test results show that the coating obtained from the motorized stage method with single spray has superior adhesive strength, exhibiting an adhesion scale of 4B in the adhesive strength chart, compared to the coating obtained

from the handheld method. When the adhesive strength between the coating made out of three different liquid precursors was compared, the Cu coating made from copper quats ranked the highest with a scale of 4B with coating area loss less than 5% during the test. Being too transparent, the adhesive strength for TiO₂ coating could not be measured using this method. However, judging by the coating remains on the 3M tape after the test, the adhesive strength of TiO₂ coating seemed to lie in between that of copper azole and copper quats coating (Figure 4.11). A recent study that used an electroless copper-plated process to create superhydrophobic Cu coatings on wood substrate produced an adhesion scale of 4B, which is very similar to the adhesion scale achieved by the Cu quats coatings produced by the TSC method [38]. It is also worth mentioning that the thickness of the coating mentioned in this reference was ~10 μm, which was nearly twice the thickness of the coating produced by the TSC method.



Figure 4.11 Images of the coating remains in the 3M tape after adhesion test for (a) copper azole, (b) copper quats, and (c) TiO₂.

4.4.3 Contact angle measurement

Table 4.7 shows the water contact angles of Cu and TiO₂ coatings on wood with varying spray methods. The control (untreated wood) had a contact angle of 57°. After application of the Cu and TiO₂ coatings by the liquid-precursor TSC method, the wood substrate became more

hydrophobic, recording the highest water contact angle of 126° for TiO₂, followed by Cu from copper azole with the water contact angle of 91° (Figure 4.12 – 4.14). A similar study that employed thermal spray method on a paperboard surface to create a TiO₂ hydrophobic layer acquired a contact angle of 160°, which is quite comparable to TSC, considering the difference in substrates employed [14]. It is also worth mentioning that despite increasing the water contact angle from 57° to 91°, the copper azole coating quickly absorbed the water droplet within 120 seconds of contact. The other Cu coating made from copper quats was too hydrophilic to perform a contact angle measurement. The water droplet instantaneously penetrated the copper quats coating, most probably due to instant wetting. Similar to the previous surface tests, the samples made by the motorized stage method had a higher contact angle than those made by handheld method, probably due to more even and consistent coating as a result of the motorized stage. The hydrophobicity and contact angle, i.e., 126° for TiO₂ produced by the TSC method, falls in line with the hydrophobicity achieved by the other surface modification techniques on a wooden surface, i.e., a contact angle of 110° - 150° [39,40,41].

Table 4.7 Contact angle measurement results.

Method	Precursor solution	Average Contact angle measured (degrees)	Standard deviation	Coefficient of variance
Control sample		57	2.1	4.2
Handheld (3 coat spray)	copper azole	80	2.4	6.0
	titanium dioxide	112	1.7	2.9
Motorized stage (1 coat spray)	copper azole	91	0.5	0.2
	titanium dioxide	126	2.4	6.0
Motorized stage (3 coat spray)	copper azole	87	0.8	0.7
	titanium dioxide	124	2.5	6.2

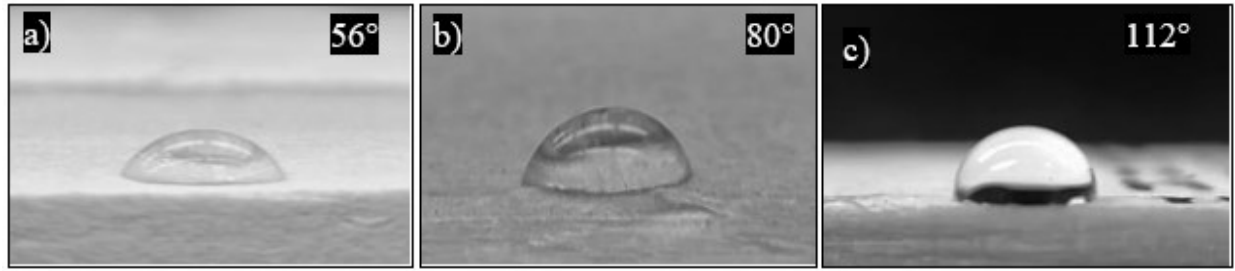


Figure 4.12 Comparison of water contact angle for the handheld method: a) control wood, b) Cu from copper azole, and c) TiO_2 from titanium tetraisopropoxide.

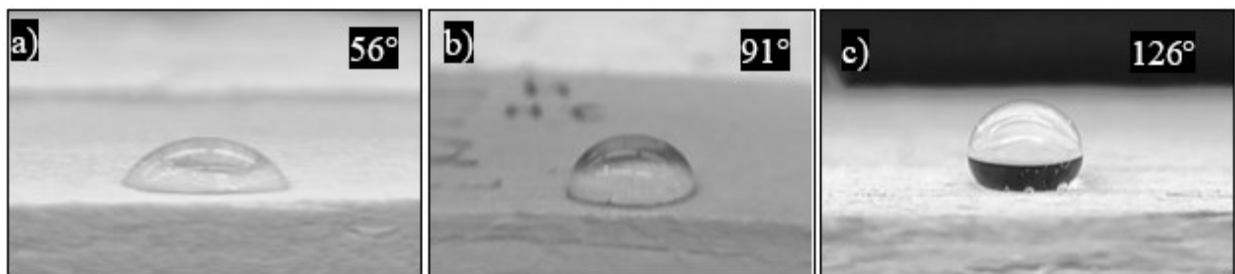


Figure 4.13 Comparison of water contact angle for the single spray motorized stage method: a) control wood, b) Cu from copper azole, and c) TiO_2 from titanium tetraisopropoxide.

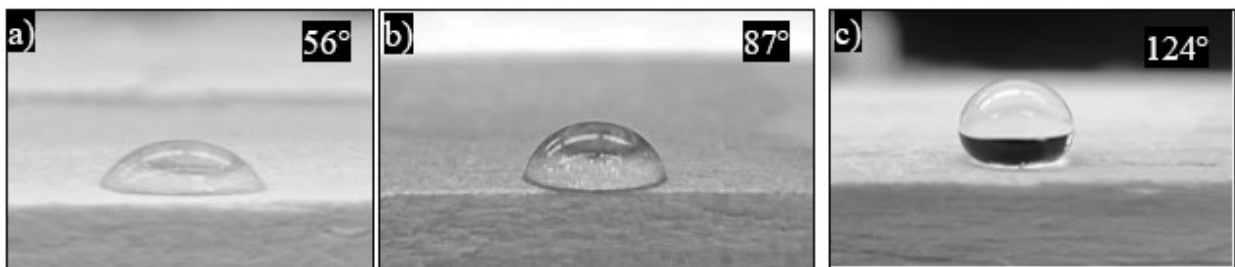


Figure 4.14 Comparison of water contact angle for the three coat spray motorized stage method: a) control wood, b) Cu from copper azole, and c) TiO_2 from titanium tetraisopropoxide.

4.5 QUV accelerated weathering test

The TSC-modified samples were subjected to a QUV accelerated weathering test for a total of 20 days, which translates into roughly six months of natural weathering conditions. Artificial weathering tests can speed up the impacts of natural weathering from 5 to 20 times, depending upon the exposure conditions [42]. Laboratory accelerated weathering tests are one of the most effective techniques accessible to researchers to predict the weathering degradation of materials. However, to avoid extrapolation of data, realistic baseline information is required [43]. The weathering pattern for the control and coated samples was studied, and pictures were taken at specific intervals (1 observation in 24 hours) throughout the 20 days. From the difference in weathering images shown in Figure 4.15 - 4.18, among all control and treated samples, color changes caused by the accelerated weathering tended to be most significant for the control samples followed by TiO_2 , copper quats, and lastly copper azole coatings, respectively. The copper coating seemed to be the least affected on the color change comparison, which could be the result of a thicker coating achieved during TSC compared to the TiO_2 coating. Furthermore, a recent study indicates that opaque coatings are generally more durable than clear coating during weathering [44]. Having said that, other studies suggest that the photo stabilization caused by Cu coatings is only limited to the cellulosic component of wood while the photo stabilization of lignin was found to be poor [45]. The copper azole coating gradually developed a brownish color as a result of the presence of Cupric ions. TiO_2 coatings showed some color change during the weathering test, as seen by the burn marks. However, it still showed appreciable protection to photodegradation, compared to the control samples. Observing weathering images for the control sample, it was found that untreated wood degraded drastically upon exposure to UV light and moisture. UV burns grew stronger with continued exposure (Figure 4.15). Comparing day 0 and day 20 images of

control sample (Figure 4.15a and e), the wood started to develop a small crack. Thus, by monitoring the weathering effects on the control and treated wood, it is apparent that TSC-modified wood was able to offer more resistance to photodegradation, compared to the untreated wood, caused by the top three natural enemies of wood, i.e., UV rays, temperature, and moisture.

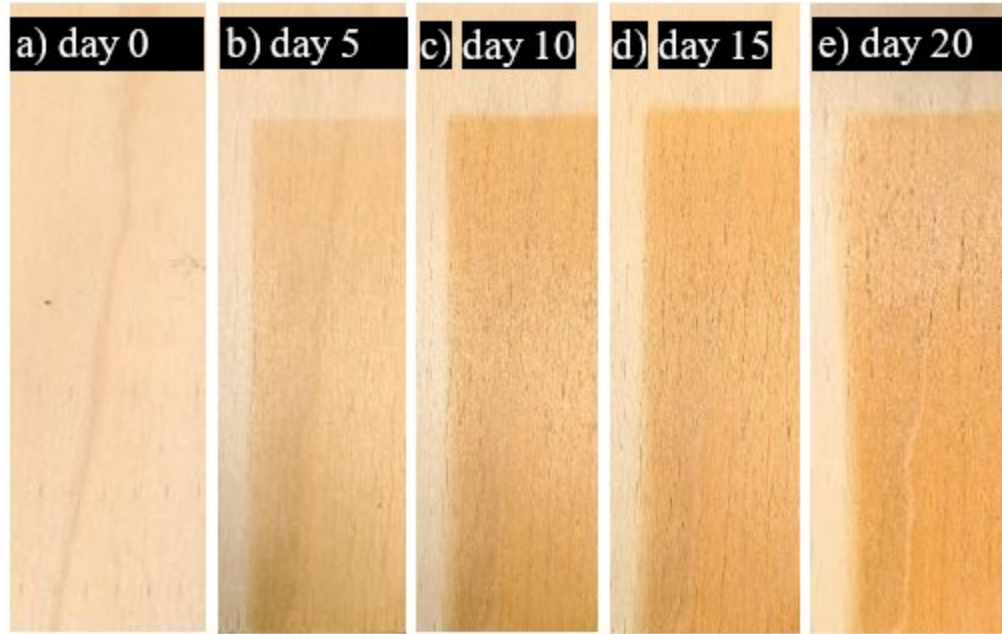


Figure 4.15 Pictures a to e: accelerated weathering images of untreated control samples on day 0 to 20, respectively.



Figure 4.16 Pictures a to e: Accelerated weathering images of modified wood created by the motorized movement method (three consecutive coatings with resting) starting from day 0 to 20 with copper azole, copper quats, and titanium tetraisopropoxide as precursor solution, respectively.

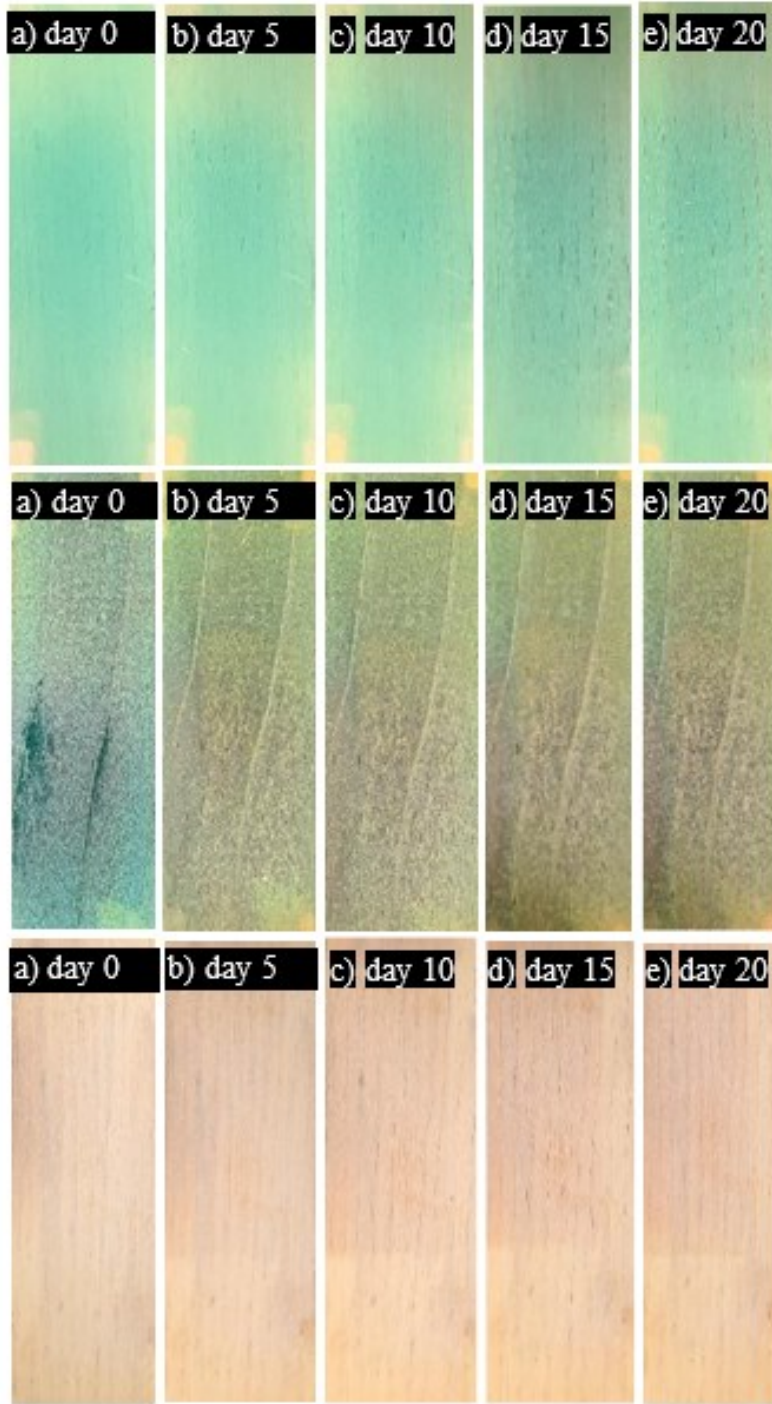


Figure 4.17 Pictures a to e: Accelerated weathering images of modified wood created by the motorized movement method (single coating spray) from day 0 to 20 with copper azole, copper quats, and titanium tetraisopropoxide as precursor solution, respectively.

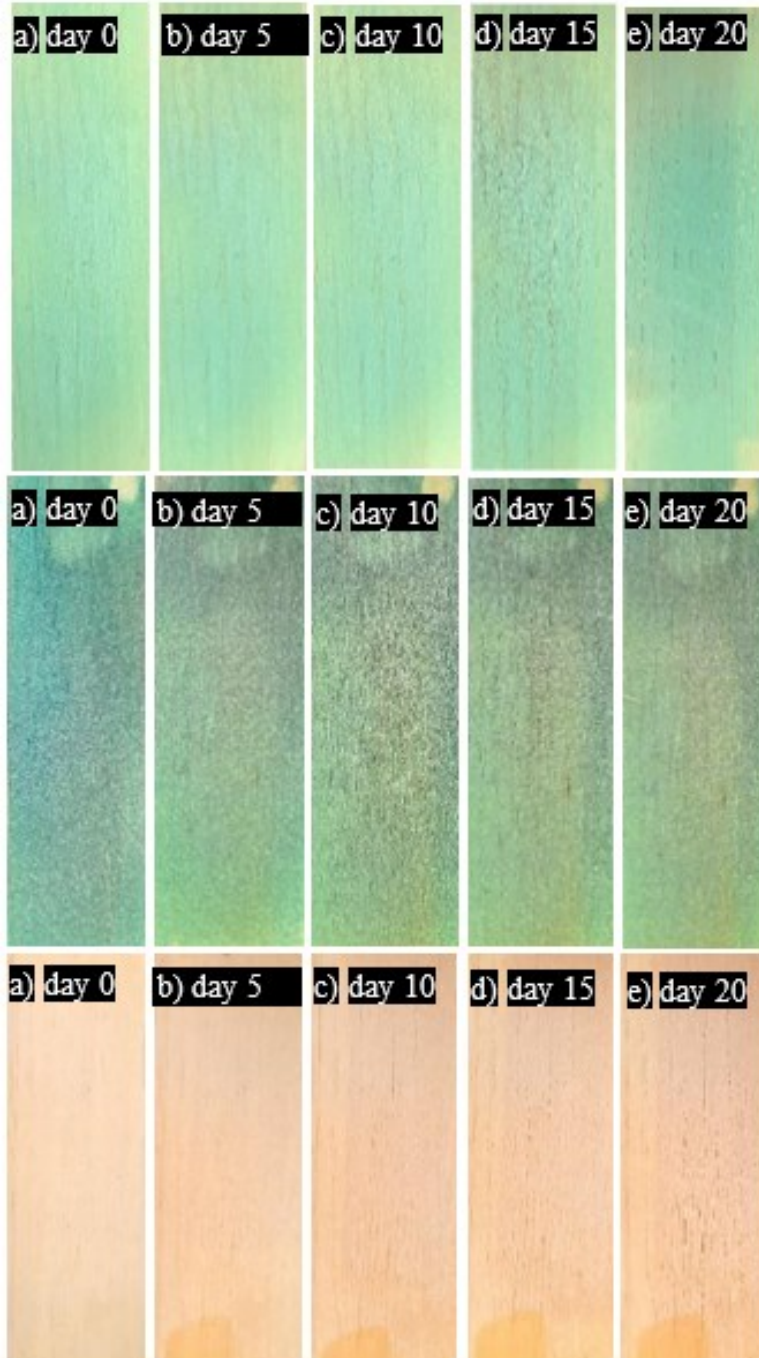


Figure 4.18 Pictures a to e: Accelerated weathering images of modified wood created by the handheld movement method (single coating spray) from day 0 to 20 with copper azole, copper quats, and titanium tetraisopropoxide as precursor solution, respectively.

CHAPTER V

SUMMARY, CONCLUSIONS AND FUTURE WORK

5.1 Summary and Conclusions

In the first portion of the study, three precursor solutions, i.e., copper azole, copper quaternary, and titanium tetraisopropoxide, were selected to test the effectiveness of the liquid-precursor TSC method as a viable process for surface modification of wood. All three precursor solutions were found to be able to deposit Cu and TiO₂ particles onto the wood surface, as confirmed by visual inspection and optical microscopic images. Optimized liquid-precursor TSC process parameters were devised, which include a torch-to-sample distance of 10 cm, an airbrush-to-torch angle of 10°, and concentrations of 5 and 15 wt% solution concentration for Cu and TiO₂ precursor solutions, respectively. Using these parameters, the average surface coverage of > 90% and an average coating thickness of > 5 µm were obtained on the SYP veneers. In the second portion of the study, the surface properties of the Cu and TiO₂ coatings and the weathering durability of the TSC-coated wood were evaluated. A hydrophobic water contact angle of 120° and a hardness level of up to 4B on the hardness scale was measured. The detailed conclusions are summarized below.

1. The motorized stage spray method was superior to the handheld spray method. The optimum distance from the substrate and the precursor solution was 10 cm, and the best angle to be used between the flame source and airbrush was 10°. Similarly, the single coating spray method for 180 seconds was superior to the multiple coating method

(samples were sprayed for three times in a row for 60 seconds, followed by a resting period of 20 seconds), determined by the surface and stability tests.

2. The average film hardness of 3H, 3H, and 4H on the ASTM 3363 standard film hardness test for coatings with copper azole, copper quats, and titanium tetraisopropoxide as the precursor solution was found.
3. The Copper quats coating had the highest adhesion strength, asserting an adhesive strength of 4B on the adhesion strength table, according to the ASTM D3359 measuring adhesion by tape test.
4. The TiO_2 coating displayed hydrophobic behavior with a water contact angle of more than 120° . The Copper azole coating also provided some level of hydrophobicity with a water contact angle of 90° .
5. Copper azole displayed high resistance against discoloration in QUV accelerated weathering tests, compared to copper quats and TiO_2 . Control samples were severely affected by discoloration, showing visible signs of UV burns and developing a small crack at the later stages of weathering tests.

5.2 Future work

One of the findings of this research is the thickness estimate of the samples coated by the liquid-precursor thermal spray coating. However, this may not accurately represent the exact thickness on the coating since the estimate was based on the fact that wood is conformal, but in fact, wood does not have a conformal surface. A new approach that can accurately estimate the thickness of the coating in the wood substrate should be tried. Possibilities are mass balance calculation from the consumed mass of precursors.

It is important to know the penetration and retention level of the inorganic particles of the coatings inside the wood substrate, which was not addressed by this research. These assessments are crucial to proving the efficiency of TSC on a wood substrate. Similarly, due to time constraints, the weathering test was limited to 480h and was evaluated by just using photographs. However, to understand the full spectrum of weathering test, accelerated weathering tests along with natural weathering will be performed for at least 1000h [ASTM G154]. Furthermore, the weathering of the coated samples will be studied with a colorimeter/spectral-photometer to accurately predict the change in color and gloss [ASTM E1347/ ASTM D523].

It is equally important to measure the dimensional stability of the coated wood using different techniques, for instance, short repeated water-swelling test [ASTM D4446] or the long humidity-cycling test [ASTM D3459] to predict the durability and stability of the modified wood. In addition, only wood veneers were used as a wood substrate during this research. The study concerning the effect of liquid-precursor TSC for other wood substrates, for instance, CLT panels need to be performed.

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